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Hydride forming metals and alloys as hydrogen acceptors in catalytic dehydrogenation

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Abstract. The use of hydride forming metals and alloys as hydrogen acceptors in order to overcome the thermodynamic limitations in catalytic reactions involving the evolution of hydrogen is examined. The high effectiveness of intermetallic hydrogen acceptors in reactions involving the dehydrogenation of cycloalkanes, isobutane, and alcohols (C_1-C_3) and the aromatisation of alkanes (C_2-C_3) is noted. The bibliography includes 36 references.

I. Introduction

A unique feature of many transition metals and alloys based on them is the ability to absorb reversibly significant amounts of hydrogen at fairly high rates of absorption and desorption. This particular feature is in fact responsible for the wide scale application of metal hydrides in power and atomic engineering for the storage and purification of hydrogen.[1-3]

The incorporation of hydrogen in the metal or alloy lattice is preceded by dissociative chemisorption with formation of atomic hydrogen, while the evolution of hydrogen from the bulk of the hydride involves the recombination of atoms with subsequent desorption of H_2 molecules into the gas phase. The heterophase exchange of hydrogen between the hydride lattice and the hydrogen in the gas phase takes place continuously. The high activity of the surface centres as regards the dissociation of H_2 and the constant presence of activated hydrogen on the surfaces of hydrides makes it possible to employ compounds of this kind as highly effective hydrogenation catalysts in petrochemistry and petroleum processing.[4-6] The formation of hydrogenation products of hydrocarbons in the presence of hydrides of intermetallic compounds depleted in hydrogen was first observed more than 20 years ago by Lunin et al.[7]

In 1985, the absorption capacity of hydride forming metals and intermetallic compounds was used successfully to overcome thermodynamic limitations in catalytic dehydrogenation processes.[8,9] The reactions involving the dehydrogenation of alkanes, alkenes, and alcohols are known to be thermodynamically unfavourable at moderate temperatures. For example, the dehydrogenation of alkanes C_nH_{2n+2} to alkenes C_nH_{2n} at 298 K is accompanied by an increase in the standard Gibbs free energy.

$$C_nH_{2n+2} \longrightarrow C_nH_{2n} + H_2, \quad \Delta G^0 > 0 \qquad (1)$$

It was found that the introduction of a suitable metal or intermetallic compound (M) into the system displaces the equilibrium appreciably towards dehydrogenation, since the formation of the hydride (MH_2) entails the evolution of energy necessary to effect reaction (1).

$$M + H_2 \longrightarrow MH_2, \quad \Delta G^0 < 0 \qquad (2)$$

The absorption capacity of the initial alloy may be restored in the subsequent regeneration cycle. The combination of reactions (1) and (2) together with the regeneration of the initial alloy can be represented in the following form:

$$C_nH_{2n+2} + M \longrightarrow C_nH_{2n} + MH_2$$
$$\uparrow \qquad\qquad\qquad\qquad \downarrow$$
$$-H_2$$

Consequently the role of the hydride-forming alloy consists in binding the hydrogen evolved on dehydrogenation with the formation of a thermodynamically more favourable compound. This process is in many respects analogous to oxidative dehydrogenation:

$$C_nH_{2n+2} + O_2 \longrightarrow C_nH_{2n} + H_2O,$$

with the sole difference that in the former case a hydride is formed and may be regenerated to the initial alloy with evolution of hydrogen, while in the oxidative version water is formed as a side product.

The first studies using hydride forming metals and alloys as hydrogen acceptors were carried out in relation to the catalytic dehydrogenation of isobutane[8] and cyclohexane.[9] Subsequent investigations made it possible to discover a positive effect, which is attained when the hydrogenation of metals and intermetallic compounds is coupled with a whole series of thermodynamically restricted catalytic reactions proceeding with evolution of hydrogen. The principal results of such investigations are summarised in the present review and the characteristic features of the reactions in the presence of intermetallic hydrogen acceptors are considered.

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II. Catalytic reactions using intermetallic hydrogen acceptors

Tables 1 and 2 present the literature data on the application of hydride forming metals and alloys as hydrogen acceptors in catalytic reactions of various organic compounds. Intermetallic hydrogen acceptors have been tested mainly in the dehydrogenation reactions of alkanes and alcohols. Both oxide and zeolite systems with deposited metals and the activated surfaces of the intermetallic compounds themselves have been used as dehydrogenation catalysts. We shall examine in greater detail the reaction conditions and the principal results achieved.

1. Reactions of hydrocarbons

The first reaction in which a hydride forming metal (Ti) was used successfully to remove the hydrogen evolved was the dehydrogenation of isobutane to isobutene.[8] The reaction was carried out in a flow system on a platinum/alumina catalyst (5 mass% Pt) mixed mechanically with titanium powder at 641 K. The mass ratio of the catalyst and the acceptor was 1 : 1.5. As a result of the removal of 60 vol.% of the hydrogen formed, the ratio iso-C_4H_{10} : iso-C_4H_8 in the reaction product was 12.5 : 1, which corresponds to 7.4% conversion of isobutane into isobutene. Under these conditions but without the removal of hydrogen, the equilibrium ratio iso-C_4H_{10} : iso-C_4H_8, calculated from thermodynamic data is 19 : 1 and corresponds to 5.3% conversion. In a repeated dehydrogenation cycle after the regeneration of titanium, the conversion reached 10.4%. Thus, by carrying out the hydrogenation of the titanium powder jointly with the dehydrogenation of isobutane, it was possible to increase by a factor of 1.5–2 the yield of the alkene compared with the equilibrium value (without removing hydrogen).

The use under the same conditions of the intermetallic compound $Ti_{0.63}V_{0.27}Fe_{0.1}$, which functions simultaneously as a hydrogen acceptor and as a dehydrogenation catalyst, did not yield a positive result owing to the low catalytic activity of the intermetallic compound. The conversion to isobutane did not exceed 1% in this case although the hydrogen formed was fully absorbed by the acceptor.

The dehydrogenation of isobutane to isobutene has also been investigated in the presence of the ZrNi and ZrCo hydrogen acceptors on the Pt/Al_2O_3 and Pt/SiO_2 catalysts for a catalyst : acceptor mass ratio of 1 : 3.[10] The reaction was carried out at 300 and 350 °C. The calculated equilibrium yield of isobutene under these conditions, without the removal of hydrogen, was 1.5% and 4.2% respectively, while in the presence of the intermetallic compound ZrNi it reached 4.3% and 11.5%, i.e. exceeded the equilibrium yield by a factor of 2.5–3. The intermetallic compound ZrCo and the Pt/SiO_2 catalyst proved to be less effective in this reaction.

The highest yield of isobutene from isobutane, amounting to 45%, which exceeds by a factor of 2 the equilibrium yield under the same conditions without the removal of H_2, was achieved at 470 °C in the presence of the Cr_2O_3/ZrO_2 catalyst mixed with the intermetallic compounds Zr_2Fe.[10]

The effect of hydride-forming intermetallic compounds on the dehydrogenation of cycloalkanes to the corresponding aromatic hydrocarbons has been considered in a number of studies.[9,12–14] In the series of intermetallic compounds tested,[9,12] $CaNi_5$ proved to be the most effective hydrogen acceptor. In its presence, the yield of benzene from cyclohexane on the Pt/Al_2O_3 catalyst at 150 °C increased by a factor of 3.5 compared with the equilibrium yield (without the removal of hydrogen) and reached 32.2% (the equilibrium yield is 9.1%). The use of the intermetallic compound ZrNi as the hydrogen acceptor in a similar system made it possible to exceed by a factor of 5 the equilibrium yield of benzene from cyclohexane and of toluene from methylcyclohexane at 190 °C.[13,14] Under these conditions, 100% conversion of cycloalkanes into the corresponding aromatic products was observed (the equilibrium yield is about 20%).

The positive effect of the lanthanide intermetallic compounds Nd_2Co_7 and Sm_2Co_7, used simultaneously as catalysts and hydrogen acceptors, has been noted in the dehydrogenation of cyclohexene to benzene and of n-heptane to methylcyclohexane.[15] The latter reaction occurred at 398 K and only traces of the n-heptane cyclisation product were observed.

The intermetallic compound Zr_2Fe proved to be an effective hydrogen acceptor in the significantly more complex multistage aromatisation of C_2–C_3 hydrocarbons.[16–20] The reaction was studied in the temperature range 450–550 °C in the presence of catalysts based on the high-silica TsVM zeolite modified by zinc, gallium, or platinum cations. When the hydrogen evolved in the reaction was bound by the intermetallic acceptor, the yield of aromatic hydrocarbons from ethane was higher by a factor of 4–6 than in the absence of the intermetallic compound, and the selectivity of the aromatisation increased by a factor of 2–2.5 as a result of the suppression of the methane-forming side reaction.[16–18] In the aromatisation of propane in the presence of hydrogen acceptors, the yield of aromatic hydrocarbons increased by a factor of 2–5 and the sensitivity of the aromatisation increased by a factor of 1.5–3.5.[19,20]

An attempt was also made to influence the equilibrium in reactions involving the direct conversion of methane into C_2 hydrocarbons, which is thermodynamically least favourable but is of extremely great practical importance.[21] The reaction was carried out at 400 K with the use of Ti and TiFe as the hydrogen acceptor and deposited metallic catalysts containing Pt, Rh, or Ni. However, the only reaction product, for a very low conversion of methane (above 1%), was coke.

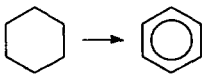
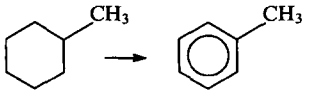
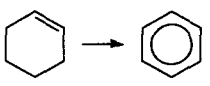
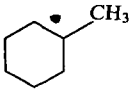
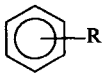
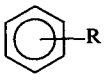
2. Reactions of alcohols

A large group of studies[15,22–27] has been devoted to the reactions of alcohols in the presence of intermetallic compounds of various compositions. In contrast to the reactions of hydrocarbons, hydride forming metals and alloys play the role of acceptors of the evolved hydrogen and of catalysts simultaneously in these processes. In certain cases, the surface of the alloys was modified by platinum, ruthenium, copper,[26] or rhodium[23] salts in order to increase the catalytic activity. The reactions were carried out in flow[24,25] and circulation systems[15,22,23,26] or in an auto-clave.[27] A direct quantitative estimate of the effect of hydride formation on the dehydrogenation of an alcohol is difficult and it can be inferred only indirectly from the decrease in the reaction temperature and the increase in the process selectivity.

In the presence of intermetallic compounds of different composition, methanol was dehydrogenated selectively under mild conditions (356–443 K) to CO and hydrogen, the latter forming part of the composition of the hydride.[15,22,23] The activity of the intermetallic compounds fell in the series $Zr_2Ni > M_2Co_7 > MFe_2$, where M is a lanthanide element. The authors explain this by the possible decrease in the catalytic activity of metals in the sequence Ni > Co > Fe. On the other hand, in terms of their absorption capacity the lanthanide intermetallic compounds were superior to Zr_2Ni: in their presence, complete removal of hydrogen from the reaction mixture was observed, whereas in the case where Zr_2Ni had been used, hydrogen was present in the gas phase from the very start and throughout the entire experiment. After the deposition of platinum or rhodium salts on the surfaces of the least active intermetallic compounds MFe_2, their properties were appreciably improved.[23] Thus the deposition of $RhCl_3$ on $DyFe_2$ increased the activity of the latter in the decomposition of methanol by a factor of 18.

Depending on the composition of the hydride-forming intermetallic compound used, the formation of various products was observed in the dehydrogenation of methanol at 523 K.[24,25] Thus the main product was formaldehyde in the presence of FeTi and $(Fe_{0.9}Mn_{0.1})Ti$. On nickel-containing alloys, methanol was con-verted into CO, while on Mg_2Cu methyl formate was also found among the reaction products in addition to CO.

Table 1. Reactions of hydrocarbons in the presence of intermetallic hydrogen acceptors.

Reaction	Intermetallic compound	Catalyst	Ref.
iso-C_4H_{10} ⟶ iso-C_4H_8	Ti	Pt/Al_2O_3	8
	$Ti_{0.63}V_{0.27}Fe_{0.1}$,	without catalyst	8
	$Ti_{0.63}V_{0.225}Fe_{0.1}Pt_{0.045}$		
	ZrNi, ZrCo	Pt/Al_2O_3	10
	Zr_2Fe	Cr_2O_3/ZrO_2	11
	FeTi, $(Fe_{0.9}Mn_{0.1})Ti$, $CaNi_5$, $LaNi_{4.7}Al_{0.3}$, Mg_2Ni, Mg_2Cu	Pt/Al_2O_3	9, 12
	ZrNi	Pt/Al_2O_3	13
	ZrNi, $ZrCr_2$, $ZrCr_2Ni_{0.1}$	Pt/Al_2O_3, Pt/SiO_2, Pd/Al_2O_3	14
	ZrNi	Pt/Al_2O_3	14
	Nd_2Co_7, Sm_2Co_7	without catalyst	15
n-C_7H_{16} ⟶ 	Nd_2Co_7, Sm_2Co_7	"	15
C_2H_6 ⟶ 	Zr_2Fe	Pt/HTsVM, Pt-Cr/HtsVM, Zn/HTsVM, Ga/HTsVM	16–18
C_3H_8 ⟶ 	Zr_2Fe	Zn/HTsVM, Ga/HTsVM, Pt/HTsVM	19, 20
CH_4 ⟶ C_2H_6	Ti, TiFe	Ni/Al_2O_3, Rh/SiO_2, Pt, Sn/Al_2O_3	21

The selective dehydrogenation of ethanol to acetaldehyde and hydride hydrogen occurred at 423 K [22] and 523 K [24] on all the intermetallic compounds tested by the authors with the exception of Mg_2Cu, in the presence of which a small amount of ethyl acetate was formed (the ethyl acetate : acetaldehyde ratio was 0.0047). The activities of the intermetallic catalysts in the reactions of ethanol and methanol depended to almost equal extents on the composition of the alloys, which indicates, according to the authors,[22,24] the similarity of the mechanisms of these reactions.

The dehydrogenation of isopropyl alcohol in the presence of the intermetallic compounds M_2Co_7 (where M = Pr, Nd, Sm) was quantitative and the selectivity in the formation of the corresponding hydride and acetone was close to 100% even at 317 K.[15,26] The rates of dehydrogenation of isopropyl alcohol on $Nd_2Co_7H_{0.1}$, $Nd_2Co_7H_{2.7}$, and $Nd_2Co_7H_{5.1}$ were respectively 1.1×10^{-3}, 6.0×10^{-4}, and 3.5×10^{-4} mmol min^{-1} per gram of the alloy. According to the authors,[15,26] this means that the formation of the hydride is the driving force of the dehydrogenation reaction. On the other hand, as in the case of methanol, modification of the surfaces of the alloys with platinum increases significantly their activity. For example, treatment of Pr_2Co_7 suspension with an aqueous solution of H_2PtCl_6 increased its activity in the dehydrogenation of isopropyl alcohol by a factor of 10.[26]

The effect of the hydride forming alloy $Mg_{2.4}Ni$ on the dehydrogenation of isopropyl alcohol in the presence of the Cu/CuO catalyst has been investigated[27] in a static system in an autoclave at 473 K and a pressure of 0.1–1.0 MPa. The absorption of hydrogen by the alloy altered appreciably the hydrogen balance in the system. However, as a consequence of the catalytic activity of the hydride in condensation reactions, the selectivity of the dehydrogenation reaction fell greatly.

Analysis shows that, in the vast majority of cases, the formation of the hydrides of transition metals and alloys under the conditions of catalytic dehydrogenation has a positive effect on the yields of the target products and on the selectivity of the dehydrogenation process.

III. Characteristic features of catalytic dehydrogenation coupled with hydride formation

Despite the wide variety of the initial organic reagents, the catalysts and the intermetallic compounds employed, and the experimental conditions, certain general features are characteristic of all the dehydrogenation reactions using intermetallic hydrogen acceptors.

1. Thermodynamics

It follows from Eqns (1) and (2) that the thermodynamic features of coupled dehydrogenation and hydride formation processes are equally important for the attainment of a positive effect.

For hydrogen to be absorbed, it is essential that its partial pressure in the gas phase should exceed the equilibrium dissociation pressure (p_{eq}) of the hydride. The pressure p_{eq} for a given metal or alloy is determined by the thermodynamics of the absorption–desorption equilibrium and tends to increase with increasing temperature.[28] The partial pressure of hydrogen in the reaction mixture is determined by the dehydrogenation equilibrium. When the temperature is reduced, thermodynamic

Table 2. Reactions of alcohols in the presence of intermetallic hydrogen acceptors.

Reaction	Intermetallic compound	Catalyst	Ref.
$CH_3OH \longrightarrow CO$	Nd_2Co_7, Sm_2Co_7	without catalyst	15
	$ErFe_2$, $DyFe_2$, Nd_2Co_7, Sm_2Co_7	"	22
	Zr_2Ni, Pr_2Co_7, Nd_2Co_7, Sm_2Co_7, $ErFe_2$, $DyFe_2$	$RhCl_3 \cdot 3H_2O$	23
	FeTi, $(Fe_{0.9}Mn_{0.1})Ti$	without catalyst	24, 25
$CH_3OH \longrightarrow HCHO$	$CaNi_5$, $LaNi_{4.7}Al_{0.3}$, Mg_2Ni	"	24, 25
$CH_3OH \longrightarrow HCOOCH_3$	Mg_2Cu	"	24, 25
$C_2H_5OH \longrightarrow CH_3COH$	$ErFe_2$, $DyFe_2$, Nd_2Co_7, Sm_2Co_7	"	22
	FeTi, $(Fe_{0.9}Mn_{0.1})Ti$, $CaNi_5$, $LaNi_{4.7}Al_{0.3}$, Mg_2Ni, Mg_2Cu	"	24
$CH_3CHCH_3 \longrightarrow$ (OH)	Nd_2Co_7, Sm_2Co_7	"	15
$\longrightarrow CH_3CCH_3$ (O)	$ErFe_2$, $DyFe_2$, Nd_2Co_7, Sm_2Co_7	"	22
	Pr_2Co_7, Nd_2Co_7, Sm_2Co_7	$RuCl_3$, $CuSO_4$, H_2PtCl_6	26
	$Mg_{2.4}Ni$	Cu/CuO	27

limitations to the dehydrogenation reactions arise (Fig. 1). In the dehydrogenation of alcohols, $\Delta G°$ shifts to the positive region at significantly lower temperatures than in the dehydrogenation of hydrocarbons, with the exception of the aromatisation of cycloalkanes (Table 3). Thus the equilibrium pressure p_{eq} and the temperature at which the free energies $\Delta G°$ for the dehydrogenation reactions shift to the positive region impose certain limitations on the choice of metals and intermetallic compounds as hydrogen acceptors. For example, the equilibrium dissociation pressure of the hydride of $Mg_{2.4}Ni$ [27] is such that this alloy can be used to remove the H_2 evolved in the dehydrogenation of ethanol or isopropyl alcohol but not propane or methanol.

The majority of binary and ternary metal hydrides have been synthesised and investigated in order to use them as hydrogen accumulators.[28] One of the main requirements which must be met by such systems is a low equilibrium dissociation pressure at room temperature. This restricts the search for intermetallic hydrogen acceptors suitable for the dehydrogenation of saturated hydrocarbons. Intermetallic compounds having the composition M(IV)$_2$M(VIII), the equilibrium dissociation pressures of the hydrides of which at 500 °C are much lower than 1 atm, appeared to be the most promising.

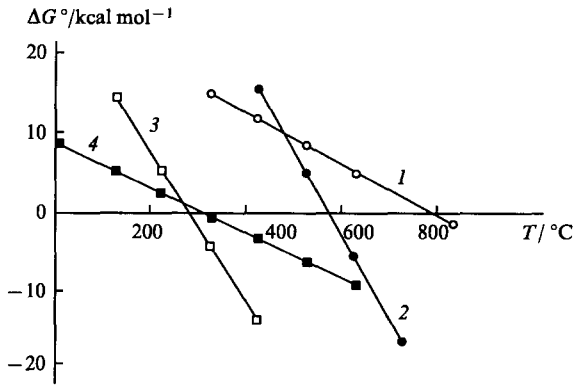


Figure 1. Temperature dependence of the change in the standard Gibbs free energy in the reactions involving the conversion of ethane into ethylene (line *1*), of ethane into benzene (line *2*), of cyclohexane into benzene (line *3*), and of ethanol into acetaldehyde (line *4*).

2. Absorption by metals and alloys of the hydrogen evolved in the dehydrogenation reaction

Evidently, for hydride formation to have a positive effect on the dehydrogenation reaction it is essential that the rate of absorption of hydrogen by the intermetallic acceptor should be equal to or greater than the rate of its formation as a result of the reaction. Indeed, in the dehydrogenation of isobutane,[10] cycloalkanes,[9,14] and alcohols[22] the rate of absorption of hydrogen by intermetallic compounds was one of the factors determining the effectiveness of their application.

The interaction of metals and alloys with hydrogen is a complex process including stages involving the dissociative adsorption of H_2, surface migration, transition from the adsorbed to the absorbed state, and finally bulk-phase diffusion.[28] Kinetic studies have shown that below 400 °C the rate of absorption is as a rule limited by the dissociation of H_2 molecules or the passage of H atoms through the surface oxide film,[30] which is formed when metals and intermetallic compounds come into contact with air under normal conditions.[31] This could have hindered the use of intermetallic hydrogen acceptors in low-temperature cycloalkane and alcohol dehydrogenation reactions. However, the presence on the surface of intermetallic compounds of Group VIII metals reduces appreciably the activation energy for the dissociative chemisorption of hydrogen, which facilitates absorption significantly even at room temperature.

The absorption of hydrogen may be promoted by sputtering isolated regions or monolayers of Ni, Pd, or Fe on to the surface of the intermetallic compound.[30,31] The introduction of Group VIII metals into intermetallic compounds at the stage where the metals are fused together does not always activate the absorption processes, since the surface oxide film is formed preferentially

Table 3. Thermodynamics of the dehydrogenation reactions of hydrocarbons and alcohols.

Reactant	Product	Temperature/ °C at which $\Delta G° = 0$ [a]
Ethane	ethylene	800
Ethane	benzene	580
Propane	propene	660
Butane	butene	540
Cyclohexane	benzene	260
Methanol	formaldehyde	430
Ethanol	acetaldehyde	330
Isopropyl alcohol	acetone	150

[a] Determined from thermodynamic data.[29]

from elements with a higher affinity for oxygen, so that the concentration of the Group VIII metal on the surface proves to be inadequate. In order to enrich the surface in the Group VIII metal, it is necessary to subject the intermetallic compound to a preliminary oxidation-reduction treatment under specific conditions[32] or to repeat the absorption-desorption cycles.[8,27]

One of the fairly important factors which determines the possibility of using particular intermetallic compounds as hydrogen acceptors is the retention of the ability to sorb H_2 under dehydrogenation conditions and after carrying out the desorption cycles. It was found that intermetallic hydrogen acceptors effectively retained their absorption properties under the conditions of catalytic reactions. In reactions involving hydrocarbons, this is probably associated with the catalytic inertness of the metals and alloys employed. In the reactions of alcohols, the dehydrogenation and H_2 absorption reactions take place at different active centres,[22,27] so that deactivation of the surface by the reaction products (observed in some cases) does not affect the absorption capacity of the acceptor.

As mentioned above, the repetition of the absorption-desorption cycles may increase the absorption capacity of the metals and alloys by activating their surfaces. For example, the acceptor properties of titanium are improved on repeating the isobutane dehydrogenation reaction after the desorption of hydrogen from the hydride.[8] On the other hand, the thermal desorption of hydrogen from the hydride of the intermetallic compound Zr_2Fe leads to an irreversible decrease in its absorption capacity as a consequence of the bulk-phase decomposition to $ZrFe_2$ and ZrH_2, which occurs at temperatures above 400 °C. However, the introduction of oxygen in the stage where the metals are fused together prevents the bulk phase decomposition of this intermetallic compound even at 850 °C.[33]

3. The activity of dehydrogenation catalysts and the change in the selectivity of catalytic processes

The yield of the products of dehydrogenation coupled with hydride formation is virtually unrestricted by the thermodynamic equilibrium and is therefore determined primarily by the rate of the reaction, i.e. by the activity of the hydrogenation catalyst. This was clearly demonstrated for the dehydrogenation of isobutane using Pt/Al_2O_3, $Ti_{0.63}V_{0.27}Fe_{0.1}$, or $Ti_{0.63}V_{0.225}Fe_{0.1}Pt_{0.045}$ as the catalyst.[8] In the aromatisation of cyclohexane,[14] the difference between the dehydrogenation activities of the Pt/Al_2O_3 and Pd/Al_2O_3 catalysts, which is not manifested in the absence of the hydrogen acceptor for thermodynamic reasons (the conversions of cyclohexane into benzene in the presence of these catalysts are respectively 19% and 21%), becomes very distinct if the product is removed by the intermetallic compound ZrNi (the conversions are 100% and 42% respectively). The yields of the dehydrogenation products of methanol[23] and isopropyl alcohol[26] increased by a large factor after deposition on the surfaces of intermetallic compounds of metals, such as platinum or rhodium, which are highly active in the dehydrogenation reactions.

The removal of hydrogen from the reaction mixture may exert a positive effect on reactions occurring with evolution of hydrogen, whereas reactions in which hydrogen is actually one of the reactants may be to a large extent suppressed in the presence of the intermetallic acceptor. The composition of the products of complex catalytic processes, in particular of the aromatisation of hydrocarbon gases, which includes several dehydrogenation stage as well as parallel hydrocracking, dealkylation, and hydrogen redistribution reactions, changes significantly in the presence of intermetallic compounds. For example, the selectivity of the aromatisation of ethane in the presence of pentasils modified by platinum increases by a factor of 2 in the presence of the intermetallic compound Zr_2Fe [18] as a result of the suppression of the methane formation side reaction and the displacement of the thermodynamic equilibrium in the rate-limiting stage involving the dehydrogenation of ethane to ethylene. The effect of the hydrogen acceptor on the secondary stage of the aromatisation reaction (the oligomerisation of ethylene) promotes the preferential formation of bicyclic aromatic products from ethane on Zn- and Ga-containing zeolites.[17]

The positive effect of the removal of hydrogen on the oligomerisation process was confirmed by the present authors in relation to the aromatisation of ethylene on the HTsVM zeolite (Table 4). In contrast to ethane, ethylene is readily activated on the acid centres of the H-form of pentasil, where rapid oligomerisation and aromatisation takes place. In the presence of Zr_2Fe, there is an appreciable increase in the yield of the aromatic products and of their content of bicyclic hydrocarbons for only a slight increase in the conversion of ethylene, but coke formation is not intensified. Evidently the removal of hydrogen has a positive effect on the stage involving the dehydrogenation of oligomers. On the other hand, the content of C_2-C_3 hydrocarbons in the gaseous reaction products diminishes. Consequently, as in the aromatisation of ethane, the removal of the hydrogen formed prevents the cracking of the intermediate and final reaction products. The slight increase in the yield of methane in the presence of the hydrogen acceptor is probably due to the demethylation of xylenes, the yield of which is reduced with a simultaneous increase in the yield of benzene.

Table 4. Aromatisation of ethylene on HTsVM (450 °C, 3600 h^{-1}) in the absence and presence of Zr_2Fe.

Parameter	Without acceptor	With acceptor
Conversion (mass%)	96.6	98.4
Yield of aromatic hydrocarbons (mass%)	38.2	44.9
Proportions of products (%):		
CH_4	1.4	3.7
C_2H_6	6.4	5.2
$C_3H_6+C_3H_8$	44.6	35.5
$C_4H_8+C_4H_{10}$	7.4	9.4
C_{5+}	0.6	0.6
Aromatic hydrocarbons	39.6	45.6
Proportions of aromatic hydrocarbons (%):		
Benzene	12.3	14.2
Toluene	39.5	40.1
Xylenes + ethylbenzene	43.7	37.6
C_{9+}	4.5	8.1
Content of coke on catalyst (mass%)	4.4	3.5
Content of hydrogen in the reaction stream (mol%)	11.8	0.2

Contrary to expectations, the removal of hydrogen by the hydrogen acceptors suppressed the dehydrogenation of ethane on oxide and on platinum-containing catalysts, both of which are inactive in the aromatisation reaction (Table 5), and at the same time no appreciable coke formation was observed.[18] This result shows that hydrogen plays a definite role in the dehydrogenation of ethane. One can postulate that it reduces to the acceleration of the desorption of the alkene from the surface of the catalyst. It has been shown[34] that the dehydrogenation of propane on gallium and zinc oxides is limited by the propene desorption stage, which is accelerated appreciably in the presence of the HZSM-5 zeolite as a result of the migration of $C_3H_7^+$ from gallium oxide to the acid centres of the zeolite, where a proton is fairly readily abstracted with the formation of propene. When H^+ is replaced by Na^+ in ZSM-5, the rate of dehydrogenation of propane diminishes by a factor of 100. It may be that this bifunctional mechanism operates in the dehydrogenation of ethane as well.

The change in the mode of reaction in the presence of hydrogen acceptors as a function of its mechanism and the catalyst composition has been observed in the aromatisation of

Table 5. The influence of the hydrogen acceptor Zr_2Fe on the dehydrogenation of ethane.

Catalyst	T/ °C	Reaction time/min	Yield of ethylene (mass %)	
			without acceptor	with acceptor
Ga_2O_3/SiO_2	550	6	5.1	5.7
	550	15	5.0	0.3
Cr_2O_3/ZrO_2	600	5	9.7	13.6
	600	22	9.8	1.9
Pt/SiO_2	550	7	7.9	1.2
	550	22	7.4	1.9
Pt/NaTsVM	550	5	7.2	1.0
	550	15	7.8	0.04

propane.[19,20] The authors suggest that, owing to the high activity of Ga/HTsVM in the dehydrogenation and oligomerisation processes, the displacement of the dehydrogenation equilibrium, occurring in the presence of the Zr_2Fe hydrogen acceptor, virtually precludes competition between the side reaction involving the hydrocracking of the intermediates and the aromatisation reaction, and the selectivity in the formation of aromatic hydrocarbons increases almost by a factor of 2. In the presence of the HTsVM and Pt/HTsVM catalysts, the removal of hydrogen from the reaction mixture activates the hydrogen redistribution processes, which increases the yield of aromatic products from propane but does not lower the amount of C_1-C_2 alkanes in the reaction products.

The dehydrogenation of methanol on intermetallic catalysts of different composition takes place with the formation of CO, formaldehyde, or methyl formate.[24,25]

Thus the activity and selectivity of the dehydrogenation catalyst as well as the process mechanism are of primary importance for the attainment of high yields of the target products when intermetallic hydrogen acceptors are used.

4. The spill-over of hydrogen

When the dehydrogenation and hydride formation reactions take place simultaneously, the catalytically active centres and hydrogen absorption centres are separated from one another by large distances. Presumably the hydrogen evolved migrates to the acceptor through the gas phase in the molecular state or it migrates on the surface in the atomic form. i.e. via spill-over.

The spill-over of hydrogen is more likely when the intermetallic compound functions simultaneously as a dehydrogenation catalyst and a hydrogen acceptor, since in this case the catalytic and absorption centres are close to one another and the transfer of hydrogen through the gas phase is energetically less favourable. The view exists[22,23,27] that the dehydrogenation of alcohols on hydride-forming intermetallic compounds is a pure example of the spill-over of hydrogen when the alcohol serves as the source of hydrogen atoms and the intermetallic compound is a solid acceptor. The activation of the surface of the intermetallic compound accelerates, according to the authors' view, not only dehydrogenation but also the spill-over of hydrogen to the absorption centres.

The ability to initiate the spill-over of hydrogen is characteristic of all hydride forming metals and alloys, because the H_2 absorption process involves the migration of the hydrogen dissociated on the surface into the bulk of the intermetallic phase. However, only some of them are active in dehydrogenation and this frequently requires a special treatment of the surface. Studies on the spill-over of hydrogen in various catalytic systems using different organic molecules as the hydrogen donors have shown that the ability of the catalysts to initiate this process depends on their activity in dehydrogenation.[35] In other words, the spill-over of hydrogen is closely related to dehydrogenation and apparently does really occur in the systems considered.

In the case where the intermetallic compound performs only the function of a hydrogen acceptor and the dehydrogenation reaction proceeds on an oxide, a deposited metal, or a zeolite catalyst, the involvement of spill-over in hydrogen transfer from the catalyst to the acceptor is less likely, but it cannot be ruled out on the basis of available data.

The appearance of molecular hydrogen in the reaction medium from the first minutes of the dehydrogenation of isobutane on Pt/Al_2O_3 in the presence of titanium presupposes, according to the authors,[8] that the transport of hydrogen takes place through the gas phase or in competition with the spill-over. The occurrence of the spill-over of hydrogen has been demonstrated indirectly in the dehydrogenation of cyclohexane in the presence of the intermetallic compound ZrNi and deposited platinum catalysts.[14] On Pt/Al_2O_3 and Pt/SiO_2 without a hydrogen acceptor, the yield of benzene was 19 mass% and 15 mass% respectively. After the removal of hydrogen, the maximum yield of benzene on the platinum/alumina catalyst reached 100%, while on Pt/SiO_2 it did not exceed 16 mass%, hydrogen being fully absent from the gas phase at the beginning of the experiment in the former case whilst in the latter it was present. This fact can be attributed to the different abilities of the Al_2O_3 and SiO_2 carriers to transfer the activated hydrogen along the surface.[36] Furthermore, for different proportions of Pt/Al_2O_3 and ZrNi in a mechanical mixture, the effectiveness of the hydrogen acceptor in the dehydrogenation of cyclohexane depends on the area of contact between the catalyst and the acceptor,[14] which can also be associated with the spill-over of hydrogen. Thus the maximum effect of hydride formation on the dehydrogenation reaction is probably attained when these processes are coupled, i.e. when the hydrogen acceptor reacts with the active hydrogen species formed as a result of dehydrogenation.

IV. Conclusion

The results examined in the present review reveal a new application of hydride-forming metals and intermetallic compounds as hydrogen acceptors for the displacement of the equilibrium in thermodynamically restricted catalytic reactions occurring with the evolution of H_2. The results indicate a high effectiveness of intermetallic hydrogen acceptors in the dehydrogenation reactions of cycloalkanes, isobutane, and C_1-C_3 alcohols and also in the aromatisation of C_2-C_3 hydrocarbon gases. This is manifested by the increase by a large factor in the yields of the target products, by the reduction of the reaction temperature by 100–150 °C, and by an increase in the selectivity of the processes.

In order to couple hydride formation with dehydrogenation, the hydrogen acceptor and the catalyst must satisfy certain requirements. It is essential that the metal or the intermetallic compound should be characterised by a low equilibrium dissociation pressure of the hydride at elevated temperatures, that the rate of absorption by the metal or the intermetallic compound should be high, and that it should retain its absorption capacity under dehydrogenation conditions and on repetition of the desorption cycles. The catalyst must have a high dehydrogenating activity and ability to initiate the spill-over of hydrogen. The process mechanism, which depends on the composition and properties of the catalyst, also affects the results of the dehydrogenation reaction occurring in the presence of an intermetallic hydrogen acceptor. All these factors create certain difficulties in the practical realisation of the processes and require additional search for new intermetallic compounds with the necessary properties and also the study of the reaction mechanisms under the conditions of hydrogen removal by the acceptor.

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