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Methods for increasing the efficiency of catalysts for the oxidative condensation of methane

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ABSTRACT. Possible ways of increasing the efficiency of catalysts for the oxidative condensation of methane by increasing the pressure, adding other gases to the reaction mixture (methane + oxygen), and carrying out the process under cyclic redox conditions have been examined. In some cases the yield of C_2-hydrocarbons can be increased to 32%.

The bibliography contains 102 references.

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I. Introduction

The oxidative condensation of methane to give C_2-hydrocarbons, which was discovered in 1981–1984, is one of the most rapidly developing and promising fields of catalysis. About 100 papers on the catalysts, mechanism, and characteristics of this reaction are published every year. A number of reviews have been published.[1–7]

There are now a number of catalytic systems showing activity and selectivity in the oxidative condensation of methane. The chemical relationships governing the selection of catalysts for oxidative condensation have not been fully determined. The most active and selective catalysts are the oxides of the non-transition metals of groups I–IV, that is the oxides of metals with outer *sp*-electrons. High and stable yields of C_2-products have been obtained on PbO deposited on Al_2O_3 or MgO; on a number of lanthanide oxides, in particular Sm_2O_3; on BaO_2; and on Li/MgO. Most transition metal oxides catalyse the extensive oxidation of methane. Among transition metal oxides, for some unknown reason, activity and selectivity are shown by manganese oxides, but only in compounds, and not in pure form.

A number of authors report the existence of various limiting yields of C_2-hydrocarbons.[8,9] According to McCarty,[9] the limiting yield of C_2-hydrocarbons is ~26%. With increase in the conversion of methane, the selectivity decreases. On most catalysts studied, the yield is lower than this value. Other authors[8] give slightly higher limiting yields of about 30%. Even higher yields have been reported: 30.8% on an Li–Mn–Ti–O catalyst,[10] 31.6% on $Ce_{1-x}Sr_xYb_xO_3$,[11] and even 32.3% on Li–Nd–O/MgO,[12] although in each case a careful analysis of the conditions giving these yields is required; they may be artefacts. High yields have also been observed on various chlorine-containing systems (see below).

The highest reaction rate has been obtained on Sm_2O_3 [4]— 828 μmol s^{-1} g^{-1} at 1023 K. The best temperature range for carrying out the reaction is 950–1100 K. Extensive oxidation of methane takes place at lower temperatures. At higher temperatures, in addition to extensive oxidation, extensive catalytic cracking takes place. Many catalysts are unstable under the reaction conditions, both as a result of the loss of the active component and as a result of overheating during this exothermic process.

The heterogeneous–homogeneous mechanism of the oxidative condensation of methane, according to which reaction with the surface gives methyl radicals

$$O_S + CH_4 \xrightarrow{k_1} OH_S + CH_3, \quad (1)$$

and their recombination in the gas phase gives ethane

$$CH_3 + CH_3 + M \xrightarrow{k_2} C_2H_6 + M, \quad (2)$$

is now generally accepted.[1–7]

The selectivity of the gas-phase stages of the reaction is determined by the equilibrium

$$CH_3 + O_2 \underset{}{\overset{K_3}{\rightleftharpoons}} CH_3O_2. \quad (3)$$

At high temperatures, equilibrium (3) is displaced to the left, and the selectivity towards C_2H_6 increases. Below 873–973 K, equilibrium (3) is displaced to the right, and the radical CH_3O_2 leads to extensive oxidation.

An examination of a stepwise mechanism for the oxidative condensation of methane for low degrees of transformation made it possible[13] to put forward the following equation for the limiting selectivity with respect to ethane

$$S_{lim} = \frac{1}{1 + K_3 p_{O_2}(K_3 p_{O_2} k_4/k_2 + k_5/k_2)}, \quad (4)$$

where k_2 is the rate constant of reaction (2), K_3 the equilibrium constant of reaction (3), and k_5 and k_4 the rate constants of the homogeneous gas-phase reactions of the further oxidation of CH_3 and CH_3O_2 radicals. Eqn. (4) does not take account of possible reactions on the catalyst surface, for example extensive catalytic oxidation. For high degrees of transformation, reactions of free radicals in the gas phase, not taken into account, may take place. The oxidative dehydrogenation of ethane gives ethylene, apparently with the intermediate formation of C_2H_5 radicals.

Under stationary conditions, the kinetics of the oxidative condensation of methane are described by an equation of the Mars–Van Krevelen type, characteristic of processes taking place by a redox mecanism

$$r = \frac{k_r p_{CH_4} k_{ox} p_{O_2}}{k_r p_{CH_4} + k_{ox} p_{O_2}}, \quad (5)$$

where k_r and k_{ox} are the rate constants for the reduction of the active centres by methane and their re-oxidation by oxygen respectively.[3]

Possible ways of increasing the efficiency of the oxidative condensation of methane are examined below.

II. Increase in pressure

According to the reaction kinetics described by Eqn. (5), increase in the pressure of oxygen and methane should increase the reaction rate. According to Eqn. (4), increase in the O_2 pressure should decrease the selectivity, but increase in the methane pressure should have no significant influence on it. These equations, however, are applicable only for small degrees of conversion. At high degrees of conversion and high pressures, the ratio between the heterogeneous and homogeneous processes may change sharply in favour of the latter. There may be an increase in the part played by processes giving undesirable products of extensive oxidation.

A decrease in selectivity with increase in the oxygen pressure has in fact been observed by a number of authors.[14–16]

Increase in pressure from 0.1 MPa and 0.8 MPa in the empty reactor increased the degree of conversion of CH_4 from a very low value (< 1%) to 32.7% at 1073 K and a volume rate of 24 min^{-1}.[17] In a study of the influence of pressure on the oxidative condensation of methane on an Li/MgO catalyst, Tyulenin and co-workers[18] filled the empty volume beyond the catalyst with the weakly active MgO, to decrease the reaction in the gas phase. Under these conditions, the degree of conversion of CH_4 increased with increase in pressure, from 28.1% to 34.3%, and the selectivity with respect to C_2-hydrocarbons decreased from 41.1% to 36.0%; the selectivity with respect to C_2H_6 decreased from 20.1% to 10.1%, and the selectivity towards C_2H_4 increased from 20.5% to 26.3%, the ratio $[C_2H_4]/[C_2H_6]$ in the reaction products increased from 1.0 to 2.62, the yield of CO increased slightly, and the yield of CO_2 remained unchanged.

An increase in the selectivity towards C_2H_4 with increase in pressure was noted in other papers.[19,20] The yield of C_2H_4 increases and even exceeds the yield corresponding to the equilibrium $C_2H_6 \rightleftarrows C_2H_4 + H_2$, that is the principal role is played by kinetic factors.

Thus increase in pressure has a positive influence mainly on the second stage of the process—the oxidative dehydrogenation of ethane to ethylene.

Increase in pressure may also have a positive influence on the first stage of the process—the formation of C_2H_6 molecules by the recombination of methyl radicals with the participation of a third molecule M. In highly porous catalysts such as MgO or Li/MgO, reaction (2) hardly takes place within the catalyst granules.[21] This is due to the diffusion of the CH_3 species formed under Knudsen conditions, when these species undergo practically no collisions with one another or with the molecule M, but react with the surface, on which extensive oxidation apparently takes place. As a result, only the outer layers of catalyst take part in the formation of C_2H_6. With increase in pressure, the probability of triple collisions according to reaction (2) increases, and the yield of C_2-hydrocarbons shows a corresponding increase. This also explains the observed[22,23] decrease in activity and selectivity in the oxidative condensation of methane with increase in the specific surface, that is decrease in the specific surface and increase in the pressure in this reaction operate in the same direction.

III. Influence of water vapour

Water vapour is formed both in the oxidative condensation and in the extensive oxidation of methane. In the stages of catalyst reduction and oxidation, water may have a negative influence on the catalysis by blocking the active centres.

Nevertheless, the opposite is also observed—an increase in the degree of conversion of methane with increase in the water vapour pressure with no change in selectivity.[24,25] A redistribution of the products of oxidative condensation towards C_2H_4 has also been observed on Sm_2O_3 + CeO_x, PbO–MgO, and ZrO_2–MgO.[26] Thus water vapour apparently influences the heterogeneous but not the homogeneous stages of the process.

At a high temperature (> 1000 K) in the presence of water vapour, steam conversion of methane takes place on oxide catalysts. The formation of H_2, C_2H_4, and C_2H_6 (the last two in smaller quantities than H_2) has been observed in the reaction of methane and water vapour on a CaO catalyst.[27]

Most interesting results were obtained by Pereira and co-workers.[28] At low temperatures (873 K and below) on a Ca–Ni–K-oxide catalyst for a mixture with $[CH_4]:[O_2]:[H_2O]$ = 3 : 1 : 6.5 at atmospheric pressure, 100% selectivity in hydrocarbon formation was observed, with a degree of conversion of ~10% in one operation. Heating in oxygen increased the activity and selectivity. Activation for 1 h gave a mixture of 38% C_2H_4, 48% C_2H_6, 5.3% C_3H_8, 5.6% C_3H_6, and 2.8% hydrocarbons. If water vapour is replaced by helium, the activity decreases rapidly, that is the catalyst is stable towards water vapour. X-Ray photoelectron spectroscopy showed that $Ni(OH)_2$ is formed on the catalyst surface, and calcium nickelate (charge on nickel > 2+) is formed in the bulk. The formation of carbonates leads to a decrease in the activity of the catalyst.

Another paper by the same authors[29] gives the results of prolonged tests confirming the earlier data. An unusually low activation energy E for the oxidative condensation of methane is reported: 84 kJ mol^{-1}, which is much lower than the activation energy of extensive oxidation (~250 kJ mol^{-1}). On most catalysts studied for the higher-temperature oxidative condensation of methane (without water vapour), the opposite was observed: E for the oxidative condensation was greater than E for extensive oxidation.[3] The most active and selective catalyst for the reaction in the presence of water vapour had the composition $Ca_3NiK_{0.1}O_x$. A much lower activity and selectivity were shown by the catalyst $CaK_{0.1}O_x$, indicating that the presence of the transition metal (nickel) in the catalyst is necessary. The transition metal acts as a promoter.

The mechanism of this low-temperature condensation of methane is not yet clear. The possible steam conversion of methane to give synthesis gas CO + H_2 followed by a Fischer–Tropsch synthesis, that is purely heterogeneous reactions, have been suggested.[29] The distribution of the reaction products—$C_1:C_2:C_3:C_4$-hydrocarbons—to some extent resembles the Schulz–Flory distribution.

The authors cited point out that the synthesis of the hydrocarbons may be influenced by carbon particles. This is confirmed by experiments with $^{13}CH_4$. Water vapour does not play a direct role in the synthesis, but has an indirect influence, probably as a result of the formation of OH groups on the surface. The authors cited also point out that $CaK_{0.1}O_x$ is a very good catalyst for the steam gasification of graphite at relatively low temperatures to give H_2 and CO.[30]

Until the radical products above the catalyst have been determined, possible explanations of the influence of water vapour on the homogeneous stages of the process should not be rejected. High concentrations of hydroxyl radicals were observed in the oxidation of methane on platinum.[31] The action of oxygen led to the hydroxylation of molecularly adsorbed water on Ag(110) and Cu(100) with the intermediate formation of O_2^-.[32] The reaction

$$4(OH)_S + O_2 \longrightarrow 4O_S + 2H_2O, \quad (6)$$

observed[33] in the re-oxidation of reduced methane by an Li/MgO catalyst possibly also involves the intermediate formation of OH or HO_2 radicals.

The characteristics of the low-temperature oxidation of methane noted by other workers are probably also related to the influence of water vapour and OH groups. Water has a strong influence on the acidic properties of a surface. Matsuhashi and co-workers,[34] using a 4.3% Na^+/ZrO_2 catalyst at 873 K, were able to carry out the oxidative condensation of methane with 26.5% conversion and 52.8% selectivity towards C_2-hydrocarbons. On the super-acid SO_4^-/ZrO_2 at 873 K, water vapour led to a marked increase in the transformation of a $CH_4 + O_2$ mixture into oxygen-containing products (to 16.2% for a degree of conversion of 10.8%). It has been shown[35] that an iron phosphate catalyst (Fe/P = 0.6), with or without a carrier, functions even at 850 K (yield of C_2-hydrocarbons up to 8%). The activity of this catalyst was very unstable, however, and its loss and reduction were observed after further heating at 973 K. Although the authors cited[35] do not point out a relationship between the observed effects and the action of water vapour, nevertheless the observed phenomenon is very similar to the analogous effects for an Ni–Ca–K–O-catalyst in the presence of water vapour.[29] The same paper also reported the unexpected deactivation of the catalyst with restoration of the activity after further heating.

IV. Influence of chlorine

In the presence of chlorine-containing compounds both in the catalyst and in the gas phase it is possible to increase considerably the yield of the products of the oxidative condensation of methane. This was first demonstrated by Otsuka and co-workers.[14,36,37] The additives LiCl, NaCl, KCl, CsCl and LiBr were deposited on MnO_x/SiO_2, NiO_y/SiO_2, and other catalysts. With a 2% $NaCl/MnO_x/SiO_2$ catalyst at 1023 K and 90 kPa, the degree of conversion of CH_4 was 46.8%, the selectivity towards C_2-hydrocarbons 66%, and the yield 31.6%, which is 8–10% greater than the yield of C_2 on the same catalyst without NaCl. It has been suggested[14] that LiCl and NaCl act as promoters as a result of the formation of chlorine atoms, which subsequently lead to the formation of additional methyl radicals

$$\begin{aligned} &LiCl + CH_4 + {}^1/_2\,O_2 \longrightarrow LiOH + CH_3Cl, \\ &CH_3Cl \longrightarrow CH_3 + Cl\,, \end{aligned} \quad (7)$$

followed by the gas-phase recombination of methyl radicals (2) and gas-phase reactions involving chlorine atoms

$$\begin{aligned} &Cl + CH_4 \longrightarrow CH_3 + HCl, \\ &Cl + C_2H_6 \longrightarrow C_2H_5 + HCl. \end{aligned} \quad (8)$$

The chlorination of methane is an important industrial process for obtaining chloro-derivatives of methane. At 1000–1200 K it takes place by a chain mechanism to give CH_3Cl, C_2H_5Cl, and ethane. The limiting stage is the removal of an H atom from CH_4 with an activation energy of 16 kJ mol^{-1}. In some experiments with chlorine-containing additives,[38] HCl was not detected in the products of the reaction of methane with chlorine. This suggested that HCl is continuously removed from the system by the reaction

$$HCl + OH = Cl + H_2O \quad (9)$$

with the regeneration of chlorine atoms, which are the active centres of the chain reaction.

The addition of ZSM-5 zeolite to MnO_x + NaCl or NiO_y + LiCl catalysts leads to the formation of aromatics.[38]

Other workers[39–43] observed an increase in the selectivity towards C_2H_6 and more particularly towards C_2H_4 when chlorides are added to oxide catalysts. The formation of chlorine is accelerated in the presence of water in the hydrolysis

$$LiCl + H_2O \longrightarrow LiOH + HCl \quad (10)$$

or the oxidative transformation on CaO + $CaCl_2$ [9]

$$\begin{aligned} &CaCl_2 + {}^1/_2\,O_2 \longrightarrow CaO + Cl_2, \\ &CaCl_2 + H_2O \longrightarrow CaO + HCl, \\ &2HCl + {}^1/_2\,O_2 \longrightarrow Cl_2 + H_2O. \end{aligned} \quad (11)$$

The introduction of water vapour into the reaction mixture on $CaCl_2$ leads to an increase in the yield of C_2-hydrocarbons and CH_3Cl, and also an increase in the ratio $[C_2H_4]/[C_2H_6]$. The high selectivity of ethylene formation is due to the high efficiency of the dehydrogenation of C_2H_6 to C_2H_4 in the presence of chlorine, compared with the dehydrogenation of C_2H_6 under the influence of O_2 alone. A decrease in the rates of the extensive oxidation of CH_4 and C_2-hydrocarbons compared with the pure oxides is also observed, making it possible to achieve a higher selectivity in the formation of ethylene. It has been shown[41] that chlorine initiates gas-phase reactions within a layer of the catalyst $SmCl_3$ or SmOCl. Reactions outside the layer increase the combustion of methane.

The introduction of C_2H_5Cl into the gas phase on $BaCO_3/\alpha$-Al_2O_3 or $BaCO_3/TiO_2$ leads to an almost two-fold increase in the yield of C_2-products. This increase in yield is due chiefly to an increase in the selectivity from 36% to 60%, while the degree of conversion decreases slightly. If C_2H_5Cl (10 p.p.m.) is added continuously to the gas stream, the yield of C_2-hydrocarbons remains constant for a long time. A very high ratio $[C_2H_4]/[C_2H_6]$ = 10.2 was obtained under these conditions on $BaCO_3/TiO_2$.[43]

A kinetic analysis of the heterogeneous–homogeneous scheme for obtaining C_2-hydrocarbons with the participation of Cl_2 showed[40] that C_2-hydrocarbons are formed preferentially at chlorine concentrations below 10^{-10} mol cm^{-3}; at a higher chlorine concentration, CH_3Cl is formed. Estimation of the concentration of CH_3 radicals based on a comparison of the experimental rates of formation of the products and the known rate constants of the elementary reactions gave high values. Increased concentrations of

the radicals possibly exist above the catalyst in a layer having a thickness of the order of the mean free path of the particles.

According to Warren,[43] chlorine has three functions in the oxidative condensation of methane: 1, it increases the conversion of CH_4 by increasing the number of active centres of the catalyst, for example by transforming surface salt centres such as carbonate, aluminate, and titanate into chlorides; 2, it decreases the number of extensive-oxidation centres; and 3, it increases the ratio $[C_2H_4]/[C_2H_6]$ (sometimes to 10). The alkali metal atoms present in the chlorides also inhibit extensive oxidation.

A particularly large number of studies have been carried out with the addition of chlorides to Mn-containing catalysts.[14,36,37,39,44–57]† In some cases a very high yield of C_2-hydrocarbons was obtained. For example, a 13% NaCl–17% MnO_x/SiO_2 catalyst at 1123 K gave a CH_4 conversion of 45.8%, and a selectivity with respect to C_2-hydrocarbons of 74.7%, that is the yield of C_2-hydrocarbons was 32% for a contact time of 0.5 s and a ratio $[CH_4]/[O_2] = 2$.[52] On an $LiCl + B_2O_3 + MnO_2$ (5:7:13) catalyst at 1023 K and a ratio $[CH_4]/[O_2] = 3:1$, the selectivity was 80%, and the yield of C_2 was 33.9%.[53]

The activity of chlorine-containing catalysts decreases during operation as a result of the loss of chlorine. It can be restored by introducing chlorine-containing additives into the gas phase: HCl,[48,51] CH_3Cl,[54] CH_2Cl_2,[40,55,56] CCl_4,[57]† Cl_2.[55] These additives restore the concentration of chlorine in the catalyst.

The phase composition of an Na–Mn–O/SiO_2 catalyst treated with a chlorine-containing reaction mixture has been studied.[58] A multi-phase oxide–halide system containing NaCl, Mn_3O_4, and MnO_2 is formed:

$$\beta\text{-}Na_{0.7}MnO_2 \xrightarrow{CH_4 + O_2 + 1\%\ HCl} NaCl + Mn_2O_3 + Mn_3O_4 + H_2O. \quad (12)$$

The phase transformations of this catalyst have been studied in detail for the oxidative dehydrogenation of ethane to ethylene by *in situ* X-ray diffraction. The initial chloride catalyst contained a phase with variable composition $NaCl.xMnCl_2$. During the $C_2H_6 + O_2$ reaction, a continuous increase in the intensity of the lines due to the NaCl phase was observed, with the appearance of oxide and the liberation of chlorine

$$3[NaCl \cdot 2MnCl_2] + 4O_2 \longrightarrow 3NaCl + 2Mn_3O_4 + 6Cl_2. \quad (13)$$

Comparison of the rates of formation of the NaCl phase (with the loss of chlorine) and ethylene showed a correspondence between these quantities. The rates, expressed in moles per minute, are fairly close to one another. Thus chlorine is generated by the redox oxidation of HCl (Deacon's process):

$$3[NaCl \cdot 2MnCl_2] + 4O_2 \longrightarrow 3NaCl + 2Mn_3O_4 + 6Cl_2 \ (\longrightarrow 12Cl),$$
$$3[4NaCl \cdot MnCl_2] + 2O_2 \longrightarrow NaCl + Mn_3O_4 + 3Cl_2 \ (\longrightarrow 6Cl),$$
$$2Cl^{\cdot} + C_2H_6 \longrightarrow C_2H_4 + 2HCl. \quad (14)$$

Ethylene is also formed in a process parallel to reaction (14), by the reaction of C_2H_6 with surface centres containing Mn^{4+}. A temperature-programmed study showed that the quantity of oxygen liberated from the oxide catalyst is four times the quantity of oxygen desorbed from the corresponding oxide halide catalyst. This weakly bound oxygen is apparently responsible for the extensive oxidation, and decreases the selectivity of the process. The selectivity increases sharply when oxygen is removed. The addition of HCl regenerates the mixed Na–Mn–Cl phase.

In some published studies, however, another opinion is found, namely that the formation of C_2H_4 on chloride catalysts is purely heterogeneous. For example, Conway and Lunsford[59] observed a selectivity in the conversion of CH_4 to ethane of 40.9% on a 65% LiCl/MgO catalyst, and selectivity in the transformation of ethane to ethylene of 70.2% for a degree of conversion of 75–79%, but the activity gradually decreased as a result of the removal of chlorine from the catalyst by its reaction with H_2O. The $LiCl/Dy_2O_3/MgO$ catalyst is even more active and stable.[60] In the opinion of the authors cited,[59,60] the presence of chlorine on the catalyst prevents the adsorption of CO_2 and alters the activity of the O^- centres in such a way that they become capable of activating the weaker C–H bond in ethane, but are still incapable of activating the stronger C–H bond in ethylene (that is for extensive oxidation).

The layer halides $MBi_3O_4X_2$, where M = Li, Na, K, Ag, Pb, Cd, and X = Cl, Br, are relatively stable under the catalysis conditions. Their activity and selectivity are not very high, however, and the yield of C_2 does not exceed 19.4%. Bromides are slightly more active than chlorides.[61,62] The so-called Arpe phases $M_{24}O_{31}Cl_{10}$, where M = Bi, La, Sm, have been studied.[63] These phases are exceptionally stable towards the removal of chlorine, and have a layer structure, but their activity is very low.

The pure chlorides of magnesium, calcium, strontium, barium, and potassium at 1023 K are selective in the formation of C_2H_6, but nonselective in the formation of C_2H_4. The mixed chlorides $LiCl/MnCl_2$ and $NiCl_2/MnCl_2$ are more selective; under the catalysis conditions they are converted into a mixture of chlorides and oxides MnO_x which is more selective.[64]

A $Bi_2O_3.MoO_3.LiCl$ melt at 1023 K gave 18% conversion, 35.8% selectivity with respect to C_2, and 6.4% yield, including only 1.4% C_2H_4. The addition of CH_3Cl to the gas phase increased the selectivity towards C_2H_4 to 100%, related to C_2-products.[65]

The aggressive nature of the halogens may prevent the practical application of reactions involving halogen-containing additives, despite the considerable increase in activity and selectivity.

V. Influence of carbon dioxide

A number of workers point out that CO_2 has a positive influence on the selectivity and a negative influence on the activity of catalysts for the oxidative condensation of methane. CO_2 forms surface carbonates on catalysts with basic properties. These carbonates decrease the number of active centres and hence decrease the activity of catalysts in oxidative condensation, but they decrease the activity in extensive oxidation to an even greater degree, so that the selectivity increases.[66,67]

Equilibrium in the decomposition of the alkaline earth metal carbonates $MCO_3 \rightleftarrows MO + CO_2$ at atmospheric pressure is established at a temperature close to that of the oxidative condensation of methane. Under the catalytic conditions, CaO was covered by a layer of $CaCO_3$,[68] and SrO by a layer of $SrCO_3$.[69] Deactivation of the catalyst with a simultaneous increase in selectivity was observed. Similar effects were observed for the Li/MgO catalyst.[70] An increase in the selectivity under the influence of CO_2 was also observed for catalysts of the oxidative dehydrogenation of ethane.[71]

† See also S Ahmed, J B Moffat *J. Catal.*, 1989, **118**(2) 281, 1190; **121**(2) 408; 1990, **125**(1) 54.

At higher temperatures, CO_2 may take part in oxidative dehydrogenation as an oxidising agent. This was first studied in detail by Aika and Nishiyama.[72] The free energies of the reactions of CO_2 with methane and ethane ΔG (kJ mol^{-1}) at 1073 K are given below:

$$CH_4 + 2CO_2 = C + 2CO_2 + 2H_2O \qquad \Delta G = -27, \qquad (15)$$

$$CH_4 + 3\,CO_2 = 4CO + 2H_2O \qquad \Delta G = -611, \qquad (16)$$

$$CH_4 + CO_2 = 2CO + 2H_2 \qquad \Delta G = -254, \qquad (17)$$

$$C_2H_6 + CO_2 = C_2H_4 + CO + H_2O \qquad \Delta G \sim 0, \qquad (18)$$

$$2CH_4 + CO_2 = C_2H_6 + CO + H_2O \qquad \Delta G = 35. \qquad (19)$$

The ΔG values are negative for the first three processes, and positive for the fifth reaction. All the reactions are endothermic. The equilibrium yield of C_2H_6 at 1073 K even according to reaction (19) should be 13%; this value is fairly high. The equilibrium yield of C_2H_4 by reaction (18) is 57%. By using a $CH_4 + CO_2 + O_2$ mixture it is possible to obtain a higher yield of C_2 and to convert the oxidative condensation of methane into a thermally neutral process, that is to solve the problem of removing heat in the oxidative condensation of methane using oxygen.

Aika and Nishiyama[72,73] studied a number of oxide catalysts of the oxidative condensation of methane. Their properties were compared in two mixtures: 1, $CH_4 + O_2$ (100:1) and 2, $CH_4 + CO_2 + O_2$ (100:100:1). A catalyst with a medium basic strength showed an even higher yield of C_2-hydrocarbons compared with the yield in a $CH_4 + O_2$ mixture. For example, on 50% PbO–MgO the yield of C_2 was 3.28% in the first case, and 4.37% in the second; on CaO–BaO–CeO_2 the yields were 2.2% and 3.5% respectively. From these results it was concluded[72] that the oxidative dehydrogenation of hydrocarbons involves oxygen atoms removed from CO_2

$$CO_2 \rightarrow CO + O_{ads}, \qquad (20)$$

$$2CH_4 + O_{ads} \rightarrow C_2H_6 + H_2O, \qquad (21)$$

$$C_2H_6 + O_{ads} \rightarrow C_2H_4 + H_2O. \qquad (22)$$

Experiments with labelled molecules $^{13}CO_2$ and $^{12}CD_4$ [74] showed that ^{13}CO and $^{12}C_2D_6$ appear. This means that all the CO is formed only from CO_2, and not as a result of the further oxidation of hydrocarbons. In the absence of hydrocarbon, CO_2 is completely unreactive on the catalyst. An initial quantity of ethane is necessary to initiate the reaction. The transformation of CO_2 apparently takes place by the reverse reaction to the conversion of water gas

$$CO_2 + H_2 \longrightarrow CO + H_2O \qquad (23)$$

by the action of the hydrogen formed in the gas-phase dehydrogenation of ethane, with intermediate dissociative adsorption (20). Thus in this case the mechanism of the activation of methane and ethane is the same as the mechanism of activation using oxygen alone.

The main processes are the formation of synthesis gas by reaction (17) on pure MgO, reactions (15) and (16) on PbO, and oxidative condensation (18) and (19) on PbO–MgO. The addition of O_2 facilitates reactions (18) and (19), and suppresses reactions (15) and (16). Catalysts with strong basic centres such as Li/MgO and Li/ZnO give less satisfactory results in a $CH_4 + CO_2$ mixture than in a $CH_4 + O_2$ mixture, and are rapidly deactivated.[74]

Reaction (17) takes place mainly at higher tempratures. On Mn–BaO/Al_2O_3 and Mn–CaO/Al_2O_3 catalysts, for example, this reaction takes palce above 1173 K.[75]

A study of the oxidative dehydrogenation of ethane to ethylene using CO_2 [76–78] showed that the most active and stable systems for the activation of CO_2 and the hydrocarbon are based on manganese oxides. The selectivity of the formation of C_2H_4 was 54% on a 17% MnO_x/SiO_2 catalyst; it increased to 65.4% on 5.5% Cr–17% MnO_x/SiO_2, and when 1.5% K_2O was added the selectivity increased to 76.8% for degrees of conversion of C_2H_6 and CO_2 of 82.6% and 52.3% respectively. The yield of C_2H_4 on the last catalyst was 55.7% at $C_2H_4/CO > 1$.

An *in situ* X-ray diffraction study of the phase composition of the K–Cr–MnO_x/SiO_2 catalyst[76,77] showed that the Mn_3O_4 phase observed initially is reduced to MnO under the reaction conditions. The same is observed for the MnO_x/SiO_2 and Fe–MnO_x/SiO_2 catalysts.[78] The addition of a second transition metal (iron or chormium) oxide apparently creates an inter-phase boundary which facilitates the redox process. The surface is oxidised both by CO_2 and by O_2. The oxygen capacity in the oxidative dehydrogenation using CO_2 on a K–Cr–MnO_x/SiO_2 catalyst was much lower (by a factor of 8) than that when O_2 was used.

The kinetics of the oxidative dehydrogenation of ethane are described by the equation

$$r = \frac{k_1 p_{C_2H_6} k_2 p_{CO_2}}{k_2 p_{CO_2} + k_3 p_{CO}}. \qquad (24)$$

With increase in the ratio $[CO_2]/[C_2H_6]$ the selectivity in the formation of C_2H_4 at first increases, and then reaches a constant value at $[CO_2]/[C_2H_6] > 2.5$. This change in selectivity differs considerably from the change in selectivity under the influence of O_2 in the oxidative dehydrogenation of CH_4 and C_2H_6, which is characterised by a decrease in selectivity with increase in p_{O_2} [see Eqn. (4)]. The increase in the extent of the oxidation of the surface with increase in p_{CO_2} possibly retards the extensive cracking of C_2H_6.

The results show that it is possible in principle to carry out the oxidative dehydrogenation of CH_4 and C_2H_6 using a mixture of the two oxidising agents O_2 and CO_2 by a thermally neutral scheme. The observed[72–74] increase in the yield of C_2H_4 in the oxidative condensation of methane using CO_2 is probably due to the continuous displacement of equilibrium (19) with the removal of ethane by reaction (18). Even higher yields of C_2H_4 than those obtained in the work cited[72–74] can be expected.

VI. Cyclic oxidation and reduction

Oxygen decreases the selectivity of the oxidative condensation of methane [see Eqn. (4)], so that many workers have tried to carry out the reaction in the absence of oxygen in the gas phase. One of the first studies[79] obtained considerable yields of C_2-hydrocarbons by the alternate reduction of the catalyst by methane and its subsequent oxidation by oxygen. Alternate reduction and oxidation also solves to a considerable extent the problem of heat removal. The most active catalyst was MnO_x/SiO_2.

The first Arco has made a detailed study of this cyclic process. The deposited oxides of manganese, indium, gallium, antimony, tin, bismuth, and praseodymium were found to be more active in the cyclic process than in the continuous process. The selectivity reached 10–15%.[80] A subsequent study[80–83] confirmed the high

activity and selectivity of manganese-containing systems and made it possible to improve them by modification. A 15% MnO_x + 5% $Na_4P_2O_7/SiO_2$ catalyst was found to be stable. Successive two-minute pulses of CH_4 and O_2 at 1123 K gave a 17% yield of C_2-hydrocarbons (77% selectivity and 22% conversion); at 1073 K and a low degree of conversion, the selectivity approached 100%.[81] Almost 30 000 cycles were carried out on an Li–B–Mn–Mg–O catalyst with almost no loss of activity. Arco constructed a pilot plant based on these experiments.[84] The firm Bechtel developed an improved pilot plant for the cyclic process with reduction of the catalyst in a fluidised bed.[85]

The $Mn-O/Al_2O_3$ catalyst was much less selective than $Mn-O/SiO_2$.[85] Its phase composition changes continuously on oxidation and reduction. In the reaction of MnO_x/SiO_2 with CH_4, the reduction of Mn_3O_4 to MnO was observed, corresponding to the removal of 0.33 g-atom of oxygen per g-atom of manganese.

A study of the reduction of PbO/Al_2O_3 and PbO/MgO catalysts under cyclic conditions showed that in the reduction, up to 23% of the oxygen of PbO is removed, and the metallic lead remaining converts CH_4 mainly into C_2H_6.[86] This result to some extent contradicts X-ray photoelectron spectroscopic data,[87] according to which a Pb phase is not formed on 0.4% PbO/MgO, and also other published data,[33] which show that the reduction of PbO to Pb leads chiefly to the oxidation of CH_4 to CO_2.

4% Na/Pr_6O_{11} was also an active catalyst in the cyclic process.[84] At 1073 K it gave 21% conversion and 76% selectivity. The selective preparation of C_2-hydrocarbons in a cyclic process was carried out on an $Li/NiO/TiO_2$ catalyst; on Li/TiO_2, however, only CO and CO_2 were obtained.[88] The pure oxides Mn_2O_3 and MnO_2 function effectively under cyclic redox conditions, but the addition of even small quantities of oxygen to methane leads to extensive oxidation.[5] Relatively high yields of C_2-hydrocarbons were also obtained under cyclic conditions on an Li/MgO catalyst.[89]

The best catalysts for cyclic redox conditions are systems containing the oxides of transition metals and reducible lanthanide oxides. Their capacity with respect to oxygen is apparently fairly high, while the absence of weakly-bound oxygen on the surface prevents extensive oxidation.

The selectivity of catalysts such as In_2O_3, Bi_2O_3, La_2O_3, and Li/MgO under cyclic conditions is also fairly high, but the capacity with respect to oxygen is much lower.[5,79,81,90]

The oxidative dehydrogenation of CH_4 [75] and C_2H_6 [76,77] using CO_2 has also been studied under cyclic alternating conditions. The selectivity is higher, but the oxygen capacity much lower, than in the case where oxygen is used as oxidant. The rate of the oxidative dehydrogenation on a $K-Cr-MnO_x/SiO_2$ catalyst increases when chromium is introduced. According to the authors cited,[76,77] the inter-phase boundary between MnO_x and CrO_y facilitates the re-oxidation of the catalyst.

One form of separated process involves the use of membranes permeable to oxygen. An advantage of this process may be the possibility of condensation in the absence of oxygen or at a low oxygen pressure.

The formation of ethane on a silver membrane with O_2 on one side of the membrane and CH_4 on the other was observed even at 743 K.[91] 100% selectivity was obtained with a low conversion (0.02%). Increase in temperature to 953 K increased the conversion to 40% for a selectivity of about 40%. C_2H_4 also began to appear in the products at 823 K. The active species is atomic oxygen, which diffuses to the silver surface through the membrane and takes part in the formation of C_2-hydrocarbons. The diffusion is apparently the limiting stage; this is confirmed by the similarity in the rate of formation of the C_2-products and the rate of diffusion of oxygen through silver. The observed activation energy of the formation of C_2-hydrocarbons is 150 kJ mol^{-1}. The authors cited[91] consider the C_2-hydrocarbons may be formed as a result of the reaction of CH_4 with atomic oxygen in the gas phase.

Membranes of PbO or MgO on Al_2O_3,[92] PbO/MgO/dynacerum (ceramic),[93] or Pd/MgO/ceramic[94] have also been studied. In the last case the catalysis took place at a low temperature, 553–683 K; 38% selectivity with 0.45% conversion was observed even at 523 K.

The separated cyclic process can be modified by the sectional introduction of oxygen into the reactor. For example, oxygen has been introduced in portions into four successive reactors.[95] This gave a much higher selectivity of up to 80% at 1103 K and 20% conversion on an La/MgO catalyst when oxygen was introduced in equal quantities into each of the four sections. A selectivity of 62% was obtained for 35.7% conversion.

Finally, an electrochemical version of the process is possible. An electrochemical cell with 80% Y_2O_3/ZrO_2 solid electrolyte, a silver anode, and an Ag/Bi_2O_3 cathode was first used by Otsuka and co-workers.[96] A CH_4 + O_2 mixture was passed over the anode. The selectivity was higher than in the continuous gas-phase process.

Other authors[97–102] carried out the electrochemical process at 1023–1123 K using the same solid electrolyte Y_2O_3/ZrO_2. The electrodes used were the catalysts $La_{0.89}Sr_{0.10}MnO_3$,[97,100] Au, Pd, Ag/Bi_2O_3,[98] Cu, Ag–Pd, La–Li–O,[101] and $LaCoO_3$.[102] The reaction rates were low, however. The electrochemical version is still far from the stage of practical application.

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