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Intermediates and mechanisms of heterogeneous catalytic reactions. Reactions involving hydrogen and the monoxides of carbon and nitrogen

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Abstract. The structure of intermediate surface compounds in heterogeneous catalytic reactions involving H_2, CO, and NO is discussed. The relative reliability of the role of various structures in catalysis is discussed. Schemes for the reaction mechanism which have been developed from information on the surface complexes are described. The bibliography includes 248 references.

I. Introduction

We have previously discussed the intermediates which have been detected by spectroscopic measurements in situ in the simplest heterogeneous catalytic reactions of hydrocarbons.[1] This review is concerned with somewhat more complex reactions involving H_2, CO, or NO. In most cases two substances are the initial reactants, and the catalysts are metals or transition metal oxides. The hydrogenation of olefins and the dehydrogenation of paraffins are reaction of the general type

$$A + B \leftrightarrows AB .$$

In the forward direction we may observe the activation of both the olefin (A) and the hydrogen (B), and therefore possible intermediates formed from both the hydrocarbons and the hydrogen must be considered.

As in our previous review[1] we shall define three levels of reliability of the existence of intermediate substances: a low level (L), obtained from spectroscopic data recorded before and after the catalysis, a medium level (M), obtained from spectroscopic data in situ but without kinetic measurements, and a high level (H), from spectroscopic data in situ aimed at comparing the kinetics of the heterogeneous catalytic reactions with those of the change in concentration of the surface compounds.

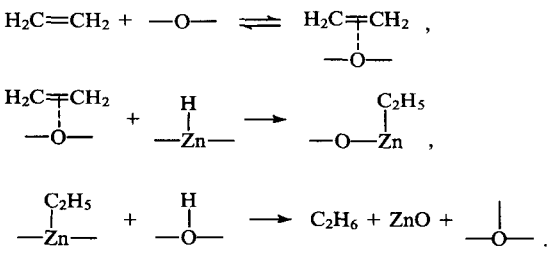
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In the reactions with H_2, CO, and NO the observed spectra are usually stronger than those seen in the reactions of the hydrocarbons. This effect is attributed to the high extinction coefficients of the C–O, O–H, and N–H bonds. Accordingly, the reliability of the results is also generally higher.

II. Hydrogenation of hydrocarbons

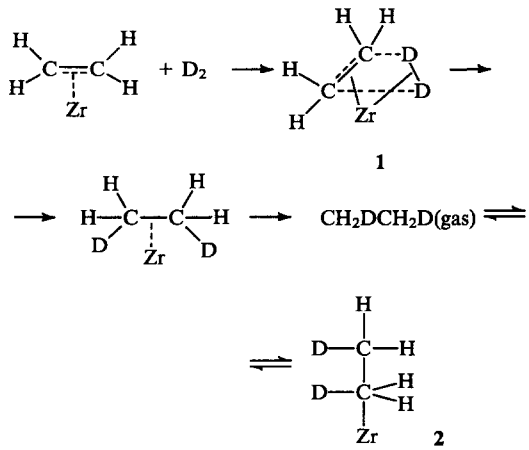
In our previous review,[1] devoted to the simplest reactions of the hydrocarbons, alcohols, and acids, we discussed the intermediate complexes formed by the isomerisation of the olefins on ZnO.[2,3] The same workers[4–6] used kinetic methods and IR spectroscopy to study the mechanism of the hydrogenation of C_2H_4 on ZnO. According to their results there are two types of adsorption of H_2 on ZnO: (1) a fast, reversible adsorption, with formation of Zn–H bonds (1710 cm^{-1}) and of O–H bonds (3510 cm^{-1}), and (2) a slow, irreversible adsorption, with diffusion of the hydrogen into the bulk of the catalyst. Adsorption of the first type occurs when C_2H_4 is hydrogenated at 300 °C. After the adsorption of C_2H_4 the Zn–H band persists in the IR spectra but the O–H band disappears. This led to the conclusion that hydrogen is adsorbed as a π complex on the oxygen atoms, with absorption bands (a. b.) at 1438, 1451, and 1600 cm^{-1}; the heat of adsorption is about 58 kJ mol^{-1}. A new band assigned to a π complex, appears when the C_2H_4 is hydrogenated in a flow reactor. When C_2H_4 is replaced by C_2D_4 the initial rate of disappearance of the C_2H_5 absorption bands is close to the stationary rate of hydrogenation: the step corresponding to this process may be rate-limiting. The proposed mechanism can be represented as



The adsorbed hydrogen can migrate over the oxygen centres of the surface towards the adsorbed C_2H_4.

The mechanism proposed[4-6] for the hydrogenation of C_2H_4 was subsequently confirmed.[7,8] However, the only deuteration products of C_3H_6, C_4H_8, and C_4H_6 were the deuterated hydrocarbons $C_3H_6D_2$, $C_4H_8D_2$, and $C_4H_6D_2$. This shows that the hydrogen takes part in the reaction in a molecular form rather than in the atomic form seen in the hydrogenation of ethylene: this difference can be attributed to the weaker chemisorption of C_2H_4 on ZnO as compared with C_3H_6, C_4H_6, and C_4H_8. Therefore C_3H_6 and C_4H_8 are adsorbed as π-allyl complexes.

The IR spectra of hydrogen adsorbed on ZrO_2 at 0-100 °C also indicate a heterolytic dissociation of H_2 with formation of Zr-H and O-H groups.[9] However, when bound in this way hydrogen does not react with ethylene from the gas phase, but is simply replaced by it: the intensity of the Zr-H band decreases, and the absorption bands of π-C_2H_4 (1446 cm^{-1}) and of the tightly bound C_2H_4 complex (1338 cm^{-1}) are formed. However, the hydrogenation of C_2H_4 is detectable even at −100 °C, when the heterolytic dissociation of H_2 is inconceivable. Under these conditions the adsorbed ethylene interacts with D_2 from the gas phase by the following mechanism:

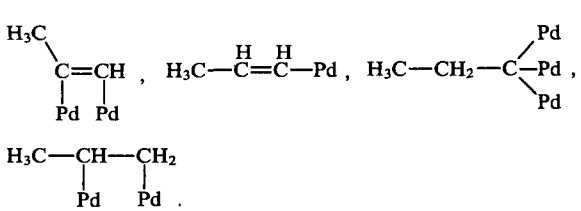


In this reaction the complex **1** is the intermediate and the complex **2** is a side product.

On clean Pd(111) and Pd-Cu(111) metallic surfaces π-C_2H_4 and ethylidene (=CH-CH_3) are observed[10] in the electron energy loss spectroscopy (EELS) spectra, whereas in the adsorption of C_2H_2 the corresponding species are π-C_2H_2 and ethylidyne (≡C-CH_3). At high temperatures (200 °C) even more highly dehydrogenated intermediates of composition Pd-C_xH_y are formed (where $x > y$). It was concluded that the hydrogenation reaction takes place through the formation of these complexes.

An IR spectroscopic study[11] of the interaction of C_2H_4 with Rh/SiO_2 and with VO_x-Rh/SiO_2 also suggested the formation of the ethylidene groups =CH-CH_3. In the presence of hydrogen these are hydrogenated to give alkyl groups, and beyond to CH_4 and C_2H_6.

An analysis[12] of the IR spectra obtained after the hydrogenation of propylene on Pd/ZrO_2 detected the formation of the surface compounds

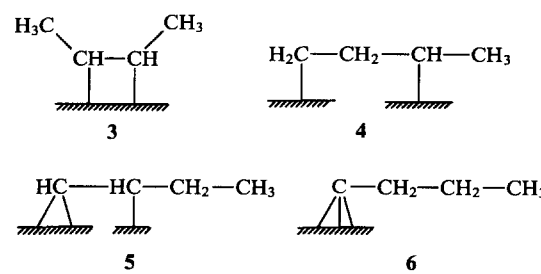


The hydrogenation of butadiene on Pt(100), studied[13] by low-energy electron diffraction (LEED) and by Auger spectroscopy, was found to proceed through the formation of the intermediate C_4H_7:

$$C_4H_6 \rightleftharpoons C_4H_6\,(ads) \underset{-H^+}{\overset{H^+}{\rightleftharpoons}} C_4H_7\,(ads) \xrightarrow{H^+} C_4H_8\,(ads) \longrightarrow C_4H_8\,(gas).$$

The conversion of butadiene into butene is the rate-limiting step, characterised by an activation energy of 39 kJ mol^{-1}. The fact that the rate of H/D exchange is an order of magnitude greater than the rate of hydrogenation of C_4H_6 points to the same conclusion.

The IR spectra of butenes adsorbed on Ni/SiO_2 [14] and on Co/SiO_2 [15] revealed absorption bands denoting the formation of metal-butane



and of π-allyl complexes. The allyl complexes are probably the precursors of the metal butanes **3**-**5**. The complex **3** is loosely bound to the surface, and is easily hydrogenated to butane. The complexes **4** and **5** are tightly bound, and are probably hydrogenated through the intermediate formation of the complex **6**. The formation of butane is observed in the range 20-100 °C, but above 90 °C the hydrogenation is accompanied by some dissociation of the C-C bond.

Data on the intermediate compounds taking part in the hydrogenation of the hydrocarbons are summarised in Table 1.

The hydrogenation of olefins on ZnO was studied by a combination of in situ spectroscopic and kinetic measurements, which unambiguously demonstrated the participation of the π-allyl complexes of C_3H_6 and of the π complexes of C_2H_4, and also the interaction of the H atoms with C_2H_4 and of the H_2 molecules with C_3H_6 and with C_4H_8. However, the kinetic parameters obtained by spectroscopic methods could not be compared with those obtained by analysing the gaseous products.[4-8]

Adequately reliable data on the intermediate compounds taking part in the dehydrogenation of the paraffins do not appear to be available.

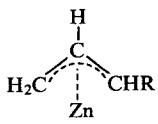
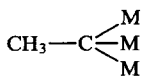
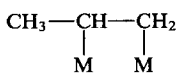
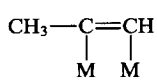
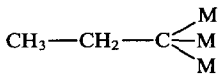
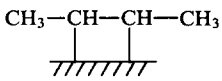
Addigo et al.[16] studied the IR spectra of the complexes of ethylbenzene and styrene adsorbed on iron oxide catalysts after the dehydration of the ethylbenzene to styrene. Under ordinary (non-reactive) conditions on non-promoted Fe_2O_3 the binding of the adsorbed styrene to the surface takes place through the aromatic ring, and the vinyl group suffers only a negligibly small perturbation. However, under the conditions favourable to the dehydrogenation reaction the interaction with the surface takes place through the vinyl group.[16]

III. Decomposition of ammonia

The synthesis of ammonia is carried out under high pressures. Spectroscopic measurements are difficult under these conditions, and therefore the reverse reaction (decomposition of NH_3) is often used in studies of the mechanism of the ammonia synthesis.

The decomposition of NH_3 on polycrystalline tungsten has been studied by Auger spectroscopy,[17] and on W(100),[18] Ru(001), and Ru(111)[19] it was studied by X-ray photoelectron spectroscopy (XPS). At 800 °C the tungsten surface (according to in situ Auger spectroscopy data) is covered with nitrogen atoms, and no NH_x species are found on the surface. The number of adsorbed

Table 1. Intermediate compounds in the hydrogenation of olefins.

Reaction, catalyst	Intermediate complex	Reliability	Ref.
Hydrogenation of ethylene on ZnO	Zn–H	H	4–6
	$H_2C{=}CH_2$ (O)	H	4–6
Hydrogenation of ethylene on ZrO_2	$H_2C{=}CH_2$ (Zr)	M	9
Hydrogenation of C_3H_6, C_4H_6, C_4H_8 on ZnO		M	7,8
		M	7,8
Hydrogenation of ethylene on metals		L	10,11
Hydrogenation of propene on Pd/ZrO_2		L	12
		L	12
	$CH_3{-}CH{=}CH{-}M$	L	12
		L	12
Hydrogenation of C_4H_6 on Pt(110)	C_4H_7(ads)	L	13
Hydrogenation of butenes on Co/SiO_2 and Ni/SiO_2		L	14,15

N atoms is much greater than the number corresponding to equilibrium adsorption

$$N_2 \rightleftharpoons 2N(ads),$$

in the absence of NH_3 and H_2 but under otherwise similar conditions. A combined study (by Auger spectroscopy) of the kinetics of the decomposition of NH_3 and of the desorption of N_2 showed that an increase in the coverage of the surface by nitrogen (θ_N) lowers the rate of decomposition of NH_3 and increases the rate of desorption of N_2, which become identical under steady-state conditions. Hydrogen from the gas phase has no effect on the adsorption of N_2 or on the rate of the reaction.

These results show that the reaction takes place by the mechanism of 'dynamic equilibrium' between two successive rate-limiting steps: (1) the formation on the catalyst surface of a layer of N atoms as a result of the decomposition of the NH_3 molecules, and (2) the desorption of the N atoms with formation of the N_2 molecule. The nitrogen is not in equilibrium with the NH_3 and H_2, as it is in the well known Temkin–Pyzhev mechanism of NH_3 synthesis on iron,[20] and for this reason the hydrogen does not affect the rate of absorption of nitrogen or the overall reaction rate. At high pressures the iron penetrates into the bulk of the catalyst and forms a nitride.

The decomposition of ammonia on Fe, W, and Re catalysts has also been studied by the electron projector method under thermal desorption conditions.[21] Nitrogen and hydrogen atoms adsorbed under the reaction conditions were detected. The activated adsorption of N_2 was observed on iron, and on rhenium and tungsten non-activated adsorption of nitrogen took place in two different forms, one of which contributes to the decomposition reaction whereas the other does not.

Thus it has been reliably shown by spectroscopic methods that adsorbed nitrogen atoms are the intermediate species in the decomposition of NH_3. Obviously, nitrogen atoms must act as intermediate complexes also in the synthesis of ammonia.

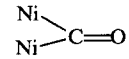
IV. Water gas conversion

Reactions involving CO are most conveniently studied by spectroscopic methods because the C≡O vibrations have high extinction coefficients. The interaction of CO with water vapour

$$CO + H_2O \rightleftharpoons CO_2 + H_2,$$

(the 'water gas conversion'), like its reverse reaction (the reverse water gas conversion'), is one of the simplest reactions involving CO. Both associative and dissociative mechanisms have been proposed for this reaction.

A purely dissociative mechanism was put forward on the basis of an IR spectroscopic study of this reaction on $Ni/(La_2O_3-MgO-Al_2O_3)$.[22] The vibration band of the bridging CO group



is shifted from 1960 to 1930 cm^{-1} after the adsorption of water, and under these conditions the linear form Ni–C≡O disappears. It was concluded that the adsorption of H_2O weakens the C=O bond in the bridging CO group (probably by shifting the electron density from H_2O towards the Ni) and thus favours its dissociation and disproportionation with formation of CO_2. The CO_3^{2-} and CH_3 groups, which do not take part in the conversion of CO, were also detected on the Ni surface. The following reaction mechanism was proposed:

$$H_2O(ads) \longrightarrow OH(ads) + H(ads),$$

$$CO(br) \longrightarrow C(ads) + O(ads),$$

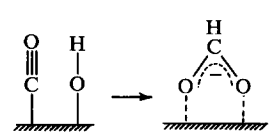
$$CO(br) + O(ads) \longrightarrow CO_2(ads),$$

$$2\,H(ads) \longrightarrow H_2,$$

$$C(ads) + OH(ads) \longrightarrow CO(br) + H(ads).$$

A dissociative mechanism for the reaction of CO with H_2O on Cu was proposed on the basis of IR spectroscopic data,[23] and for the same reaction on Co–Mo oxides by interpreting the results obtained by the response method.[24]

Most of the workers engaged in IR spectroscopic studies of the conversion of CO by water vapour observed the formation on the catalyst surface of formate groups (in addition to CO groups of various types). Therefore the formates are treated as intermediates in the mechanisms proposed for the reaction. The following formal mechanism was proposed after a study[25,26] of the conversion of CO on Cu–ZnO and $Cu-ZnO-Al_2O_3$ catalysts:



$$\rightleftharpoons H_2 + CO_2.$$

A similar mechanism was discussed for the reaction of H_2 with CO on Ru/NaY at 200–300 °C, but the observed first-order kinetics with respect to P_{H_2O} exclude the participation of tightly bound OH groups in the reaction.[27] An in situ study of the UV spectra allowed the valence state of the Ru to be determined: the results led to the reaction mechanism

$$Ru^+(H)(CO) + H_2O \longrightarrow Ru^{2+}(HCOO^-) + H_2,$$

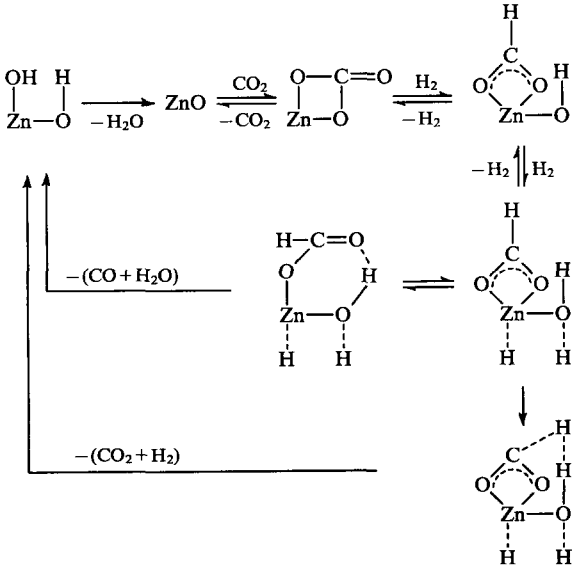
$$Ru^{2+}(HCOO^-) \rightleftharpoons Ru^+(H) + CO_2,$$

$$Ru^+(H) + CO \rightleftharpoons Ru^+(H)(CO),$$

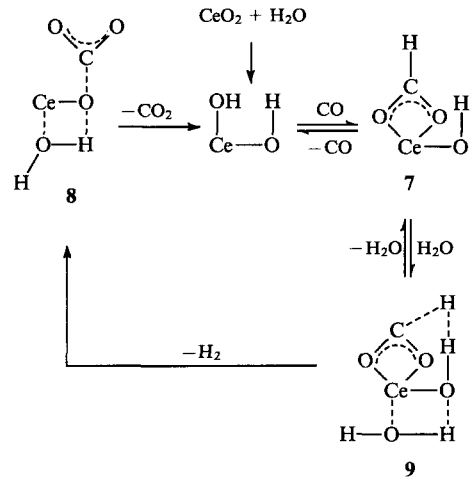
in which the formation of formate is the rate-limiting step.

On ZnO at 230 °C the rate of dissociation of the surface formate is equal to the rate of evolution of H_2O and CO into the gas phase after the hydrogenation of the CO_2.[28,29] On the other hand, if CO + H_2O is used as the initial mixture the production of formate is not observed. The opposite state of affairs is found on MgO:[28] formate is produced more easily from a mixture of CO + H_2O than from H_2 + CO_2. Under the conditions of the catalysis the MgO surface is covered mainly (90%) by carbonate, but the latter does not take part in the reaction.

The difference in structure between the surface complexes formed in the forward (CO + H_2O) and in the reverse reaction (CO_2 + H_2) on ZnO was reported also by Shido and Iwasawa.[30] By combining IR spectroscopy and labelled atom methods these workers showed that two types of formate complex exist on the surface. The first, formed from H_2 and CO_2, is 70% decomposed into H_2 and CO_2 at 250–300 °C, and 30% into H_2O (or surface OH groups) and CO. A different formate complex is obtained from OH and CO: this species is 70% decomposed with formation of OH and CO and 30% with formation of H_2 and CO_2. The activation energy for the decomposition of the formate complexes of the second type is 15–18 kJ mol^{-1} lower than for the first type. The rate of decomposition of the formate is much lower (by a factor of 10–30) in the presence of CO_2 than in a vacuum. Conversely, in the presence of H_2 the decomposition is faster. Under stationary conditions a balance is established between the promotion of the reaction by hydrogen and its suppression by CO_2. As reported,[30] the rate-limiting step is the dissociation of H_2 on a pair of Zn(HCOO)(OH). The overall reaction scheme can be written as follows.



The study of the interaction of CO and H_2O was extended to CeO_2 promoted by rhodium.[31] The activation energy for the decomposition of the formate complex produced from CO and OH was 56 kJ mol^{-1} (for the decomposition into H_2 + CO_2) and 122 kJ mol^{-1} (for the decomposition into OH + CO). In the presence of water vapour the rate of decomposition of $HCOO^-$ by the first path is increased 100-fold, and the activation energy falls to 33 kJ mol^{-1}. The rate-limiting step is assumed[31] to be the decomposition of the bidentate formate **7** into H_2 and the monodentate carbonate **8**. The evolution of CO_2 from the monodentate carbonate is promoted by H_2O through the intermediate complex **9**.



8 **7** **9**

The proposed mechanism differs from the mechanism of the same reaction on ZnO by the presence of the carbonate complex **8**. Rhodium itself is not active, but when added to CeO_2 it induces a rearrangement of the charges in the Ce–O pair which results in the activation of the C–H bond in the intermediate formate, in a closer approach of the formate to the neighbouring OH bridging group in the transition state **9**, and in a lowering of the activation energy.

Of the intermediates suggested above as participants in the water gas conversion the possible existence of the bridging carbonyl and carbonate complexes **8** can be assigned a reliability level L, and the existence of the formate complexes **7** a level M. However, the associative mechanism seems to be the most probable for the reaction: in this case the intermediate complex is not simply the formate but its associative complex with H_2O or H_2. The observation of various formate complexes, dissociating with different activation energies, suggests the possible migration of $HCOO^-$ from some centres to centres of other types.

V. Synthesis and decomposition of methanol

Methanol is synthesised at high pressures from a mixture of CO + H_2. According to Rozovskii[32] the species hydrogenated is CO_2, and not CO. The carbon dioxide is formed in the first step of the water gas conversion discussed in the previous section. The mechanism of the synthesis of methanol from CO + H_2 and from CO_2 + H_2 has been studied extensively.[33–47] The reverse reaction (decomposition of CH_3OH) has also been studied, because it takes place at low pressures and is therefore experimentally easier.

The Cu–ZnO–Al_2O_3 system is the most generally used methanol synthesis catalyst: most of the reported spectroscopic studies have relied on the use of this catalyst and of its components. IR spectroscopy measurements on the catalyst surface have revealed the presence of formates,[29,33–46] carbonates,[33,37–39,41,43] methoxy groups,[29,34,35,44,47] and formyl groups HCO,[34,36,40,43,46] as well as adsorbed forms of CO and CO_2. Adsorbed CH_2O has also been reported.[47] Many of these workers have formally proposed the following series of transformations for these compounds:

$$H_2 + CO\,(ads) \rightleftharpoons HCO \rightleftharpoons HCOO^- \overset{H_2}{\rightleftharpoons}$$

$$\rightleftharpoons CH_3O^- \overset{H_2}{\rightleftharpoons} CH_3OH.$$

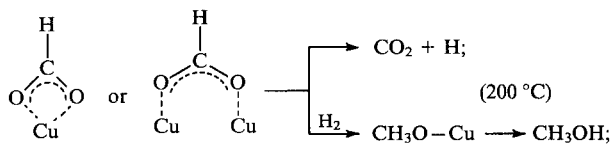
The same sequence of reactions was assumed[48] for the synthesis of methanol from CO_2 and H_2 on $Cu-ZnO-SiO_2$, in which the IR spectra of the surface compounds were examined after the reaction.

A detailed study[49] of the kinetics and of the mechanism of synthesis of CH_3OH on $Cu-ZnO-Al_2O_3$ led to the following scheme:

$$H_2 \rightleftharpoons 2\,H(ads),$$
$$CO_2 \rightleftharpoons CO_2(ads),$$
$$CO_2(ads) + H(ads) \rightleftharpoons HCOO(ads),$$
$$HCOO(ads) + 3\,H(ads) \rightleftharpoons CH_3OH + O(ads),$$
$$CO + O(ads) \longrightarrow CO_2,$$
$$H_2 + O(ads) \longrightarrow H_2O.$$

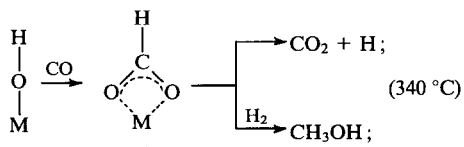
The location of these complexes is a problem of the greatest importance. Three types of adsorbed formate were detected by combining IR spectroscopic methods with temperature-programmed desorption (TPD) and with the method of chemical traps:

(1) formates adsorbed on Cu



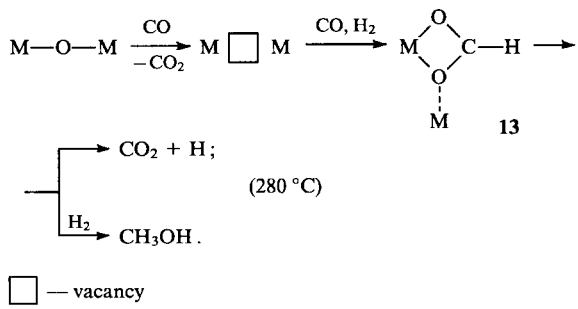
10 **11**

(2) formates adsorbed on Zn and Al atoms (with the participation of OH groups)



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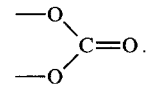
(3) formates produced after the partial reduction of the surface by carbon monoxide (evidently, near the boundary between Cu and ZnO)



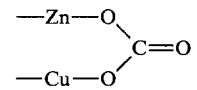
Many workers have detected a proportionality between the rate of the reaction of CO with H_2 (or of CO_2 with H_2), or of the amount of formate produced, and the copper content of the catalyst (or the surface area of the copper phase).[35,39,40,42] They concluded that the reaction takes place on the copper. There are also suggestions that $HCOO^-$ is formed near the Cu–ZnO boundary.[41,47] The hydrogenation of $HCOO^-$ to CH_3O (and even to CH_3OH) is treated as rate-limiting in the synthesis of CH_3OH from CO and H_2 (see Neophytides et al.[39]) or from CO_2 and H_2 (see Amenomiya and Tagawa[40]).

However, according to other workers[38,46,47] the formate is not an intermediate but a side-product of the methanol synthesis and decomposition processes. In a study of the synthesis of CH_3OH from CO and H_2 or from CO_2 and H_2 the IR spectra were obtained under high-pressure conditions.[38,48] At 200–220 °C both carbonate and formate complexes were detected on both Cu and ZnO. It was found that the formate complexes **10–13** are stable under the reaction conditions, and that upon further heating they decompose with evolution of CO (and not CO_2, as had been previously thought). Thus adsorbed CO is not a source of CH_3OH. On the other hand carbonate complexes are formed immediately after the adsorption of CO_2 and are converted into methanol during the subsequent hydrogenation. Thus it was concluded, in keeping with Rozovskii's views,[32] that the CH_3OH is formed from CO_2 and not from CO.

The role of carbonates in the synthesis of methanol was studied on the basis of IR spectroscopic measurements.[37,41,44] On ZnO the weakly bound bicarbonate HCO_3^- and the strongly bound carbonate CO_3^{2-} are formed, but on Cu we find the bidentate carbonate



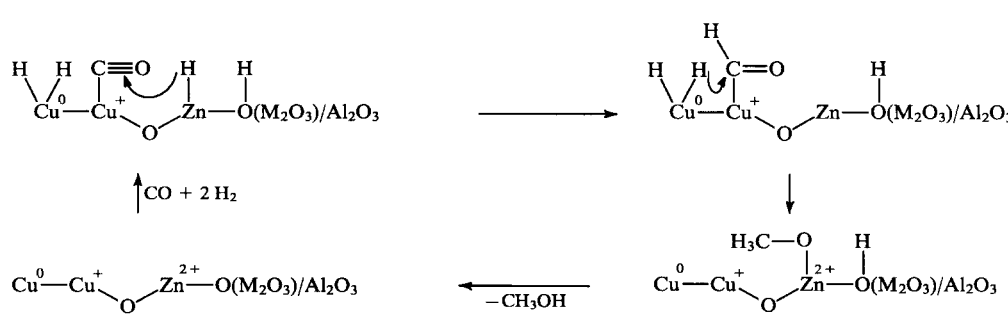
On mixed Cu–ZnO catalysts an absorption band at 1615 cm^{-1} was also found, and assigned to the carbonate



located at the phase separation boundary (known to be an active complex in the synthesis of methanol).[41] The hydrogenation of this carbonate produces formate. The formation of CO_3^{2-} during the adsorption of CO_2 is associated with the $Cu^0 \rightleftarrows Cu^+$ transition. It was also found that the formation of carbonates is approximately eight times greater in the adsorption of a mixture of $CO_2 + 2H_2$ than in the adsorption of CO_2 only,[37] i.e. that the hydrogen not only assists the adsorption of CO_2 (associative mechanism) but it also regenerates the centre needed for the subsequent adsorption of CO_2.

The adsorption of H_2 on ZnO at low temperatures results in the formation of Zn–H and O–H bonds, but at higher temperatures these bonds are not formed.[46] On this mixed catalyst we observe the migration (spill-over) of the hydrogen from the Cu to the ZnO and backwards, and this hydrogen contributes to the hydrogenation of the carbonate groups.[42]

Scheme 1



The nature of the synergism observed in the synthesis of methanol on a $Cu-ZnO-M_2O_3$ catalyst (M = Sc, Cr, V) has been studied by in situ Raman spectroscopy.[45] The Cu–H, Cu–O–H, Cu–CO, and Cu–CHO groups were detected on the catalyst surface. The mechanism of this reaction is shown in Scheme 1.

According to the Raman spectra additions of N_2O promote the adsorption of CO.

The simultaneous use of in situ IR spectroscopy and kinetic response methods showed that the formation of methanol from $CO + H_2$ and $CO_2 + H_2$ mixtures takes place by different mechanisms.[36] In the first of these mixtures surface formyl is produced from M–CO and M–H, and this step is rate-limiting, as shown by the appearance in the IR spectrum of an absorption band due to HCO immediately after the passage of a pulse through the $H_2 + CO$ mixture. In the $CO_2 + H_2$ mixture carbonates and formates are formed:

$$CO_2 + M \rightleftharpoons M{-}CO_2,$$

$$H_2 + M \longrightarrow M{-}H,$$

$$M{-}CO_2 + M{-}H \longrightarrow M{-}O{-}C(=O){-}H + M,$$

$$M{-}O{-}C(=O){-}H + 2\,M{-}H \longrightarrow M{-}O{-}CH_2{-}OH + 2\,M,$$

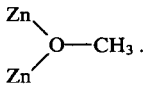
$$M{-}O{-}CH_2{-}OH + M{-}H \longrightarrow CH_3OH + M{-}OH + M,$$

$$M{-}OH + M{-}CO \longrightarrow M{-}O{-}C(=O){-}H + M.$$

In this case the rate-limiting step is (apparently) the dissociative adsorption of H_2 on ZnO and Cu and the migration of the hydrogen from the ZnO to the Cu. However, this dissociation is faster than the synthesis of CH_3OH from CO and H_2. Furthermore the CO_2 inhibits the disproportionation of CO into CO_2 and C, thus preventing the poisoning of the catalyst.

It has been shown[29] that the decomposition of the surface formates, which is very slow in the absence of a gas phase, is greatly accelerated by the presence of CH_3OH in the gas phase, i.e. the decomposition takes place by an associative mechanism.

The mechanism of the decomposition of CH_3OH on a $Cu-ZnO/Al_2O_3$ catalyst has been studied also by in situ ^{13}C and ^1H NMR methods.[50] The methanol is adsorbed on Al_2O_3 as $Al-OCH_3$, and on ZnO as



When heated on copper the OCH_3 group is oxidised to the symmetrical formate and beyond (to HCO_3^- and CO_3^{2-}), and CO_2 is evolved when the system is further heated to 250 °C. Under the conditions of the synthesis of CH_3OH many intermediate substances are adsorbed on ZnO and Al_2O_3, but in order to contribute to the synthesis these must migrate towards the copper. Experiments on the adsorption of CH_2O also show that this species can participate in the reaction, for example by disproportionation into CH_3O^- and $HCOO^-$, though in the synthesis process CH_2O is not adsorbed on the surface. Carbon dioxide is easily adsorbed on $Cu-ZnO/Al_2O_3$, giving a carbonate, whereas CO is adsorbed to a much smaller extent. The carbon monoxide also is converted into a carbonate during the oxidation. This indicates the participation of CO_2 (rather than CO) in the synthesis of methanol.

An NMR study[51] of the decomposition of CH_3OH on $Cu-ZnO/Al_2O_3$ detected methoxy among the adsorbed compounds.

Fu and Somorjai[52] studied the interaction of CH_3OH with Cu–ZnO by a combination of XPES, LEED, and temperature-programmed reaction (TPR) methods. The methanol reduces the ZnO and removes the adsorbed oxygen from the copper centres. The formate produced on clean copper decomposes into CH_2O and H_2. On Cu–ZnO also we observe the decomposition of $HCOO^-$ into $CO_2 + CO + H_2O$ at 380 °C and the decomposition of CH_3O^- into CH_2O and H_2 at 280 °C. The decomposition of $HCOO^-$ on ZnO produces a mixture of $CO + CO_2 + H_2O + CH_4$.

The formation of compounds on the individual components of the catalyst was studied in parallel with the mechanism of the synthesis of CH_3OH on $Cu-ZnO/Al_2O_3$. It was found that copper can catalyse all the stages. Nevertheless under the conditions of the synthesis of CH_3OH many compounds formed as intermediates are found on the support phases (ZnO and Al_2O_3): we should therefore stress the important role of synergism and spill-over effects in this process.

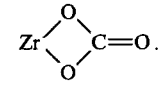
Spectroscopic methods have been used also in the study of other catalysts. For example, in situ IR spectroscopy was used to study the synthesis of CH_3OH on a K–Cr–Zn–O catalyst.[53] After the reaction CH_3O^- and $HCOO^-$ fragments were detected on the surface. In the presence of potassium we note a large increase in the $HCOO^-:CH_3O^-$ ratio. Methyl formate ($HCOOCH_3$) is formed at low temperatures on catalysts containing potassium, evidently as a result of the interaction of the unstable $HCOO^-$ with methane. The methyl formate can then take part in the synthesis of higher alcohols.

$HCOO^-$ and CH_3O^- groups were detected[17] during the decomposition of CH_3OH on Cr_2O_3. The adsorbed formate groups are stable in a vacuum, but in the presence of $^{13}CH_3OH$ vapour the ^{13}C isotope is easily incorporated into the $HCOO^-$ surface groups and hence into the reaction products. At the same time, according to IR spectroscopic data, the concentration of formate stays constant. This shows that the decomposition of CH_3OH takes place by an associative mechanism through 'desorption at the expense of adsorption', (in Tamaru's terminology[17]).

The synthesis of CH_3OH from CO and H_2 on ZrO_2 has been studied by IR spectroscopy and temperature-programmed desorption (TPD) methods.[54,55] It is accelerated by the presence of water, but ^{18}O atoms from $H_2{}^{18}O$ water do not penetrate into the CH_3OH. The following sequence of reactions is suggested:

$$CO(ads) \xrightarrow{OH^-} HCOO^- \xrightarrow{2\,H^+} OCH_3^- \xrightarrow[-OH^-]{H_2O} CH_3OH.$$

Thus, water is needed for the desorption of the methanol. A similar sequence of reactions was proposed by Onishi et al.[56] on the basis of an IR spectroscopic investigation, but these workers stipulated the formation of a bidentate carbonate group as the first stage after the adsorption of CO:



Formate is produced (with the participation of an oxygen atom from the oxide) in the interaction of H_2 with CO on MgO, CaO, La_2O_3, ThO_2, and ZrO_2 at 200–300 °C.[57] Comparing the IR with the TPD spectra showed that the formation of $HCOO^-$ is preceded by the formation (as an intermediate) of the formyl group HCO^-. The main product of the reaction was CH_3OH on La_2O_3 and ZrO_2, and CH_2O on MgO.

On Pd or Rh catalysts supported on SiO_2, Al_2O_3, or ZrO_2 (promoted with LiCl, NaCl, or KCl) formate was observed[58,59] by IR spectroscopy after the admission of a mixture of $CO + H_2$ at 180 °C. It was found that the higher the concentration of

adsorbed $HCOO^-$, the greater is the rate of the synthesis of CH_3OH. No absorption bands could be seen in the IR spectra of nonpromoted samples. The rate of formation of C_2H_5OH on $Rh-Na-Al_2O_3$ was approximately proportional to the intensity of the CH_3COO^- bands. These results led to the suggestion that the active centres contain oxidised compounds which stabilise the acetates and formates.[58]

Studies of the mechanism of the formation reaction of CH_3OH and C_2H_5OH at 240–280 °C on platinum catalysts prepared from $Pt_9(CO)_{18}.2NEt_4$ clusters supported on MgO, ZrO_2, and Al_2O_3 revealed the CO_2^{2-}, CO_3^{2-}, and CH_3O^- fragments stabilised on the carrier.[60] They are apparently formed by the interaction of Pt–CO with the OH groups (or the O^{2-} groups) of the carrier. Their hydrogenation produces the alcohols.

The decomposition of CH_3OH into CO and H_2 on Fe, Ni, or Pd foil was studied by molecular beam relaxation spectrometry.[61] The process was divided into several stages, and the kinetic parameters of each stage were determined:

$$CH_3OH \xrightarrow{(1)} CH_3OH(ads) \xrightarrow{(2)} CH_3O(ads) \xrightarrow{(3)}$$

$$\longrightarrow CH_2O(ads) \xrightarrow{(4)} \ldots \longrightarrow CO(ads) + 2\,H(ads),$$

$$CO \rightleftharpoons CO(ads),$$

$$H_2 \rightleftharpoons 2\,H(ads).$$

The reality of some of these stages was confirmed by the XPES method. On Ni the slow step was the third, with an activation energy of 104 kJ mol^{-1}. On Pd the desorption of CH_3OH could not be observed because its conversion into the subsequent products is very fast. In this case the desorption of CO becomes the rate-limiting step. On Fe the adsorbed CH_3OH can be converted into CO and H_2 through intermediate products, but it can also pass into another, unreactive form (CH_3OH^{II}):

$$CH_3OH^{I}(ads) \begin{cases} \longrightarrow CH_3OH^{III}(ads) \longrightarrow \ldots \longrightarrow CO + H_2, \\ \longrightarrow CH_3OH^{II}(ads). \end{cases}$$

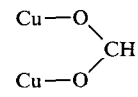
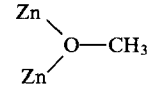
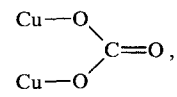
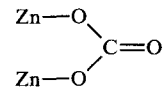
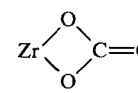
The activity of the Fe is determined by the relative probability of the reaction taking place by these two pathways. In terms of their activation energy (E_a) these metals can be arranged in the series Ni ≫ Pd > Fe, i.e. the highest E_a values are observed when the intermediates appear in the later stages of the reaction.

According to XPES and TPR data the decomposition of alkoxy groups on Fe(100) can follow one of three paths: (1) with formation of CO + H_2; (2) with formation of CH_3OH; (3) with full breaking of the C–H and C–O bonds. The last of these paths has been reported also by Benziger and Madix.[62]

Data on the intermediate compounds taking part in the synthesis and decomposition of CH_3OH are summarised in Table 2.

To conclude this section we note that, in spite of the large number of publications in which spectroscopic methods are used to study the synthesis and decomposition of CH_3OH, information on spectro-kinetic studies of these systems is almost totally absent (with a few exceptions[36,38,48,61]). The detection of the $HCOO^-$, CO_3^{2-}, CH_3O, and HCO groups on the catalyst surface is often interpreted as a proof that these species take part in the reaction as intermediates. However, direct kinetic confirmations of this conclusion are seldom put forward. Most probably the $HCOO^-$ groups contribute not to the synthesis or the decomposition of CH_3OH but to the corresponding conversion of water gas. A contribution from intermediate carbonates to the synthesis of CH_3OH is a more realistic suggestion. Furthermore, $M-CO_3$ complexes are formed simultaneously on the various phases of a complex catalyst, and it is essential to establish which of these contribute to the main reaction and which are a blind end-product or a reservoir for the former. Obviously, the spill-over phenomenon plays a very important role in the reaction mechanism. In many cases it has been established that the reaction follows an associative mechanism.

Table 2. Intermediates in the synthesis and decomposition of methanol.

Reaction, catalyst	Intermediate complex	Reliability	Ref.
Synthesis and decomposition of CH_3OH on $Cu-ZnO/Al_2O_3$	$HCOO^-$,	M	21, 29, 33–37, 39, 40, 41, 45, 50, 52
			
	CH_3O-Cu, 	M	29, 34, 35, 46, 47, 50, 51
	HCO	L	34, 36, 40, 43, 46
	CH_2O	L	47, 50
	$Cu-CO$, $Cu-H$, $Cu-HCOO$	M	36
		M	37, 38, 41, 44
			
Synthesis of CH_3OH on $Cu-ZnO-M_2O_3$	$Cu-H$, $Cu-CO$, $Cu-OH$, $Cu-HCO$	M	43
Decomposition of CH_3OH on $K-Cr-Zn-O$	CH_3O^-, $HCOO^-$	L	53
Decomposition of CH_3OH on Cr_2O_3	CH_3O^-, $HCOO^-$	L	17
Synthesis of CH_3OH on ZrO_2		L	54–56
	$HCOO^-$, CH_3O^-		
Synthesis of CH_3OH on MgO, CaO, SrO, La_2O_3, ThO_2, ZrO_2	$HCOO^-$	L	57
Synthesis of CH_3OH on Pd/SiO_2, Al_2O_3, ZrO_2	$HCOO^-$	M	58, 59
Synthesis of CH_3OH and C_2H_5OH on Pt/MgO, Al_2O_3 on ZrO_2	CO_2^{2-}, CO_3^{2-}, CH_3O^-	L	60
Decomposition of CH_3OH on Fe, Ni, Pd	CO(ads), H(ads), CH_3O(ads), CH_2O(ads)	L	61, 62

VI. Synthesis of hydrocarbons from carbon monoxide and hydrogen

The hydrogenation of CO to hydrocarbons (or Fischer–Tropsch synthesis) takes place on metals. Iron catalysts are most widely used for this reaction. However, they were studied mainly from the standpoint of their structural phase transformations under the reaction conditions. Less attention has been devoted to the forms adsorbed on the surface.

The state of the carbon on the iron surface was studied by XPES,[63–65] Raman,[66,67] and IR spectroscopy methods,[68] and also by the kinetic and the isotopic response method.[63,69–71] Three main forms of carbon were detected: graphite (which is universally known to be inactive in the Fischer–Tropsch synthesis), carbide carbon (which contributes to the synthesis of methane and of higher paraffins), and partially hydrogenated carbon CH_x (which can be hydrogenated further to give CH_4 and C_nH_m). There are also reports[64,69] of the formation of an amorphous, relatively porous form of carbon which can also be hydrogenated by hydrogen. According to Tan and Bennet[71] the real intermediate in the Fischer–Tropsch synthesis is the CH species. By using the method of 'interception' (with pyridine) of intermediate substances it was shown that alkyls can act as intermediate species of this type. Surface formates, carbonates, and carboxylates have also been detected: these are probably formed from the CO_2 produced by the disproportionation of CO.[72]

There are two contrary mechanisms for the hydrogenation of carbon monoxide by hydrogen: a dissociative and an associative mechanism.[73,74] According to the former the CO produces carbidisation of the metal (or other forms of carbon attributed to the dissociation of CO):

$$2\,Fe + CO + H_2 \longrightarrow Fe_2C + H_2O,$$

and

$$2\,Fe + 2\,CO \longrightarrow Fe_2C + CO_2,$$

and the carbide then interacts with hydrogen to give hydrocarbons

$$Fe_2C + 2\,H_2 \longrightarrow 2\,Fe + CH_4.$$

According to the associative mechanism the CO and H_2 from the gas phase react with atoms of the metal, forming complexes: for example[75]

$$H(ads) + CO(ads) \rightleftharpoons HCO(ads) \longrightarrow H_2CO(ads) \longrightarrow CH_3O(ads) \longrightarrow CH_3(ads) + O(ads).$$

The CH_3 group can be hydrogenated to methane or it can add on a CH_2 group, forming C_2 (and higher) hydrocarbons.

According to results from our laboratory[74] on iron catalysts this reaction involves oxides and carbides. The following mechanism can be proposed for the reaction at the metal–oxide boundary:

$$MO + CO = M\square_O + CO_2,$$

$$M\square_O + CO = C + MO,$$

$$2\,M + H_2 \longrightarrow 2\,M{-}H,$$

$$4\,M{-}H + C \longrightarrow 4\,M + CH_4.$$

$\square_O$ — oxygen vacancy on the catalyst surface

Here the hydrogenation of the carbon monoxide takes place mainly by a dissociative mechanism:

$$2\,CO + 2\,H_2 = CH_4 + CO_2.$$

An alternative reaction path for the hydrogenation of CO,

$$2\,CO + 3\,H_2 = CH_4 + H_2O,$$

is probably realised by an associative mechanism, involving the formation of HCO complexes in the presence of an excess of H_2 and a deficit of CO:

$$M'CO + M{-}H = M'COH + M,$$

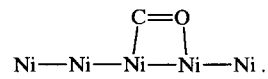
$$M'COH + 2\,M{-}H \longrightarrow M'OCH_3 + 2\,M,$$

$$M'OCH_3 + M \longrightarrow MO + M'CH_3 \xrightarrow{H_2} CH_4 + H_2O + M' + M.$$

It may be assumed that the activation of H_2 and CO takes place on different active centres: M and M'.

Nickel (unlike iron) is mainly a catalyst for the formation of methane from CO and H_2. Different forms of carbon (carbide, and hydrogenated) have been detected on a Ni surface by IR spectroscopy,[76–86] XPES,[87] and Auger spectroscopy.[88]

Bands corresponding to linear and to bridging CO groups were observed in the IR emission spectra for the interaction of CO and H_2 on 10% Ni/Al_2O_3; HCO groups were not detected.[82] It has been suggested[79] that the shift of the CO band in the IR spectra measured on Ni/SiO_2 and Ni/Al_2O_3 can be attributed to the formation of an associative HCHO complex. The pre-adsorption of H_2 on Ni(111) produces a shift in the bands of the adsorbed linear carbonyls (Ni–C≡O) towards the positions corresponding to the bridging C=O groups.[83] Evidently this can be explained by the formation of a surface carbonyl hydride in which the energy of the C–O bond is low and the dissociation of the carbonyl into carbide and oxide is facilitated. A possible precursor of the dissociated forms could be the 'recumbent' carbonyl



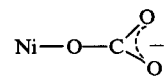
The 2050 cm^{-1} band in the IR spectrum of CO adsorbed on Ni/SiO_2 has been assigned to this form.[86]

Active carbon exists on the Ni surface in the relatively narrow temperature range between 200 and 450 °C. Above 450 °C it is rapidly converted into the inactive graphite, and below 200 °C there is no dissociation of the CO.[76,77] The following sequence of conversions of the carbon during its hydrogenation on a Ni plate has been established by in situ XPES[87] and 'absorbance-reflectance' IRS[81] methods:

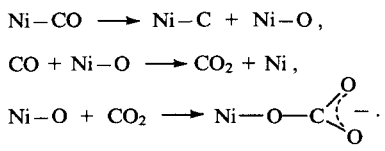
$$C \rightleftharpoons CH \longrightarrow CH_2 \rightleftharpoons CH_3 \rightleftharpoons CH_4.$$

Under reaction conditions the Ni surface is mostly covered with CH groups (Ni–CH), and their hydrogenation is probably rate-limiting.[81,87] At low temperatures we also find Ni–CH_2–Ni bridging groups, but these are lost from the surface even before the methanation temperature is reached. It is assumed[82] that under different conditions the rate-limiting step can be either the rate of formation of the CH_x species or the rate of their hydrogenation.

It has been reported[88] that the rate of methanation on Ni(100) increases with the concentration of carbon on the surface, whereas the yield of higher hydrocarbons increases with the oxygen concentration. The oxidised forms $HCOO^-$ and CH_3O^- are also found[76,77] on a Ni surface treated with a mixture of H_2 and CO, but they are hydrogenated less actively than the surface carbon. The appearance of carbonate



is apparently associated with the CO disproportionation reaction:[81]



The hydrogenation of CO to hydrocarbons on a cobalt film also includes the dissociation of CO, and probably takes place through carbide formation.[89]

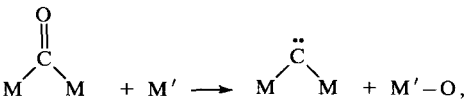
Cobalt favours the dissociative adsorption of CO more markedly than nickel.[90] This accounts for the preferential formation of methane on Ni and of methane with higher hydrocarbons on Co. However, if the Co is supported on metallic gold the rate of the hydrogenation reaction increases, the character of the CO adsorption changes, and the process takes place through the formation of HCHO complexes (or other 'associative' complexes) without dissociation of the CO.

Carbonyl groups, as well as hydrocarbons, formates, and carbonates, have been detected[91] by IR spectroscopy on Co/SiO_2 and Co/Al_2O_3 under conditions compatible with the hydrogenation of CO at 200–250 °C. The time-changes in the intensity of the bands show that these are reaction products accumulating on the surface.

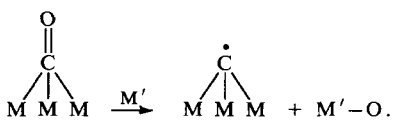
According to Loran et al.[92] the hydrogenation of CO on Ni, Ru, and Fe goes mainly via the breaking of the C–O bond in carbon monoxide, whereas on Rh and Mo it goes mainly via the breaking of the same bond in the HCHO complex.

The behaviour of bimetallic catalysts (for example, Ni–Fe and Co–Fe) towards the same reaction has also been studied.[74] The activity of the latter catalyst is attributed to the presence of cobalt, and the selectivity of the formation of olefins to the presence of iron. Obviously, the more active component contributes to the activation of H_2, and the less active to the activation of CO. It has been assumed, on the basis of IR spectroscopic data,[93] that the CO is more easily activated at the boundary between the oxidised and the reduced phase.

Also according to IR spectroscopic data[94] the most stable form of CO on Fe or Co is the bridging CO (ν_{CO} = 1800–1900 cm^{-1}), retained until the reaction temperature is reached. Its dissociation is accompanied by the formation of carbide and oxide:



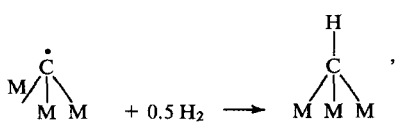
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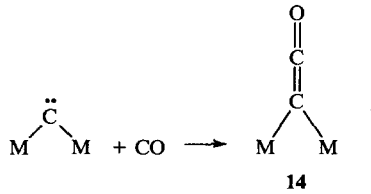


The surface carbides can then undergo hydrogenation or carbonylation.



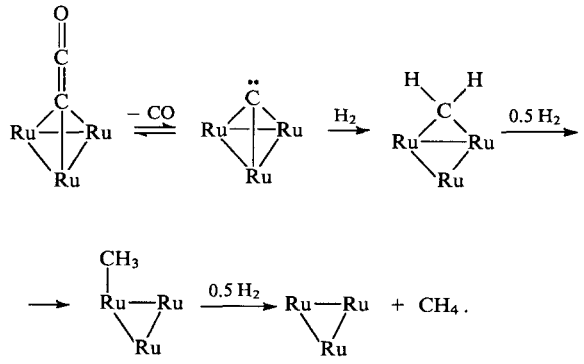
or





14

The transformations of the keten complex of ruthenium **14** supported on SiO_2 have been studied under the conditions of hydrogenation of CO at 200–300 °C:[91]



The reaction takes place by a dissociative mechanism: the associative mechanism, including (for example) the hydrogenation of the keten, is not observed.

We note that the dissociation of the C=C bond in the keten $CH_2=C=O$ added to a mixture of CO + H_2 in the hydrogenation of CO to hydrocarbons was observed by isotopic labelling more than 30 years ago.[95] The radioactivity of the hydrocarbons was found to be proportional to their carbon content. It was concluded from these results that the CH_2 species contribute to the chain initiation.

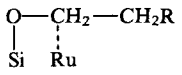
The transformation of the dissociative form of adsorption of CO into the molecular form during the carbidisation of the V(110) surface[96] is also of interest. As shown by an analysis of the EELS spectra, the C–C bond is produced during the adsorption of CO on VC, and this could be the initial stage in the subsequent synthesis of hydrocarbons.

On the platinum group metals (Ru, Rh, Pd) compounds containing oxygen are formed in addition to hydrocarbons. This is attributed to the high dissociation energy of CO on these metals.[97] On the platinum group metals (unlike iron) the energy of formation of the M–C and M–O bonds is of the same order of magnitude as the dissociation energy of CO. Many workers have studied the mechanism of the Fischer–Tropsch reaction by using a combination of physical methods. Ruthenium[97–119] and rhodium catalysts[102,120–134] were investigated most extensively.

According to IR spectroscopic measurements linear and bridging forms of CO and of the dicarbonyl $Ru(CO)_2$ are formed[97,102,104,105,108,116] on Ru/Al_2O_3. Under the catalysis conditions the linear CO groups are hydrogenated almost exclusively: the dicarbonyl groups do not contribute to the hydrogenation. Disproportionation of the CO by Boudart's reaction has also been observed.[109,123] The hydrogenation of CO takes place (apparently) through the intermediate dissociation of the linear form Ru–CO.[97,109] In the absence of H_2 the activation energy of the dissociation of CO is much higher than in its presence. The promoting action of H_2 is explained by the formation of H_2O, O(ads), and H(ads), which suppress the recombination of C and O and shift the equilibrium towards the dissociation of CO.[115] An alternative explanation of the decrease in the activation energy of the dissociation of CO in the presence of H_2 is the formation of the HCO complex.[99,117]

By using IR [97,111,114] and NMR [97,108,109] spectroscopy in conjunction with kinetic and isotopic response methods it was found that carbon is adsorbed on the surface of ruthenium in two forms: C_α and C_β. The first of these consists of adsorbed carbon atoms which are rapidly hydrogenated to CH_4 (few of these are found on a surface in a stationary state). The rate of formation of methane is directly proportional to the concentration of the C_α surface form. The C_β form consists of CH groups which accumulate on the surface and do not contribute significantly to the yield of CH_4. They are hydrogenated much more slowly than C_α CO groups are also found on the ruthenium surface, but practically no H(ads), since this is rapidly removed [98] as H_2O.

Further studies by NMR of the adsorption forms of carbon revealed the presence of four distinct forms on Ru: C_α (carbon atoms), and $C_{\beta1}$, $C_{\beta2}$, $C_{\beta3}$ (different alkyl groups). [99,101,108] The $C_{\beta1}$ form is a possible intermediate in the formation of the C_2 product. The $C_{\beta2}$ form apparently acts as a source for the formation of long hydrocarbon chains, most of which remain on the surface, and $C_{\beta3}$ is a source of branched products. The intensity of the CH_2 bands observed in the in situ IR spectra is not correlated with the rate of the reaction: evidently, these bands are due to the accumulation of reaction products on the surface. [106,107] Under the synthesis conditions (at high pressures) the hydrocarbons accumulated on the Ru surface are also bound to the support: [112]



The oxygen compounds HCO and $HCOO^-$ are also formed on the surface of supported ruthenium catalysts. [114,117] On Ru(001) promoted by potassium we find carbonate and formate:

$$CO \longrightarrow CO_2 + C\,,$$

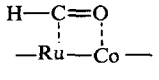
$$CO_2 + K_2O \longrightarrow K_2CO_3 \xrightarrow{H_2} KHCOO\,.$$

The conversion of water gas under the influence of alkaline additives also takes place through formate as an intermediate:

$$CO + H_2O \longrightarrow HCOO^- + H^+ \longrightarrow CO_2 + H_2\,.$$

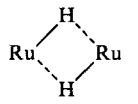
The formate is then hydrogenated to CH_4 and CH_3OH. In the absence of potassium only methane is formed.

According to calculations [94] the activation energy for the hydrogenation of HCO is smaller than for the dissociation of HCO. Therefore HCO can be hydrogenated to H_2CO(ads), CH_3O(ads), and beyond (to alcohols and hydrocarbons). As reported, the intensity of the 1584 cm^{-1} HCO band is correlated with the rate of the synthesis of oxygenated compounds. [117,134] On $Ru-Co/SiO_2$ catalysts this absorption band corresponds to the complex



The conversion of HCO into $CH_3C{=}O$ and $C_mH_nC{=}O$ groups bound to Ru and Co has been studied spectroscopically.

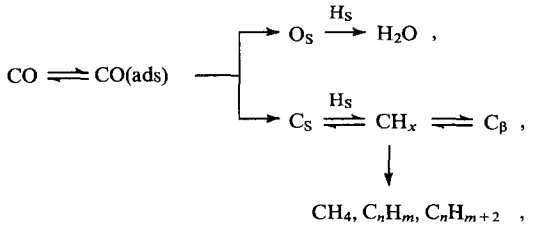
The role of carbides in the hydrogenation of CO has been studied by IR and EXAFS spectroscopic methods in the case of $[Ru_6C(CO)_{16}(CH_3)]^-$ complexes supported on MgO, ZnO, La_2O_3, TiO_2, ZrO_2, and Al_2O_3. [118,119] Whereas the carbide complex of Ru takes part in the synthesis of oxygenates, hydrocarbons and CH_4 are formed on the ordinary (carbonyl) Ru complex. It has been shown [118,119] that the central carbide atom in the cluster determines the structure of the intermediate complex, enabling it to add reversibly 8 – 11 molecules of CO onto each cluster. Under these conditions the cluster continuously expands or shrinks. The presence of a large number of adsorbed CO molecules in the bridging form (Ru_2CO) suppresses the dissociation of CO and favours the synthesis of the oxygenated compounds CH_3OH, CH_3OCH_3, and CH_2O. The expanded Ru_6C structures are more active than the compressed structures because they favour the dissociative adsorption of H_2:



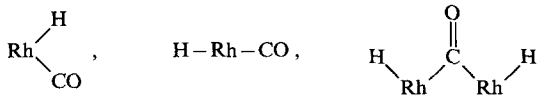
The H/D isotope exchange on the Ru_6C/MO carbide cluster is 3000 times faster than the stationary synthesis of oxygen compounds.

The low activity of rhodium towards the dissociation of CO accounts for its high activity towards the synthesis of the higher hydrocarbons (the Fischer – Tropsch reaction) and of oxygenated compounds. The Rh^0 form plays an important role in the synthesis of hydrocarbons, and Rh^+ in the synthesis of alcohols. [132] Obviously, the Rh^0-Rh^+ pairs in catalysts such as Rh/ZnO and Rh/TiO_2 can assist both the dissociation of carbon monoxide and the introduction of CO into the growing chain. [132,133]

The analysis of the IR [102,121,127] and NMR spectra [124] of the products adsorbed on supported Rh catalysts also indicates the formation of different carbonyl groups, and also of the C_α and C_β forms of carbon. The following reaction scheme was proposed: [206]

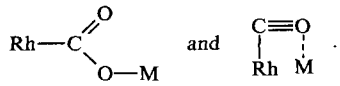


(the subscript S denoting surface atoms) according to which the form C_β does not take part in the hydrogenation of CO. The presence of H_2 assists the adsorption of CO on Rh as a result of the formation of complexes of the CH_2O type. In the methanation of CO on Rh/Al_2O_3 the formation of carbonyl hydrides has been reported: [123]

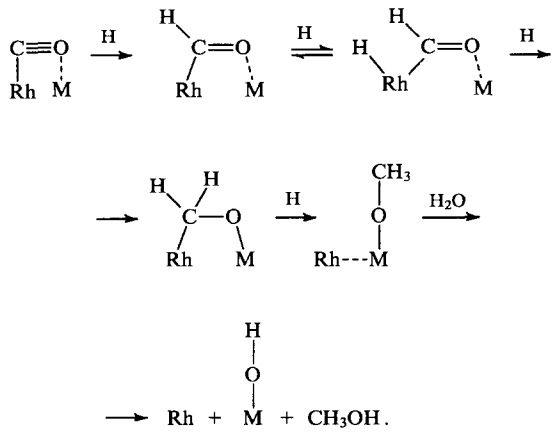


15

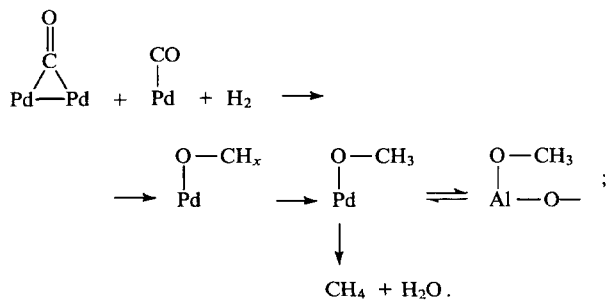
The formation of the complex **15** and the synthesis of hydrocarbons take place below the temperature of the Boudart reaction, i. e. the dissociation of CO is not observed under these conditions. The oxygenated groups OCH_3, OC_2H_5, HCOO, HCO, CH_3CO, CH_3COO, and CO_3 were detected on the rhodium surface by IR [127–130] and NMR spectroscopy. [124] The formate is produced mainly on the support: under the catalysis conditions it is fairly stable and it cannot act as an intermediate, whereas $HCOO^-$ adsorbed on metallic rhodium can play this role. [120,127] The same is true of the carbonates and acetates, which are also adsorbed mainly on the support. [128] Evidently, the active centres for the formation of oxygen compounds are on the boundary between Rh and the support. [122] Two adsorption complexes of CO, formed at the metal – support interface, have been observed [130] on Rh and Mo catalysts supported on ZrO_2:



Their dissociation is facilitated in the presence of hydrogen by the formation of the intermediate complex Rh–CHO, which is then (apparently) converted into $Rh{=}CH_2$ and methane. Methanol is obtained by the series of reactions



The properties of palladium are similar to those of Ru and Rh.[102,135–140] A scheme for the methanation of CO on Pd, involving the fully dissociated forms C(ads), H(ads), and O(ads), has been proposed.[131] The maximum coverage of the Pd/TiO_2 surface by linear carbonyls is 1%, and the maximum coverage by bridging carbonyls is 0.1%. Carbonyl groups and CH_3O, HCOO, and HCO groups, stabilised mainly on the carrier, have been observed[137] in the hydrogenation of CO on Pd/Al_2O_3. Spill-over of these species between the palladium and the Al_2O_3 was also noted. According to these workers[137] the source of the formation of CH_4 are the CH_3-O-Pd groups:



According to Hindermann et al.[138] the key intermediate in the hydrogenation of CO on $Pd-MgO-SiO_2$ is the formyl group HCO. This was confirmed by the chemical interception method with dimethyl sulfate. The presence of surface formate was also noted. Its hydrogenation has been stated[140] to be the rate-limiting step.

No correlation between the catalytic activity and the concentration of CO groups on the surface was observed[141] in a study of the hydrogenation of CO on Pt/TiO_2 by IR spectroscopy. It was concluded that only a very small part of the surface CO contributes to the hydrogenation. The active centres are, apparently, the steps or kinks on the platinum crystallites, which do not appear in the spectra.

The formation of CH_3O, which is rapidly hydrogenated to methane, was observed[142] during the hydrogenation of CO on Pt/Al_2O_3. Most of the CH_3O is adsorbed on the carrier, and the H(ads) species can move from the Pt to the Al_2O_3 (and hydrogenate the CH_3O) by the spill-over effect.

According to in situ IR spectroscopic data[76] on supported iridium the reaction proceeds by the scheme

$$CO \rightleftharpoons CO(ads),$$

$$H_2 \rightleftharpoons 2\,H(ads),$$

$$CO(ads) + H(ads) \longrightarrow C(ads) + OH(ads),$$

$$2\,CO(ads) \longrightarrow C(ads) + CO_2(ads),$$

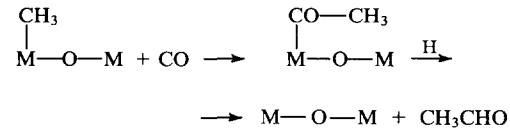
$$C(ads) + H(ads) \longrightarrow CH(ads) + CH_4,$$

$$OH(ads) + H(ads) \longrightarrow H_2O.$$

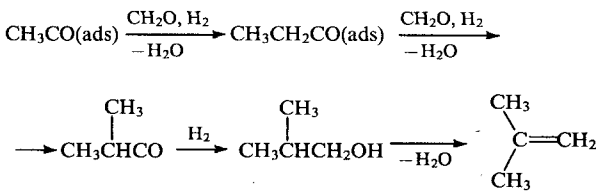
The contribution of the disproportionation of CO to the overall transformation is not substantial (only 0.8% of CO_2 is detected for a 60% conversion of the CO). The rate of hydrogenation of the adsorbed carbon is much higher than that of CO, but the adsorbed carbon is formed not by the direct dissociation of CO but by the interaction of CO with the adsorbed hydrogen (possibly through the HCO stage) by an associative mechanism.

A similar dissociative mechanism has been proposed for the hydrogenation of CO on $Ir_4(CO)_{12}$ clusters supported on α-Al_2O_3.[143] The formation of carbide, carbonyl, and oxide surface compounds has been observed by IR spectroscopy when the reaction was carried out at 250–300 °C. The rate-limiting step is the hydrogenation of the carbonyls. The formation of $Ir_xC(CO)_y$ carbide–carbonyl clusters under the reaction conditions has also been suggested, but these clusters have not been observed directly.

The hydrogenation of CO on ZrO_2 can lead to the selective synthesis of isobutene. HCOO and CH_3O groups were observed on the surface by using in situ NMR and IR spectroscopic methods.[144,145] The presence in the reaction of CH_3 and CH_2 species was also demonstrated by the kinetic interception method, using special acceptors. The introduction of the CO group into the $M-CH_3$ bond results in the formation of a new C–C bond:



The synthesis of isobutene can also take place by the aldol condensation mechanism[145]



The HCOO, CO_3, and CH_3O groups have been observed[146] by in situ IR spectroscopy at 200–400 °C on the catalyst surface during the hydrogenation of CO on Sm_2O_3. This led to the suggestion of a chain of transformations leading to the formation of methanol at temperatures below 300 °C and of hydrocarbons above that temperature.

Table 3 lists the data on the intermediate compounds which take part in the hydrogenation of CO to hydrocarbons (the Fischer–Tropsch synthesis and methanation).

In spite of the many reported studies of the CO hydrogenation mechanism by spectroscopic and kinetic methods very few truly spectroscopic investigations can be found. The best publications[97,98,104,108,109] show that the hydrogenation of CO on ruthenium catalysts takes place through the dissociative (C_α) forms of carbon. However, even these results were based on an

Table 3. Intermediates in the hydrogenation reactions of CO to hydrocarbons.

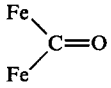
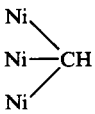
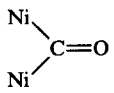
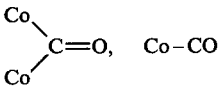
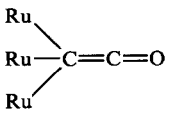
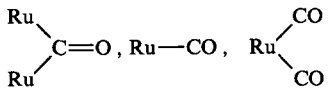
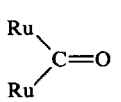
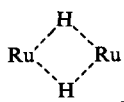
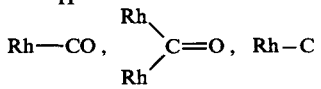
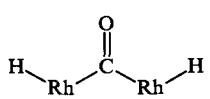
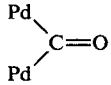
Reaction, catalyst	Intermediate complex	Reliability	Ref.
Hydrogenation of CO on Fe	FeC_x carbides	L	64–71
	$Fe-CH_x$	L	71
	Fe_5C_2, Fe–O, 	M	74
Methanation of CO on Ni (metallic or supported)	NiC_x, C(ads)	L	76–78
		L	81, 87
	Ni–CO, 	M	79, 82
		L	79, 86
Hydrogenation of CO on Co (metallic or supported)	C(ads), O(ads)	L	89
		L	74, 91
Hydrogenation of CO on Ru/SiO_2 and Ru/Al_2O_3		M	94
		M	98, 102, 104, 105, 108, 116
	C(ads), CH(ads)	M	97–99, 101, 108, 109, 111, 114
Hydrogenation of CO on Ru(001)	$HCOO^-$, CO_3^{2-}	L	113
Hydrogenation of CO on a $[Ru_6C(CO)_{16}(CH_3)]^-$ cluster supported on MgO, ZrO_2, Al_2O_3, SiO_2, etc.		M	118, 119
			
Hydrogenation of COO on Rh/SiO_2		L	106, 121, 123, 124
		M	123
	$HCOO^-$, OCH_3, OC_2H_5, CH_3COO^-, HCO	L	120, 122, 124, 127, 128

Table 3 (contd)

Reaction, catalyst	Intermediate complex	Reliability	Ref.
Hydrogenation of CO on Pd/SiO_2 and Pd/Al_2O_3	Pd–CO, Pd–OCH_3, 	M	136
	Pd–C, Pd–O, Pd–H, Pd–OH	L	102, 135–139
	HCO	L	138
Methanation of CO on Ir/SiO_2 and Ir/Al_2O_3	C(ads), OH(ads), CH(ads), O(ads), CO(ads)	L	77, 141
Hydrogenation of CO on Pt/TiO_2	Pt–CO	L	142
Hydrogenation of CO on Pt/Al_2O_3	Al–OCH_3, Pt–H	M	143
Hydrogenation of CO on Sm_2O_3	$HCOO^-$, CO_3^{2-}, CH_3O	L	146
Hydrogenation of CO on ZrO_2	$HCOO^-$, CH_3O^-, $^{\cdot}CH_3$, $:CH_2$	M	144, 145

analysis of NMR spectra, which cannot always be obtained directly under the experimental conditions because of experimental difficulties. The existence of the intermediate compound HCO seems very likely, but a direct spectroscopic proof of this assumption is still not available. The HCOO, CH_3O, and other groups observed under catalysis conditions are usually stabilised on the carrier and not on the active phase of the catalyst.

Most of the results point to a dissociative mechanism for the hydrogenation of CO, but associative mechanisms cannot be excluded.

VII. Hydrogenation of carbon dioxide

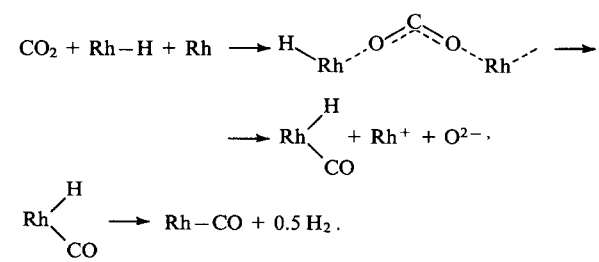
We have already discussed the hydrogenation of CO_2 as the reverse reaction of the conversion of water vapour (see Section IV), and also in connection with the synthesis of methanol on zinc–copper catalysts (see Section V). In this section we shall examine some data on the methanation of CO_2 on metallic catalysts.

The methanation of CO_2 on Rh/Al_2O_3 has been studied [147–151] by IR spectroscopy. An analysis of the IR diffuse reflectance spectra revealed HCOO groups on Rh/Al_2O_3 and HCOO and CH_3O groups on $Rh/Lu-Al_2O_3$.[147] In the first case the activation energy for the formation of CH_4 is 67 kJ mol^{-1}, and in the second case 96 kJ mol^{-1}. When CO_2 is added to the catalyst it is dissociated into CO and O(ads), and the further addition of H_2 produces formates. Stopping the addition of CO on Rh/Al_2O_3 lowers the intensity of the CO bands in the IR spectra to zero, whereas the intensity of the HCOO bands also falls but not to zero. On $Rh/Lu-Al_2O_3$ the concentration of CO groups decreases rapidly, but that of HCOO decreases slowly. From this evidence the authors conclude that the formates contribute to the conversion of water gas rather than to the synthesis of methane: the HCOO decomposes with formation of CO, which is then hydrogenated to CH_4.

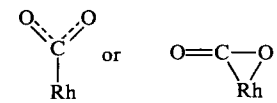
The CO, HCOO, and HCO_3 surface groups have been observed [148–151] by IR spectroscopy and EELS in the reaction of $H_2 + CO_2$ on Rh/Al_2O_3. On the unsupported catalyst HCOO groups are not formed, and on the catalyst with a carrier they appear mainly as a result of the spill-over of hydrogen from the Rh onto the carrier. The dissociation of CO_2 on Rh is assisted by the presence of H_2 because in the bent structure



an electron can be transferred from the adsorbed H_2 through the Rh to the π orbital of CO_2:



The formate group produced by the hydrogenation of Rh–CO is transferred (by spill-over) to the Al_2O_3, where it is stabilised. On the $K-Rh/SiO_2$ catalyst the band of the CO_2^- anion bound to potassium can be seen: this group is then hydrogenated to give $HCOO^-$.[151] In the absence of K or Rh no formate is produced. On massive Rh a weakly bound molecular form was observed by the EELS method during the adsorption of CO_2:



In the presence of potassium the following reactions take place:[152]

$$2\,CO_2^- \longrightarrow CO_3^{2-} + CO,$$

$$2\,CO_2^- \longrightarrow C_2O_4^{2-},$$

$$K^+ + CO_2^- \longrightarrow KO^- + CO(ads).$$

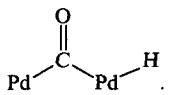
In the hydrogenation of CO_2 on $Rh-Mo/ZrO_2$ linear and bridging carbonyl forms are produced, as well as carbonate and formate, on the ZrO_2.[153]

CO(ads) and $HCOO^-$ have been detected on Ru/TiO_2 under the CO_2 hydrogenation conditions by IR diffuse reflectance spectroscopy.[154,155] The stationary concentration of CO(ads) is correlated with the rate of formation of CH_4. It was shown by the response method that the concentration of $HCOO^-$ is rapidly suppressed by the removal of H_2 from the gas mixture, but unfortunately these workers [154,155] did not provide a quantitative comparison of the concentrations of $HCOO^-$ and H_2. The formate

(or even HCOOH) produced can decompose into H_2O and CO (i. e. it can undergo a reaction which is the reverse of the conversion of water gas), or it can be hydrogenated to $CH_4 + H_2O$ in several stages. The hydrogenation of CO takes place only on a small number of Ru centres, and therefore the direct spectroscopic observation of the formation of CH_4 is experimentally difficult.

On $Ru-RuO_x/TiO_2$ the formation of various carbonyls has been observed by IR spectroscopy after the adsorption of CO_2, and after exposure to a $CO_2 + H_2$ mixture the complexes RuO_x-CO and $H-Ru-CO$ were observed.[156] Under these conditions the H or O atoms adsorbed on Ru facilitate the dissociation of the C–O bond. The much lower methanation temperature of CO_2 (as compared with CO) has been stressed: this effect is ascribed[154] to the high reactivity of the carbonyls at the instant of the dissociation of CO_2 (and also, possibly, to the formation of CO free radicals), which are subsequently converted into active carbon and methane. At high temperatures the hydrogenation mechanism of CO can include the formation of CO_2 by the Boudart reaction and its subsequent dissociation.

A study[149] of the hydrogenation of CO_2 on Pd supported on SiO_2, MgO, TiO_2, and Al_2O_3 showed that the interaction of CO_2 with Pd is facilitated in the presence of H_2 by the formation of the complex



On an iron foil the only product of the hydrogenation of CO_2 is CH_4, i. e. the process has a high selectivity.[157] On the other hand in the presence of surface oxide some CO is formed by a process which is the reverse of the water gas conversion. The high selectivity is attributed to the rapid coverage of the surface by a layer of carbon: the reaction then proceeds on the active Fe and FeC_x centres.

Magnetic studies have shown[158] that in the hydrogenation of CO_2 on Ni the carbide Ni_3C is produced by the scheme

$$CO_2 + Ni \rightleftharpoons Ni_xCO(ads) + NiO(ads),$$

$$Ni_xCO(ads) \rightleftharpoons Ni_3C + NiO(ads).$$

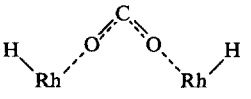
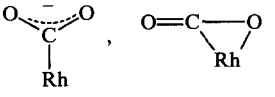
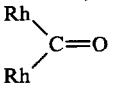
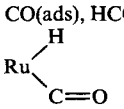
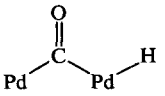
The carbide is then hydrogenated to CH_4. The methanation of CO_2 on Ni is faster than the methanation of CO.

The formates observed by IR spectroscopy during the hydrogenation of CO_2 on $La_{1-x}M_xCoO_3$ perovskites are probably intermediates in the equilibrium of the water gas conversion and of its reverse reaction. The hydrogenation of CO_2 to hydrocarbons takes place through the dissociated forms of CO_2 and H_2.[159]

Table 4 shows some data on the compounds proposed as intermediates in the hydrogenation of CO_2 to methane.

Some attempts to use spectrokinetic methods in studies of the hydrogenation mechanism of CO_2 have been reported,[154,155] but they gave ambiguous results (evidently because of the low

Table 4. Intermediates in the hydrogenation of CO_2.

Reaction, catalyst	Intermediate complex	Reliability	Ref.
Hydrogenation of CO_2 on Rh/Al_2O_3	CO(ads)	M	147–151
		L	148–150
		L	148–150
	Rh–HCOO	L	148–150
	CH_3O^-,	L	147
Hydrogenation of CO_2 on metallic Rh		L	152
Hydrogenation of CO_2 on $Rh-Mo/ZrO_2$	Rh–CO, $HCOO^-$, CO_3^{2-}, 	L	153
Hydrogenation of CO_2 on Ru/TiO_2	CO(ads), $HCOO^-$, RuO_x-CO, 	M	154–156
Hydrogenation CO_2 on Pd supported on SiO_2, MgO, TiO_2, Al_2O_3		L	149
Hydrogenation of CO_2 on Fe foil	C(ads)	L	157
Hydrogenation of CO_2 on Ni	Ni_3C	L	158
Hydrogenation CO_2 on spinels	C(ads)	L	159

sensitivity of the method). The only conclusion from this work was that adsorbed carbonyl is a likely intermediate in the hydrogenation reaction, whereas formate is an intermediate in the reverse water-gas formation reaction, i. e. in the reduction of CO_2 to CO.

VIII. Carbonylation and hydroformylation

The mechanism of carbonylation on heterogeneous catalysts containing rhodium or iridium is similar to the homogeneous carbonylation mechanism. In the homogeneous carbonylation on carbonyl complexes of Rh, Ru, Ir, and Co, intermediate compounds including carbonyl hydrides were detected, and in some cases CH_3OH and CH_3 species were found in the form of ligands bound to a metal atom.[160] Zeolites, which can be treated as solid quasihomogeneous systems, are mostly used as heterogeneous catalysts.

In situ IR spectra were obtained under methanol carbonylation conditions on zeolites containing rhodium at 150–200 °C.[161] On RhNaX we observe the conversion of CO under the influence of water vapour:

$$Rh^{3+} + H_2O + 3\,CO \longrightarrow Rh^{+}(CO)_2 + CO_2 + 2\,H^{+}.$$

During the interaction of CO with CH_3OH bands corresponding to CH_3COOCH_3, $(CH_3)_2O$, H_2O, CH_3O^-, and perhaps also to adsorbed CH_3COOH can be observed.

The following reaction has been studied[162] on IrNaY and RhNaY in the presence of CH_3I:

$$2\,CH_3OH + CO \longrightarrow CH_3COOCH_3 + H_2O.$$

It was found that initially the active species $[I_2Rh(CO)_2]^-$ is formed on RhNaY. The rate-limiting step of the reaction is the oxidative addition of CH_3I

$$[I_2Rh(CO)_2]^- + CH_3I \longrightarrow [I_3Rh(CO)_2CH_3]^-,$$

followed by the fast rearrangement of $[I_3Rh(CO)_2CH_3]^-$ into the rhodium acetyl derivative $[I_3Rh(CO)(COCH_3)]^-$, accompanied by the evolution of methyl acetate (in methanolysis) or of acetic acid (in hydrolysis). The rate of the reaction on rhodium catalysts is described by the equation $v = kP^1_{CH_3OH}P^0_{CO}P^0_{CH_3I}$, whereas in homogeneous carbonylation the rate equation is $v = kP^0_{CO}P^0_{CH_3OH}P^1_{CH_3I}$. On the IrNaY catalyst the rate of the reaction is described by the equation

$$v = k\frac{P_{CH_3OH}}{1 + k'P_{CH_3OH}}.$$

The rate-limiting step of the reaction is the adsorption of CH_3OH. Subsequently, under the influence of CH_3OH, the methyl group in $I-Ir(CH_3)(COOCH_3)(CO)_2$ is converted into the alkoxycarbonyl group, forming methyl acetate. The mechanism of the reaction can be described by the scheme

$$Ir + 3\,CO \longrightarrow [Ir(CO)_3] \xrightarrow{CH_3I} [I-Ir(CH_3)(CO)_3].$$

The hydroformylation or oxo-synthesis, i. e. the reaction of olefins with CO and H_2 (by which aldehydes are produced), also takes place on homogeneous and on heterogeneous catalysts. A study of the hydroformylation of C_2H_4 on Rh/SiO_2 by in situ IR spectroscopy has shown the presence of various forms of adsorbed CO. The introduction into adsorbed ethylene of the linear form of adsorbed CO produces the acyl group C_2H_5CO. The addition of CO takes place more readily than the synthesis of hydrocarbons from CO and H_2.[163–165] A study of some special features of the reaction kinetics[165] showed that acyl is not the main intermediate in the reaction.

According to in situ IR spectroscopy results[166] the CO group in the $Rh_6(CO)_{16}/SiO_2$ complex bound to the terminal Rh atom (1805 cm^{-1}) is more difficult to introduce into the Rh–C bond than the dicarbonyl group and the lienar form of CO on Rh crystallites. The low activity of this group is attributed to the absence of the rhodium centres needed for the adsorption of C_nH_{n+1}, C_2H_4, and H_2 from the surrounding of the rhodium atom. In the stationary state the rhodium is in the oxidised form Rh^+, and the limiting step is the hydrogenation of C_2H_5CO into C_2H_5CHO.

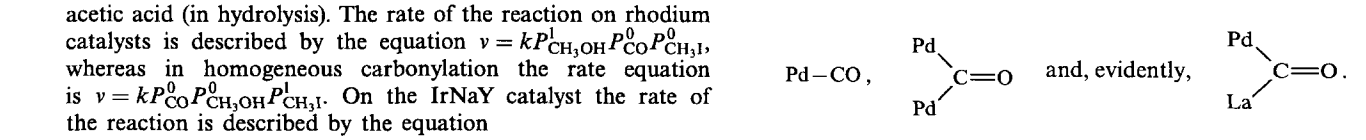
Two carbonyl complexes of rhodium, $Rh_6(CO)_{16}$ and $Rh(CO)_2$, have been detected[167] under the conditions of hydrocarbonylation of C_2H_4 on RhY. When the first complex is dissociated it is converted into CH_3CH_2CHO by the loss of several CO molecules. The second complex becomes active after lengthy exposure to a $C_2H_4 + H_2$ mixture. A likely intermediate compound in the hydroformylation of ethylene is $HRh(CO)_x$.

According to Natio and Tanimoto[168] the hydroformylation of propene on Rh/SiO_2 and Pd/SiO_2 takes place by the scheme

$$H_2 + 2\,Z \overset{(1)}{\rightleftharpoons} 2\,HZ,$$
$$CO + Z \overset{(2)}{\rightleftharpoons} COZ,$$
$$C_3H_6 + Z \overset{(3)}{\rightleftharpoons} C_3H_6Z,$$
$$C_3H_6Z + HZ \overset{(4)}{\rightleftharpoons} C_3H_7Z + Z,$$
$$C_3H_7Z + COZ \overset{(5)}{\rightleftharpoons} C_3H_7COZ + Z,$$
$$C_3H_7COZ + HZ \xrightarrow{(6)} C_3H_7CHO + 2\,Z,$$
$$C_3H_7Z + HZ \xrightarrow{(7)} C_3H_8 + Z.$$

where Z is an active surface centre. The competition between the stages (*5*) and (*7*) determines the selectivity of the reaction. On palladium step (*5*) is limiting, and on rhodium step (*6*). The activation energy of the hydroformylation is 57 kJ mol^{-1} on Rh/SiO_2 and 69 kJ mol^{-1} on Pd/SiO_2, i. e. the activation energy of step (*6*) is lower than that of step (*5*).

Bridging and linear carbonyls are observed on the surface under the conditions of the hydroformylation of propene and hex-1-ene on Pd/SiO_2 and $Pd-La/SiO_2$ at 250 °C and 10 atm:



Carbon monoxide adsorbed on La and on Pd does not contribute to the addition reaction on the $Pd-C_3H_7$ bond.[169] Spill-over of hydrogen between the Pd and the SiO_2 has been observed by the programmed temperature desorption (PTD) method. The magnitude of the spill-over is well correlated with the yield of reaction products.[169]

The hydroformylation of C_2H_4 and C_3H_6 has also been studied on the $RhFe_2$, $PtFe_2$, and $PdFe/SiO_2$ clusters.[170] A possible reaction mechanism is

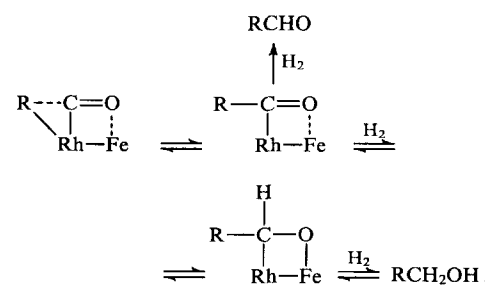
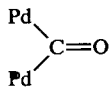
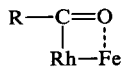


Table 5. Intermediates in carbonylation and hydroformylation reactions.

Reaction, catalyst	Intermediate complex	Reliability	Ref.
Carbonylation of methanol onRhY	$Rh^+(CO)_2$, CH_3O^-, CH_3COOH(ads)	M	161
Carbonylation of methanol on RhY	$[I_2Rh(CO)_2]^-$ $[I_3Rh(CO)_2CH_3]^-$ $[I_3Rh(CO)(COCH_3)]^-$	M	162
Carbonylation of methanol on IrY	$[Ir(CH_3)(CO)_2]^-$ $Ir(CH_3)(COCH_3)(CO)_2$	M	162
Hydroformylation of C_2H_4 on Rh/SiO_2	CO(ads), $C_2H_5CO^-$	L	163–165, 167
Hydroformylation of C_2H_4 on RhY	$Rh_6(CO)_{16}$, $Rh^+(CO)_2$	L	166
Hydroformylation of C_3H_6 and 1-C_6H_{12} on Pd/SiO_2	Pd–CO	M	168, 169
		M	169
Hydroformylation of C_2H_4 and C_3H_6 on Rh–Fe/SiO_2		L	170

A summary of the data on the intermediate compounds taking part in the carbonylation and hydroformylation reactions is shown in Table 5.

Thus definite reaction sequences have been established from IR spectroscopic data for the carbonylation and hydroformylation reactions: their reliability is confirmed (essentially) by comparing the sequences with those of the analogous homogeneous reactions. Some stages of the process can take place by associative mechanisms involving hydrogen. It is stated that the intermediates in these reactions are adsorbed carbon monoxide and the alkyl and acyl groups. Spectro-kinetic studies have not been reported.

IX. Reduction of NO_x with CO

The interaction of NO_x with CO has been widely studied by spectroscopic methods because of the high sensitivity of the C–O and N–O absorption bands in the IR spectra. This reaction is of great practical importance in relation to the problem of removing CO and NO_x from the exhaust gases of automobile engines. The reaction can follow two paths: with formation of N_2 and CO_2 or with formation of N_2O and CO_2. The first mechanism is usually predominant on metals, the second on oxides.

The NO + CO reaction on platinum foil was studied by absorbance-reflectance IR spectroscopy.[171] It was established that below 150 °C the surface is covered with CO, and that the activation energy for desorption is 14.2 kJ mol^{-1}. Above 150 °C the activation energy is governed by the dissociation of NO and is equal to 36 kJ mol^{-1}. The reaction follows a dissociative mechanism:[171]

$$CO + Z \overset{(1)}{\rightleftharpoons} COZ, \qquad NO + Z \overset{(2)}{\rightleftharpoons} NOZ,$$
$$NOZ + Z \overset{(3)}{\longrightarrow} NZ + OZ,$$
$$COZ + NOZ \overset{(4)}{\longrightarrow} CO_2 + NZ + Z,$$
$$2\,NZ \overset{(5)}{\longrightarrow} N_2, \qquad COZ + OZ \overset{(6)}{\rightleftharpoons} CO_2 + 2\,Z.$$

The rate of removal of CO (calculated from IR spectra) is determined by the kinetics of step (*4*).

On Rh(100) the reaction of NO_x with CO with studied by LEED, Auger spectroscopy, and TPD.[172] A dissociative mechanism similar to that described by Skarf and Benziger[171] was proposed. A study of the interaction of CO with NO on a Rh(331) surface has also been reported.[173] The changes in the 520 cm^{-1} absorption band (assigned to adsorbed oxygen) show that the oxygen atoms formed by the dissociation of the NO molecules are immediately removed from the surface and interact with CO molecules. The oxygen atom formed by the dissociation of the NO molecule on the surface is less active towards the adsorbed CO molecule than the oxygen atoms produced by dissociatively adsorbed O_2.

The oxygen formed on the surface by the decomposition of NO_2 under the conditions of the reaction of NO_2 with CO has properties similar to those of the oxygen formed by the decomposition of O_2. Thus, NO and CO_2 are formed on platinum at temperatures below 430 °C under the conditions of this reaction.[174] The rate of formation of CO_2 is an order of magnitude higher than the rate of interaction of CO with NO, and is almost equal to the rate of the reaction of CO with O_2.

Most of the studies have been devoted to the reaction between NO and CO on metals of the platinum group supported on SiO_2, Al_2O_3, and other carriers.[175–194] The formation of isocyanate groups (NCO) on the surface was invariably observed. For example, in the interaction of a mixture of CO and NO on Pt, Rh, and Ir supported on TiO_2, MgO, Al_2O_3, and SiO_2 carriers the IR spectrum was found to include bands at frequencies between 2180 and 2318 cm^{-1}, assigned to the NCO vibrations on the surface of both the metal and the carrier.[175] The isocyanate groups are formed by the interaction of adsorbed nitrogen atoms and CO molecules:

$$Pt–N + Pt–CO \rightleftharpoons Pt–NCO.$$

It should be noted that cyanides adsorbed on platinum or palladium absorb in the same spectroscopic region (1980–2200 cm^{-1}).[181–183] Detailed spectroscopic studies using nitrogen, oxygen, and carbon isotopes have shown that two different forms of the complex can exist on the platinum metal surface: isocyanates Rh–NCO (2172 cm^{-1}) and cyanates Rh–OCN (2225 cm^{-1}). The migration of NCO from the metal to the carrier is very fast. Its driving force is the formation of a stronger bond with the Lewis-acid centres on the carrier.

Several forms of adsorbed CO, including bridging forms (at 1875 cm^{-1}), have been observed on a binary $Pt–Rh/SiO_2$ catalyst. NCO groups are adsorbed on the Rh, but they are not observed on the Pt.[177]

Studies in situ by IR spectroscopy of the reaction of CO + NO on $Pt–WO_3/SiO_2$ at 280 °C showed that the slow step in this case is the dissociation of NO. The CO groups on Pt are rapidly replaced by NO groups, and therefore the absorption bands of the NO groups are predominant in the in situ IR spectra. Bands corresponding to CO groups are observed also on WO_x; NCO, NO_3, or NO_2 groups were seen only under the conditions of the experiment, and they were assigned[177] not to intermediates but to side-products of the reaction, because they are formed in large quantities under conditions which suppress the reaction of carbon monoxide. The active centres are located at the boundary between Pt and WO_3.

The most active of the platinum metals (rhodium) has been studied the greatest detail.[178–184] According to Hecker and Bell[178,179] the reaction of NO_x with CO on Rh/SiO_2 takes place by the scheme

$$NO + Rh \overset{(1)}{\rightleftharpoons} RhNO, \qquad CO + Rh \overset{(2)}{\rightleftharpoons} RhCO,$$
$$NORh + Rh \overset{(3)}{\longrightarrow} NRh + ORh,$$
$$NORh + NRh \overset{(4)}{\longrightarrow} N_2O + 2\,Rh,$$

$$NORh + NRh \xrightarrow{(5)} N_2 + {}^1/_2O_2 + 2\,Rh,$$

$$CORh + ORh \xrightarrow{(6)} CO_2 + 2\,Rh,$$

$$NRh + CO \overset{(7)}{\rightleftharpoons} RhNCO,$$

$$NRh + CORh \xrightarrow{(8)} RhNCO + Rh,$$

$$2\,RhNCO \xrightarrow{(9)} N_2 + 2\,CO + 2\,Rh.$$

The absorption bands of NCO on Rh (2170 cm^{-1}) appear during the catalysis; they are strongest if the reaction is carried out at 230 °C. However, there is no proof that their formation determines the rate of the catalytic reaction. The coverage of Rh by NCO groups is low as compared with the coverage by NO groups (1685 cm^{-1}) and by N atoms (1610 cm^{-1}). A high concentration of NCO is found on SiO_2 (2300 and 1960 cm^{-1}); the CO groups are observed on the carrier as a result of migration from the metal. Under the reaction conditions these groups are stable, and apparently do not contribute to the catalysis. The exposure of Rh/SiO_2 to a mixture of $N_2 + H_2 + CO$ also produces bands corresponding to the NH and NH_2 groups.[180] The activation energy for the reduction of NO in the presence of H_2 is very substantially lowered (from 34 to 23 kJ mol^{-1}). An intermediate compound [urea, $(NH_2)_2CO$] is formed on the reduced catalyst, probably by the reaction

$$HNCO + NH_3 \longrightarrow NH_4OCN + (NH_2)_2CO.$$

HNCO is formed on an oxidised catalyst.

When the reaction of NO_x with CO is carried out on Rh/Al_2O_3 Rh–NCO complexes are not formed, but Rh(CO)(NO) groups have been observed[186] and suggested as the source of the reduction of NO. The formation of dicarbonyls suppresses the reaction. However, Dictor[181] has noted the formation of $Rh(CO)_2$, but was unable to detect Rh(CO)(NO) groups. The $Rh-NO^-$, Rh–NO, $Rh-NO^+$, Rh–CO, Rh_2CO, Rh–CN, and a large number of NCO groups adsorbed mainly on the Al_2O_3 were also detected. It is suggested that NO dissociates on the reduced Rh and easily oxidises the catalyst. The NCO groups are probably formed at the Rh – carrier boundary (but not on the Rh^+).

It has also been shown[182] that the stability of NCO increases in the presence of O_2, and therefore isocyanate could be an intermediate in the catalytic reaction of $NO + CO + O_2$.

The $NO + CO + O_2$ reaction has been studied[186] on Pt/SiO_2. At low coverages of the surface by CO groups the $CO + O_2$ reaction takes place much more readily than the CO + NO reaction. A dissociative mechanism is suggested, with the dissociation of chemisorbed NO as the rate-limiting step.

The forms $NO-Ru^{2+}$ and NO_2-ZnO have been observed[188] on the Ru/ZnO catalyst. Carbon monoxide adsorbed on Ru reacts with NO when the latter is dissociated, forming NCO and CO_3. As a result of spill-over the NCO and CO_3 species move from the metal to the carrier, where they are stabilised even for temperatures above the catalysis temperature.[188]

Under catalytic conditions the formation of NCO groups and their migration towards the carrier have been observed[185] on Ir catalysts supported on SiO_2, Al_2O_3, TiO_2, or MgO. As reported, the dissociation of NO takes place on reduced iridium centres by the scheme

$$Ir(CO)(NO) \longrightarrow IrN + CO_2.$$

NNO groups, which are intermediates in the formation of N_2O, are formed in parallel with NCO:

$$IrN + NO \longrightarrow IrNNO \longrightarrow Ir + N_2O.$$

On an oxidised Ir surface no interaction between NO and CO was detected.

The only systematic spectroscopic investigation of the interaction of CO and NO on supported platinum group metals appears to be a group of studies from our laboratory.[189–194] This work involved the simultaneous measurement of the rate of conversion of the surface compounds [CO(ads), CO_2^{2-}, and NCO] and of the rate of formation of the reaction products (N_2, N_2O, and CO_2). As a result we were able to establish the following series of steps in the interaction of CO with NO:

$$CO + M \overset{(1)}{\rightleftharpoons} M-CO,$$

$$NO + M \overset{(2)}{\rightleftharpoons} M-NO,$$

$$M-NO + M \xrightarrow{(3)} M-N + M-O,$$

$$M-N + M-CO \xrightarrow{(4)} M-NCO + M,$$

$$M-NCO + M-NO \xrightarrow{(5)} M-CO_2 + N_2 + M,$$

$$M-CO + M-O \xrightarrow{(6)} M-CO_2 + M,$$

$$M-CO_2 \xrightarrow{(7)} CO_2 + M,$$

$$M-N + M-NO \xrightarrow{(8)} N_2O + 2\,M,$$

$$O_2 + 2\,M \xrightarrow{(9)} 2\,MO.$$

I: $2\,CO + 2\,NO = 2\,CO_2 + N_2$,

II: $CO + 2\,NO = N_2O + CO_2$,

III: $2\,CO + O_2 = 2\,CO_2$.

It was found that this sequence is identical for all the catalysts examined.[189–194]

The NO + CO reaction was studied on a Ni/SiO_2 catalyst by IR spectroscopy and microgravimetrically.[195] The adsorbed NO [mainly in the form of $Ni(NO)_2$] reacts with CO, giving NiNCO + CO_2. The stoichiometry of the reaction corresponds to the equation

$$4\,NO(ads) + 3\,CO \longrightarrow NCO(ads) + 2\,O(ads) + 3\,N(ads) + 2\,CO_2.$$

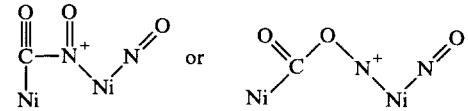
Weakly adsorbed CO is formed also by the interaction

$$NiNCO + Ni \longrightarrow NiN + NiCO.$$

In the absence of CO the following reaction takes place;

$$Ni + Ni(NO)_2 \longrightarrow 2\,NiNO \longrightarrow 2\,N(ads) + 2\,O(ads).$$

A correlation between the decomposition of NO and the formation of NCO is established 10 min after the beginning of the reaction. The possible formation of associative intermediate complexes has been suggested:[195]



16 or **17**

The formation of NCO in the reaction of surface nitride NiN (after the dissociation of NO) with CO has not been observed.

The same reaction (NO + CO) has been studied on a reduced copper catalyst (Cu/Al_2O_3) by in situ IR spectroscopy and TPD.[196] The products (CO_2 and N_2) are formed in a single elementary step. The adsorption of CO groups on Cu^0 and Cu^+ centres has been observed. The action of NO on the reduced

surface leads to the reoxidation of the copper and subsequently to the formation of NCO, probably on the carrier. The following reaction mechanism has been suggested:

$$NO \rightleftharpoons NO(ads) \longrightarrow N(ads) + O(ads),$$

$$N(ads) + N(ads) \longrightarrow N_2,$$

$$N(ads) + NO(ads) \longrightarrow N_2O,$$

$$NO(ads) + NO(ads) \longrightarrow N_2O + O(ads),$$

$$O(ads) + 2\,Cu^0 \longrightarrow Cu_2O,$$

$$Cu_2O + CO \longrightarrow 2\,Cu + CO_2,$$

$$N(ads) + CO(ads) \longrightarrow NCO(ads),$$

$$NCO(ads) + NO(ads) \longrightarrow N_2 + CO_2.$$

The last step is rate-limiting. The possible spill-over of N particles from the copper towards the carrier and their interaction with CO on the carrier have also been suggested.[196]

Absorption bands corresponding to the complexes $Cu^{2+}-NCO$, $Cu^{+}-NCO$, $Cu^{+}-NO$, $Cr^{2+}-NO$, $Cu^{2+}-CO$, $Cu^{2+}-NO$, and $Cu^{+}-CO$, and also absorption bands from carbonates, carboxylates, nitrites, and nitrates, have been observed in the IR spectra obtained under reaction conditions on a $Cu-Cr/Al_2O_3$ catalyst.[197,198] The NCO group is formed by the NO + CO reaction, and also by the sequential exposure of the catalyst first to NO and then to CO. However, not all the NCO takes part in the catalysis. Its formation and decomposition on the copper are also possible:

$$Cu^{+}-N + CO \longrightarrow Cu^{+}-NCO,$$

$$Cu^{+}-NCO + NO \longrightarrow Cu^{+} + N_2 + CO_2.$$

NCO groups are obtained also in the CO + NO reaction on oxide catalysts, for example on Cr_2O_3 [199] and on $LaMO_3$, where M = Cr, Mn, Fe, Co, or Ni.[200]

The interaction of CO and NO has also been studied[201,202] on CuO supported on Al_2O_3. Bands from carbonate–carboxylate complexes (1200–1650 cm^{-1}), from adsorbed CO_2 (2350 and 2370 cm^{-1}), and from CO bound to the reduced copper ions ($Cu^{+}-CO$, 2130 cm^{-1}) have been observed in the spectra for the adsorption of CO on Cu/Al_2O_3. The adsorption of NO produces nitrate–nitrite structures (1200–1660 cm^{-1}) and NO complexes bound to the Cu^{2+} ions (1880 cm^{-1}). $Cu^{+}-NO$ complexes (1740–1780 cm^{-1}) can also be formed. After the adsorption of a CO + NO mixture bands at 2130 ($Cu^{+}-CO$), 1880 ($Cu^{2+}-NO$), and 1780 cm^{-1} ($Cu^{+}-NO$), were observed in the spectra, and also bands at 2270, 2240, and 2140 cm^{-1} which were assigned to vibrations of the isocyanate complex. The role of the latter in the reaction was not examined. A scheme for the interaction of CO and NO in which $Cu^{+}-NO$ is the intermediate complex was proposed on the basis of spectroscopic data.

A quantitative proof that the surface carbonyl $Cu^{+}-CO$ is the intermediate complex in the interaction of CO and NO was produced[203,204] by simultaneous measurements of the diffuse reflectance spectra in the IR region and of the reaction rate on CuO/Al_2O_3.

Reports of simultaneous measurements of the rate of transformation of surface compounds and of the rate of the reaction on copper catalysts are few. In particular, one investigation of this type on CuO/SiO_2 has been described.[205,206] Comparing the spectroscopic and the kinetic results produced a scheme in which the adsorbed NO form acts as an intermediate in the formation of nitrogen. Under the reaction conditions weak adsorption bands from the isocyanate complex were observed. This suggests the possibility of the dissociative adsorption of NO:

$$Cu + NO \rightleftharpoons CuNO,$$

$$CuNO + Cu \longrightarrow CuN + CuO,$$

$$CuNO + NO \longrightarrow Cu + N_2O,$$

$$Cu^{+} + CO \rightleftharpoons Cu^{+}-CO,$$

$$Cu + N_2O \rightleftharpoons CuONN,$$

$$CuONN \rightleftharpoons CuO + N_2,$$

$$Cu_2O + CO \longrightarrow Cu^{+} + CO_2,$$

$$CuO + CO \longrightarrow Cu + CO_2,$$

$$CuN + CO \rightleftharpoons CuNCO.$$

The existence of centres of different types on the surface has been proposed: Cu, Cu^{+}, and Cu^{2+}. The dissociation and the formation of the isocyanate complex take place on the reduced centres.

A similar study was carried out on Cr_2O_3/SiO_2.[207] The activity of the catalyst was measured in a gradient-free reactor which also allowed simultaneous spectroscopic measurements. A correlation was observed between the rate of formation of CO_2 and the intensity of the absorption band at 1735 cm^{-1}, corresponding to the vibrations of NO adsorbed in the dinitrosyl form.

The interaction of NO and CO with formation of N_2O and CO_2 was studied[208] on an Au–ZSM-5 catalyst at 70 °C. Under the reaction conditions the $Au^{+}-CO$, $Au^{+}-NO$, $Au^{+}-(NO)_2$, and $Au^{+}-NO_2$ bands were observed.

It should be noted that studies in which the measurements of the reaction rate were accompanied by simultaneous measurements of the rate of conversion of surface complexes were more generally reported than in previous work.

The N_2O + CO reaction on MgO was studied by IR emission spectroscopy and by the response method.[209] An intermediate formate complex was observed, and found to be removed by the reaction

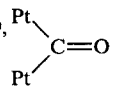
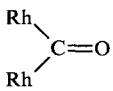
$$HCOO^{-} + N_2O \longrightarrow CO_2 + N_2 + OH^{-}.$$

On oxidation-reduction catalysts the N_2O + CO interaction follows a different path, involving an alternation of oxidation and reduction processes.

Table 6 lists the intermediate compounds observed in the study of the CO + NO reaction on different catalysts. Compounds such as **16** or **17**, which were proposed but not experimentally observed, are not included in the table.

To conclude the present section we note that many surface species have been considered in in situ studies of the CO + NO reaction by IR spectroscopic methods, but few direct kinetic confirmations of the reality of their contribution to the catalysis have been put forward. Both a dissociative mechanism (with dissociation of the CO and NO molecules) and an associative mechanism [with formation of NCO, NNO, and M(CO)(NO) species] have been suggested by different workers. There have been extended discussions of the participation in the catalysis of the NCO isocyanate species, which can be adsorbed on both the metal and the carrier. The most widely held view is that NCO adsorbed on the carrier does not contribute to the catalysis whereas NCO adsorbed on the metal. The rate of its transformation on the metal is fairly high, and after the reaction this species is not usually observed. There are also assumptions of the formation of more complex associative complexes such as **16** and **17**.

Table 6. Intermediates in the NO + CO reaction.

Catalyst	Intermediate complex	Reliability	Ref.
Pt foil	CO(ads), NO(ads)	H	171
Rh(100)	CO(ads), NO(ads)	H	172
Pt, Rh, Ir on TiO_2, MgO, Al_2O_3, SiO_2	M–NCO, carrier–NCO	M	173
Pt–Rh/SiO_2	Rh–NCO, 	M	177
Pt–WO_3/SiO_2	Pt–CO, Pt–NO, WO_x–CO, NCO	L	176
Rh/SiO_2	Rh–NCO, SiO_2–OCN, Rh–NO, Rh–CO	M	178–180
Rh/Al_2O_3		L	186
	Rh–$(CO)_2$, Rh–NO^+, Rh–NO, Rh–NO^-, Rh–CO, Rh–CN, Al_2O_3–OCN,	L	181, 182
			
Pt/SiO_2	NO(ads)	L	186
Ru/ZnO	Ru^{2+}–NO, ZnO–NO, Ru–CO, Ru^{2+}–CO, NCO, CO_3	L	188
Ir on SiO_2, Al_2O_3, TiO_2	, Ir–NCO	M	185
Pt, Pd, Rh, Ru on Al_2O_3	M–NCO, M–CO, $M–CO_2^{2-}$	H	190–194
Ni/SiO_2	Ni–$(NO)_2$, Ni–CO, $Ni–NO_2$	M	195
Cu/Al_2O_3	Cu^+–CO, Cu^0–CO, NCO	L	196
Cu–Cr–O/Al_2O_3	Cu^{2+}–NCO, Cu^+–NCO, Cu^+–NO, Cr^{2+}–NO, Cu^{2+}–CO, Cu^+–CO,	L	197, 198
Cr_2O_3, $LaMO_3$	NCO	L	199, 200
CuO/Al_2O_3	Cu^+–NO	L	202, 203
Cr_2O_3/SiO_2	Cr–$(NO)_2$	M	205
CuO/Al_2O_3	Cu^+–CO	H	206, 207
Au–ZSM-5	Au^+–CO, Au^+–NO, Au^+–$(NO)_2$, Au^+–NO_2	M	208

X. Reduction of NO_x with other reducing agents

The reduction of NO_x with other reducing agents has been studied intensively in recent years with the aim of removing nitric oxide impurities from oxygen-containing exhaust gases from industry and transport. Ammonia is often used as a reducing agent to purify industrial gases and gases from electrical power stations, and the V_2O_5–TiO_2 system usually provides the catalyst.

On pure V_2O_5 the mechanism of the reduction of NO_x was first studied by Takagi et al.[210] An analysis of the IR spectra recorded at room temperature showed that in the absence of oxygen NO is not adsorbed on V_2O_5, but in the presence of oxygen it is adsorbed [as NO_2(ads)]. Upon adding ammonia they observed NH_4(ads). From these results they proposed the following reaction mechanism:

$$NO + {}^1/_2O_2 \longrightarrow NO_2(ads),$$

$$ZOH + NH_3 \longrightarrow ZO^- + NH_4^+(ads),$$

$$ZO^-...NH_4^+(ads) + NO_2(ads) \longrightarrow N_2 + 2\,H_2O + ZO^-,$$

$$ZO^- + H_2O \longrightarrow 2\,ZOH.$$

On TiO_2 the following forms of adsorbed NO_x were observed by IR spectroscopy: NO on Ti^{4+} ions (Lewis centres), N_2O on Ti^{3+} (through the reduction of NO), and NO_3^- on Ti^{3+} (through the oxidation of NO).[211] In the adsorption of NO_2 nitrates are formed, and in the adsorption of NH_3 we find coordinatively bound ammonia (on the Ti^{4+} Lewis centres), which is stable up to 300 °C. The ammonia displaces NO from the surface, but does not react with it.

Another communication from the same authors[212] describes a study of the reaction between NO_x and NH_3 on the V_2O_5–TiO_2 system. In the adsorption of NO the surface is rapidly covered with nitrosyl groups and slowly with NO_3 and NO_2. NH_4^+ and coordinatively bound ammonia are formed on the V–OH centres as a result of the adsorption of ammonia. At 250 °C the intensity of the coordinated ammonia bands in the IR spectra decreases, and the NH_4^+ bands disappear, but they are replaced by NH_2 bands. Heating a surface covered with ammonia in an NO atmosphere leads to the reaction

$$VO^{2+} + NH_3 \longrightarrow [HO–V–NH_2]^{2+},$$

$$NO + [HO–V–NH_2]^{2+} \longrightarrow \underset{\textbf{18}}{[HO–V–NH_2–NO]^{2+}},$$

$$[HO–V–NH_2–NO]^{2+} \longrightarrow N_2 + H_2O + [VOH]^{2+},$$

$$[VOH]^{2+} + {}^1/_4O_2 \longrightarrow VO^{2+} + {}^1/_2H_2O.$$

The overall reaction is

$$NH_3 + NO + {}^1/_4O_2 = N_2 + 1\,{}^1/_2H_2.$$

Thus the reaction of NO_x with NH_3 on V_2O_5 takes place through the decomposition of the associative complex **18**. NO or NO_2 can contribute to the reoxidation stage instead of O_2:

$$[VOH]^{2+} + {}^1/_2NO \longrightarrow VO^{2+} + {}^1/_2\,H_2O + {}^1/_4\,N_2,$$

$$2\,[VOH]^{2+} + {}^1/_2NO_2 \longrightarrow 2\,VO^{2+} + H_2O + {}^1/_4\,5\,N_2.$$

Data obtained[213] by Fourier transform IR spectroscopy and by electrical conductivity methods lead to a similar conclusion:

$$3\,V_2O_5 + 2\,NH_3(ads) \longrightarrow N_2 + 3\,H_2O + V_2O_4,$$

NH_3 reduces the V^{5+} by the reaction

$$2\,V_2O_4 + NO \longrightarrow N_2 + 2\,V_2O_5.$$

and NO reoxidises the V^{4+} to V^{5+}:

At 200 °C the formation of the intermediate complex $V^{5+}-ONH_4$ was observed:

$$2\,V^{5+}-ONH_4 + V^{5+}-O-V^{5+} + 2\,NO \longrightarrow$$

$$\longrightarrow 2\,N_2 + 3\,H_2O + 2\,V^{5+}-OH + V^{4+}\square V^{4+}$$

A study of the reaction[214] by Auger spectroscopy and by TPD showed that NH_3 is adsorbed on both TiO_2 and V_2O_5, but NO is adsorbed only on TiO_2.

Ammonia reduces V_2O_5 by a reaction which produces N_2O. In the presence of N_2O, NO, and O_2 the V_2O_5 surface is reoxidised, and N_2 is evolved. NO and NH_3 molecules adsorbed on TiO_2 do not interact, but they interact on $V_2O_5-TiO_2$. The reaction apparently takes place near the Ti–V interface. Of all the possible intermediates the NH_2 groups are adsorbed on the V_2O_5:

$$V_2O_{5-x} + x\,NH_3 \longrightarrow V_2O_5 + 1^1/_2\,x\,(NH_2)_x + {}^1/_2\,x\,H_2O,$$

$$V_2O_5 + 1^1/_2\,x\,(NH_2)_x + x\,O_2 \longrightarrow V_2O_{5-x} + {}^1/_2\,x\,N_2O + H_2O,$$

$$V_2O_{5-x} + x\,N_2O \longrightarrow V_2O_5 + x\,N_2.$$

The interaction of NO with NH_3 has been studied also on metallic catalysts. On Pt(111) at low temperatures the IR spectra include a band at 1280 cm^{-1} assigned[215] to the associative complex NH_3NO. Upon being heated to 350 °C the system again breaks down into NH_3 + NO. Absorption bands due to adsorbed NO and NH_3 have also been observed. The NH_3 + NO reaction begins only at temperatures above 400 °C, stimulated by the dissociation of NH_3 into NH_2 and H.

When the NO + NH_3 reaction was carried out on FeY zeolite the bands corresponding to NH_3(ads) and NH_4^+ appeared in the IR spectra.[216] Contributions to the catalysis from HNO and N_2O species have also been suggested.

Several papers have dealt with the mechanism of the reduction of NO by hydrogen on metals, including the faces of Pd,[217] Rh,[218] and Ru monocrystals.[219]

An analysis of the EELS spectra obtained uring the reaction of NO with H_2 on Pt(III) under stationary conditions (100–350 °C, pressure $10^{-9}-10^{-8}$ Torr) showed[220] that with an excess of NO the main product of the reaction is N_2, whereas with an excess of H_2 it is NH_3 (in the temperature range 20–200 °C) or N_2 (at higher temperatures). The same precursor appears in both reactions. The NH_3NO complex which is observed (a wide band at 1280 cm^{-1}) inhibits the reaction; when heated it dissociates into NH_3 and NO. At low temperatures the Pt surface is covered with linear and with bridging NO groups, but the NO apparently contributes to the reaction in its dissociated form.

The reaction of NO + H_2 on Pt(111) under the same conditions ($10^{-9}-10^{-8}$ Torr) was studied by EELS and thermosorption methods.[221,222] Two forms of linear NO and two of bridging NO were detected in the low-temperature adsorption of NO: on the (111) plane and on defects (atomic steps). The α form of NO is desorbed at temperatures close to 100 °C, and the β form dissociates at 200–250 °C with formation of N_2. The HNO, N, NH, NH_2, and NH_3 groups are also observed on the surface.

The following mechanism is proposed for the reduction:

$$NO \xrightarrow{(1)} \alpha_1\text{-}NO(ads),$$

$$H_2 \xrightarrow{(2)} 2\,H(ads),$$

$$H(ads) + \alpha_1\text{-}NO(ads) \xrightarrow{(3)} HNO(ads),$$

$$HNO(ads) + H(ads) \xrightarrow{(4)} N(ads) + H_2O,$$

$$N(ads) + 3\,H(ads) \xrightarrow{(5)} NH_3,$$

$$2\,N(ads) \xrightarrow{(6)} N_2.$$

The NO + H_2 reaction has been studied also on supported metal catalysts. A mechanism in which the first stage is the adsorption of NO and the dissociation of H_2 was proposed[223] for the reaction on Rh/SiO_2. Nitrogen is formed by the interaction of N(ads) and NO rather than by the recombination of adsorbed N atoms. On other centres this interaction leads to the formation of N_2O:

$$NO \overset{(1)}{\rightleftharpoons} NO(ads),$$

$$H_2 \overset{(2)}{\rightleftharpoons} 2\,H(ads),$$

$$NO(ads) + H(ads) \xrightarrow{(3)} N(ads) + OH,$$

$$NO(ads) + N(ads) \xrightarrow{(4)} N_2O,$$

$$NO(ads) + N(ads) \xrightarrow{(5)} N_2O + O(ads),$$

$$O(ads) + H(ads) \xrightarrow{(6)} OH(ads),$$

$$OH(ads) + H(ads) \xrightarrow{(7)} H_2O,$$

$$N(ads) + H(ads) \xrightarrow{(8)} NH(ads),$$

$$NH(ads) + H(ads) \xrightarrow{(9)} NH_2(ads),$$

$$NH_2(ads) + H(ads) \xrightarrow{(10)} NH_3.$$

The Rh–NO and Rh–N=O···Sn complexes, and also Rh–O–Sn, were observed by IR spectroscopy and XPES under the conditions of the reaction of NO with H_2 at 100 °C on a $Rh-Sn/SiO_2$ catalyst. Their interaction with hydrogen produced N_2, N_2O, and H_2O.[224]

A study of the reaction of NO with H_2 on Au/SiO_2 and Au/MgO by in situ Fourier transform IR spectroscopy[225] revealed a wide band at 2400–2700 cm^{-1}, which could not be identified. It was assumed that the reaction includes the intermediate dissociation of NO and involves adsorbed atomic nitrogen.

With one exception[223] none of the studies mentioned above was spectroscopic, amd therefore the proposed mechanisms must be treated as tentative. Obviously, associative and dissociative steps are combined in the mechanism of the NO reduction reaction: the NO molecule takes part (as a whole) in the interaction with NH_3 or with H_2. The formation of the $NO{\cdot}NH_3$ complex assists the formation of N–N bonds and the dissociation of the NO molecule.

Reactions leading to the selective reduction of NO_x to nitrogen by using the hydrocarbons contained in the 'lean' mixtures (i.e. mixtures with an excess of oxygen)[226] characteristic of the exhaust gases of Diesel engines were recently discovered on the Cu–ZSM-5 zeolite catalyst. These have stimulated a new series of studies[227–231] aimed at establishing the mechanism of this reaction and the mechanism of the decomposition of NO_x on zeolites.

The state of the copper in the zeolites was studied by ESR (including under reaction conditions[227–229]), XPES, Auger spectroscopy,[230] and IR spectroscopy.[231] All these workers point out that the zeolite contains bivalent and univalent copper, but that the Cu^+ is predominant under the reaction conditions. As reported,[227,231] the reaction

$$2\,Cu(OH)^+ \rightleftharpoons [Cu-O-Cu]^{2+} + H_2O$$

takes place on Cu–ZSM-5. However, the formation of paired copper clusters raises some doubts, since the H^+ ions in the H–ZSM-5 zeolite are located too far from each other to allow a paired cluster to be retained near these centres. A mechanism for the autoreduction of Cu^{2+} with formation of free-radical centres has been proposed:[229]

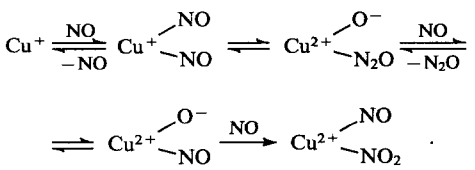
$$Cu(OH)^+ = Cu^+ + \dot{O}H,$$

$$Cu(OH)^+ + \dot{O}H = CuO + H_2O,$$

$$2\,Cu(OH)^+ \rightleftharpoons Cu^+ + CuO + H_2O.$$

According to this scheme the water oxidises the Cu^+ centres. We know[232] that water acts as a catalyst poison in the reaction between NO and hydrocarbons in the presence of oxygen. Therefore it follows that the Cu^+ centres are the active centres under the catalysis conditions.

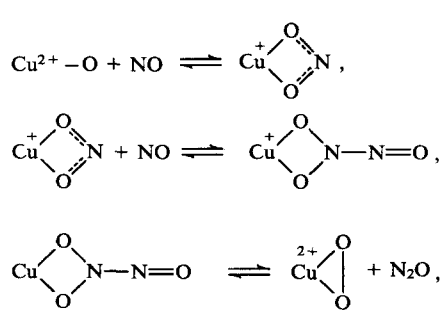
The decomposition of NO on Cu–ZSM-5 takes place at the same temperatures as its reduction by hydrocarbons. Therefore the decomposition of NO has been widely studied by spectroscopic methods.[227–229,232–234] In almost every case the formation of dinitrosyl complexes $Cu^+(NO)_2$ was observed. The following sequence of these complexes, leading to the formation of N_2O, has been proposed:[236]



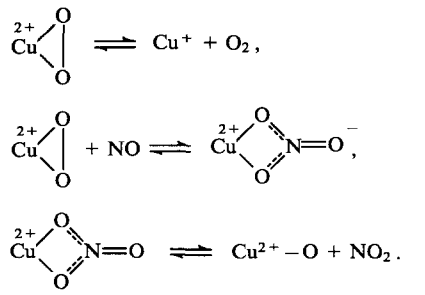
N_2 and O_2 are evolved during the dissociation of the last of these complexes. Complexes of the species $NO^{\delta+}$, $NO^{\delta-}$, $(NO)_2^{\delta-}$, and $NO_2^{\delta-}$ with Cu^{2+} have been detected.[233] During the decomposition of NO the intensity of the $NO^{\delta-}$ and $(NO)_2^{\delta-}$ bands decreases, and that of $NO^{\delta+}$ increases. The decomposition accompanied by the formation of nitrate ($NO_3^{\delta-}$), nitrite ($NO_2^{\delta-}$), and associative ($NO_2 \cdot NO$) complexes:[234]

$$NO_2(ads) + NO(ads) \longrightarrow [NO_2 \cdot NO] \longrightarrow O(ads) + N_2 + O_2.$$

Many different complexes have been observed in an analysis[229] of the IR spectra of the products of the reaction of NO with H_2. Bands corresponding to the following complexes were found after the adsorption of NO on Cu–ZSM-5 at room temperature: $Cu^{2+}-N=N$ (2156 cm^{-1}), $Cu^{2+}-NO$ (1910 cm^{-1}), Cu^+-NO (1811 cm^{-1}), $Cu^+(NO)_2$ (1734, 1827 cm^{-1}), and $Cu^{2+}-O-N=O$ (1631 cm^{-1}). At higher temperatures, and under conditions corresponding to the onset of the decomposition of NO, bands assigned to the following complexes were observed: $Cu^{2+}-NO_2$ (2130 cm^{-1}), $Cu^{2+}-NO$ (1910 cm^{-1}), Cu^+-NO (1811 cm^{-1}), $Cu^{2+}-O-N=O$ (1616, 1590, 1574 cm^{-1}) and $Cu^{2+}-NO_3$ (1502 cm^{-1}). The following scheme for the transformations of these complexes during their adsorption and decomposition was proposed:[229]



$$Cu^+ + N_2O \rightleftharpoons Cu^{2+}-O + N_2,$$



The mechanism of the interaction of hydrocarbons with NO in the presence of O_2 has been studied by spectroscopic methods.[235–241] In most cases propene was used as the reducing agent, but propane[237] and isobutane[241] were also used. Ideas on the intermediate forms of the hydrocarbons taking part in the reaction are not so definite as the ideas on the forms of NO. According to one suggestion, based on experiments in a TAP (temporal analysis of products) reactor,[236] the product obtained from the hydrocarbons is coke, which is a reducing agent for NO_x on Cu–ZSM-5 in the presence or in the absence of oxygen. The zeolite has a positive effect on both the formation of coke and on keeping the copper in the Cu^+ state.

Some workers have observed the formation under the reaction conditions of isocyanate[238–240] and of cyanide complexes.[240] The isocyanate groups can be bound both to the Cu and to an Al atom in the zeolite. As reported,[239] the process takes place by the following scheme:

$$C_xH_y \rightleftharpoons C_xH_y(ads),$$

$$C_xH_y(ads) + O_2 \longrightarrow C_mH_nO + CO_2 + H_2O,$$

$$C_mH_nO + m\,NO \longrightarrow m\,NCO + z\,H_2O,$$

$$NCO + NO \longrightarrow N_2 + CO_2 \text{ (rate limiting)},$$

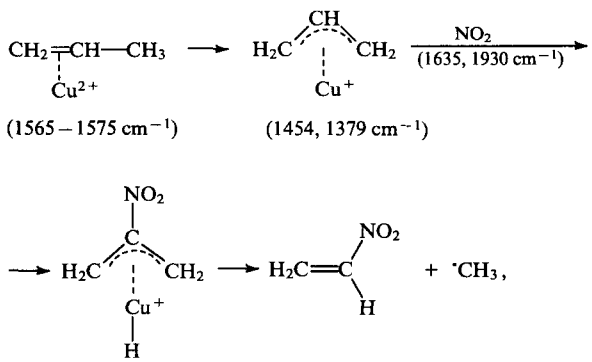
$$2\,NCO + O_2 \longrightarrow N_2 + 2\,CO_2,$$

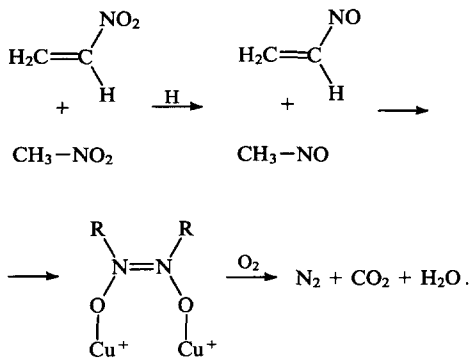
$$C_xH_y(ads)\ (\text{or } C_mH_nO) + NO \longrightarrow N_2O + CO_2 + H_2O,$$

$$C_xH_y(ads) + O_2 \longrightarrow x\,CO_2 + y/2\,H_2O,$$

$$C_mH_nO + O_2 \longrightarrow m\,CO + n/2\,H_2O.$$

There is also a more detailed scheme, based on in situ IR spectroscopic studies:[240]





In this scheme cyanides are dead-end compounds, and isocyanates are not formed.

The interaction of NO with hydrocarbons in the presence of O_2 was studied by spectroscopic methods also on other zeolites of the ZSM-5 type (containing ion-exchange cations). The reaction of $C_3H_6 + NO + O_2$ on Ce–ZSM-5 was studied by in situ spectroscopy combined with the kinetic response method using gas-phase analysis.[242, 243] The absorption bands of the NO_2, NO_3, NCO, and CH_3NO_2 species adsorbed on the surface were detected in the IR spectra under the catalytic conditions. According to these workers[242] the reaction takes place by the mechanism

$$CH_3NO_2 + NO \longrightarrow N_2 + CO_2 + H_2O.$$

The Ga–ZSM-5 catalyst was found to be very selective in the processes associated with the interaction of NO with methane and ethane.[242–244] Its unique properties are attributed to the dissociative adsorption of methane on Ga–ZSM-5 (in contrast to its adsorption on Cu–ZSM-5. This was confirmed, in particular, by isotope exchange experiments between CH_4 and CD_4 on Ga–ZSM-5.

The reduction of NO_x by hydrocarbons in the presence of O_2 has been studied also on other catalysts. Thus, in particular, the $C_3H_6 + NO + O_2$ reaction takes place on Rh/Al_2O_3.[247] According to published data NO_2^- and NO_3^- are formed in an excess of O_2, and they subsequently react with C_3H_6 giving the $^{\cdot}C_3H_5$ radical and HNO_x. The weakly bound $^{\cdot}C_3H_5$ radical is rapidly oxidised to CO_2 by nitrates and nitrites.

The species $R-NO_x$, NO_x, NCO, nitrate, and nitrite were detected[248] spectroscopically in a study of the reduction of NO by hydrocarbons on various zeolites, and also on modified ZrO_2 and on complex oxides supported on γ-Al_2O_3.

We should stress that studies of the reduction of NO_x by hydrocarbons began only 2 or 3 years ago. Nevertheless there are already numerous reports of the spectroscopic detection of various surface forms, though only few spectro-kinetic studies could be traced. The existence of adsorbed intermediate forms of NO is most convincingly established, that of the complexes of NO with hydrocarbons is still arguable. The NCO species observed by several workers may play a key role in the reduction of NO both by CO and by hydrocarbons, though detailed schemes are still to be developed.

Table 7 gives a summary of data on the intermediate compounds which take part in the reduction of NO by ammonia, hydrogen, and hydrocarbons.

Table 7. Intermediates in the NO_x reduction reactions.

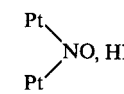
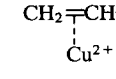
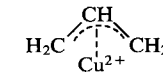
Reaction, catalyst	Intermediate complex	Reliability	Ref.
Reduction of NO with NH_3 on V_2O_5	NO_2(ads), NH_4^+	L	210
Interaction of NO with NH_3 on TiO_2	$NO-Ti^{4+}$, N_2O-Ti^{3+}, $NO_3^- - Ti^{3+}$, NH_3-Ti^{4+},	L	211
Interaction of NO with NH_3 on $V_2O_5-TiO_2$	$V^{5+}ONH_4$, $[HOVNH_2]^{2+}$, $V^{5+}OH$, NO, NO_2^-, NO_3^-, NH_3-Ti^{4+}	L	212, 213
	NH_3-V^{5+}, $NO-Ti^{4+}$, NH_2-V	L	214
Interaction of NO with NH_3 on FeY	NH_3(ads), NH_4^+	M	216
Interaction of NO with NH_3 on Pt(111)	NH_3(ads), NO(ads), NH_3NO, NH_2	L	215
NO + H_2 reaction on Pt(111)		L	220–222
NO + H_2 reaction on Rh/SiO_2	NO(ads), NH_2(ads)	M	223
NO + H_2 reaction on Au/SiO_2, Au/MgO	NO(ads), N(ads)	L	225
Decomposition of NO on Cu–ZSM-5	O(ads)	M	227
	Cu^+NO, $Cu(NO_2)$, $Cu(NO_2)^-$	M	228
	$(Cu-O-Cu)^{2+}$, $CuOH^+$	L	230, 231
	CuNO, $Cu(NO)_2$	M	232
	$Cu^+NO^{\delta+}$, Cu^+NO^{2-}, $Cu^+(NO)_2^{\delta-}$, $Cu^{2+}NO^{\delta+}$	M	233
	$Cu^{2+}-N=N$, $Cu^{2+}-NO$, Cu^+-NO, $Cu^+(NO)$, $Cu^{2+}-O-N=O$, $Cu^{2+}-NO_2$, $Cu^{2+}-NO_3$	H	229
$C_3H_6 + NO + O_2$ on Cu–ZSM-5	Cu^+NO, $Cu^{2+}(NO)(NO_2)$	M	236
		M	240
			
	NO_2(ads), $H_2C=CH-NO_2$, CH_3NO_2, HCN, CH_3CN, $-CN$, $-NCO$	M	238
	$Cu^{2+}(NO)_2$, Cu^+O(ads)	L	235
	NCO, C_mH_n, C_xH_y	M	239

Table 7 (contd)

Reaction, catalyst	Intermediate complex	Reliability	Ref.
$C_3H_8 + NO + O_2$ on Cu–ZSM-5	NO_2(ads), C_xH_yO	L	237
i-$C_4H_8 + NO + O_2$ on Cu–ZSM-5	C_x, NO(ads)	L	241
$C_3H_6 + NO + O_2$ on Ce–ZSM-5	NO_2^-, NO_3^-, CH_3NO_2, NCO	H	242, 243
$CH_4 + NO + O_2$ on Ga–ZSM-5	CH_3(ads)	L	244, 246
$C_3H_6 + NO + O_2$ on Rh–Al_2O_3	C_3H_5(ads), HNO_x	L	247
$C_3H_6 + NO + O_2$ on ZrO_2	R–NO_x, NO_x, NCO, NO_2, NO_3^-	M	248

XI. Conclusion

The reactions discussed in this review had been more carefully studied than those which were examined in our previous article.[1] This is because the extinction coefficients of the C–O, N–O, O–H, and N–H bonds are substantially higher than those of the C–H and C–C bonds. As a result, in reactions involving CO and NO (and sometimes also hydrogen) the sensitivity of the spectrokinetic measurements is higher, but the measured characteristic times of the elementary processes are lower. However in this case, as can be seen from the above tables, the confidence level of the great majority of the reported studies is only moderately high. We consider the studies of the catalytic reduction of NO by carbon monoxide, ammonia, and hydrocarbons to be the most reliable. These reactions began to be studied relatively late, but for this reason the methods used for the detection of surface compounds were more sensitive and up-to-date than the methods used in the earlier work.

In many cases the observed surface compounds (carbonates, formates, NCO) were stabilised on the carrier rather than on the active phase. They could be dead-end compounds, but they could also take part in the catalytic reaction as a result of their migration (spill-over) towards the active surface or towards the phase separation boundary.

A generalising analysis of all the reactions so far considered will be given in the third (closing) part of the present series of reviews.

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