Hydrogenation of CO_2 conjugated with dehydrogenation of cyclohexane over an intermetallic catalyst

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Transformations of carbon dioxide catalyzed by the hydride form of $[TiFe_{0.95}Zr_{0.03}Mo_{0.02}]H_x$, by the industrial Pt/Al_2O_3 catalyst, and by a mixture of the above materials were studied. Study of the thermal desorption of H_2 showed the presence of two forms of absorbed hydrogen, namely, the weakly bound hydrogen, which is evolved from the intermetallic structure on heating to 430 °C under Ar, and the strongly bound hydrogen (SBH), which remains in the intermetallic compound at higher temperatures (up to 700 °C). In a carbon dioxide medium, the SBH enters into selective CO_2 reduction to give CO at 350—430 °C and 10—12 atm. The selectivity of the formation of CO reaches 80—99% for conversion of CO_2 between 50—70%, the SBH being consumed almost entirely for the reduction of CO_2. In the presence of the mixed catalyst, conjugate reactions proceed efficiently; dehydrogenation of cyclohexane yields hydrogen, which is consumed for CO_2 hydrogenation.

Key words: intermetallic compound, heterogeneous catalysts, hydrogen, absorption, thermal desorption, weakly bound and strongly bound hydrogen, activation, hydrogenation, carbon dioxide, selectivity.

Utilization of carbon dioxide is an important problem in the chemistry of one-carbon compounds.

In the presence of metal-containing catalysts, hydrogenation of CO_2 to give methanol, a number of gaseous C_1—C_4 hydrocarbons, and CO proceeds most readily.[1—5] Carbon dioxide also enters into reverse water gas shift reaction (RWGS), which gives rise to CO and light hydrocarbons, mainly methane.[1,6] A more selective transformation of CO_2 into CO occurs in the presence of metal oxide and sulfide catalysts.[6,7] Thus the selectivity of transformation of CO_2 into CO in the presence of preliminarily reduced iron/alumina catalyst reaches 97%; however, the degree of CO_2 conversion remains low.[7,8] Selective formation of CO also takes place in CO_2 hydrogenation on a Pd—Ru membrane modified by a nickel coating.[9] In the presence of cobalt and iron filamentary crystals with special-purity quartz particles, direct transformation of CO_2 into ethylene and propylene was attained; the content of these products in the gas mixture was[10] up to 10%.

The hydride form of the $[TiFe_{0.95}Zr_{0.03}Mo_{0.02}]H_x$ intermetallic compound ($x \approx 2$) reacts with CO_2 to give CO and small amounts of methane even at 20 °C.[11,12] The selectivity of the formation of CO_2 hydrogenation products varied depending on the way of hydrogen supply to the reaction volume.

It is known that hydride phases obtained from hydrogen-accumulating intermetallic compounds are characterized by different strengths of hydrogen binding.[13—15]

In this work, we studied the influence of the strength of hydrogen binding to the lattice of the intermetallic compound on its catalytic activity and selectivity in CO_2 reduction and attempted to perform the catalytic hydrogenation of CO_2 conjugated with the dehydrogenation of cyclohexane.

Experimental

The catalytic experiments were performed in a laboratory high-pressure flow-circulation setup made of stainless steel. The functional diagram and the description of units of the setup are shown in Fig. 1. The $TiFe_{0.95}Zr_{0.03}Mo_{0.02}$ intermetallic (**1**),[16] an industrial platinum/alumina catalyst (AP-64) (**2**), and their mixture (**3**) were used as catalysts.

Prior to loading into the reactor, catalyst **1** (see Fig. 1, block *4*) was crushed to ~2—3-mm pellets using a ball mill with corundum balls.

Catalyst **3** was a thoroughly mixed blend consisting of pellets of the intermetallic compound **1** and small cylinders of

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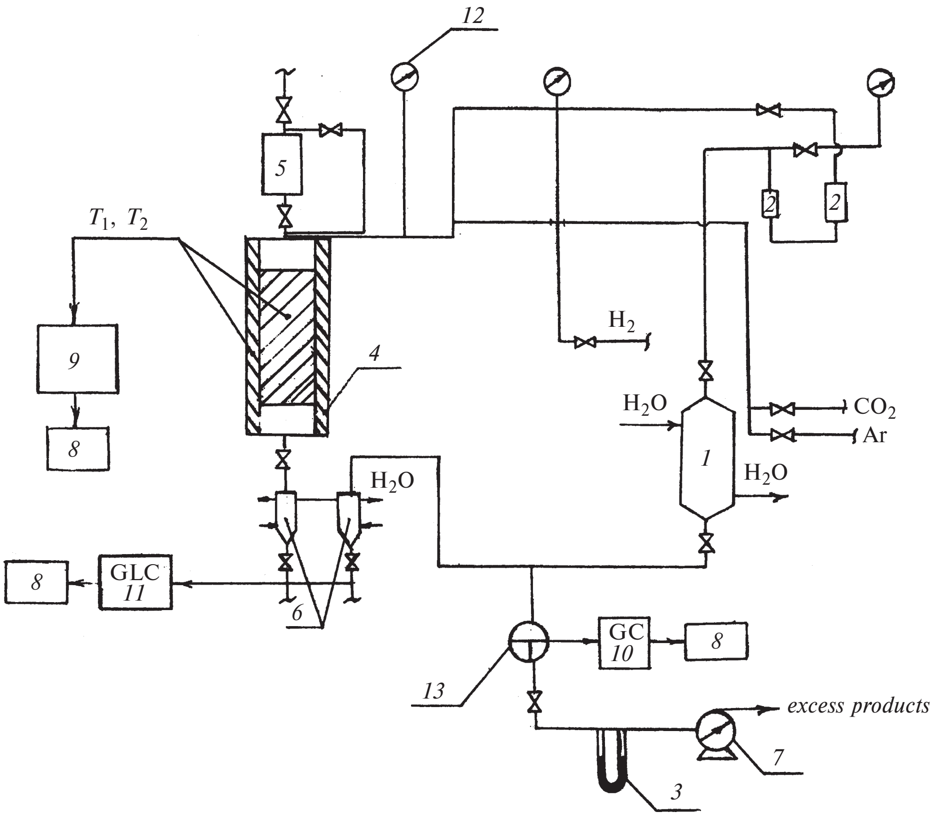


Fig. 1. Functional diagram of the laboratory catalytic setup: (*1*) gas circulation pump, (*2*) flowmeters, (*3*) pressure gage, (*4*) reactor, (*5*) dropping device; (*6*) cooled gas separators, (*7*) gas meter, (*8*), (*9*) control unit, (*10*), (*11*) LKhM-8M and LKhM-80 chromatographs, (*12*) pressure gage; (*13*) three-way valve.

the industrial Pt/Al_2O_3 catalyst **2**. In reference experiments, intermetallic compound **1** and catalyst **2** were loaded in the reactor in such a way as to exclude their mixing: the upper layer of the reaction volume contained catalyst **2**, and the lower layer was intermetallic compound **1**.

Finely ground intermetallic compound **1** (60 g) and catalyst **2** (6.3 g) were loaded in the reactor and the resulting heterogeneous system was treated with hydrogen at 100 °C and 1 atm under flow conditions for 10—14 h (activation). After activation, the system was cooled to 25—30 °C, and high-pressure (120—135 atm) H_2 was rapidly fed in the circulation mode.

Absorption of H_2 by intermetallic compounds is considered to include a step of hydrogen activation on a solid surface.[2,13,15,17] In air, the surface of hydrogen-accumulating systems is quickly coated with an oxide film, which prevents hydrogen absorption.[2,15] To increase the rate of H_2 absorption, the temperature of its interaction with intermetallic compounds is usually raised.

The temperature of the initial absorption of H_2 was found to depend on the catalyst composition and on the way of catalyst loading. In the presence of **1**, absorption of H_2 takes place at ~60—70 °C, whereas in the presence of **3**, it occurs at ~30—40 °C. In the case where catalysts **1** and **2** were arranged as separate layers that could not mix, the temperature of the onset of H_2 absorption was the same as in the case of intermetallic compound **1** alone, namely, ~60—70 °C. The initial absorption of H_2 was accompanied by a fast decrease in the reactor pressure. After completion of H_2 absorption and cooling of the reaction zone to room temperature, the pressure established in the system was determined using a high-precision secondary reference pressure gage and the amount of H_2 absorbed by the intermetallic compound was found. Then H_2 was displaced from the reactor by Ar and the curves of thermal desorption of H_2 in the mode of heating with linear programming (~5 °C min^{-1}) with circulation were recorded.

After heating to 430 °C, the system was kept at this temperature until H_2 evolution from the catalyst could not be further recorded; after that, Ar was replaced by CO_2 and the reduction of CO_2 was studied at 350 and 430 °C and at an initial pressure of 10—12 atm. When the degree of hydrogenation had markedly decreased, the reaction products, together with the remaining CO_2, were replaced again by fresh CO_2. This operation was repeated several times until no hydrogenation of CO_2 could be traced.

After completion of CO_2 reduction, the gas phase was replaced by fresh CO_2 and, under conditions of its circulation, cyclohexane was added onto the catalyst layer from a dropping device with a flow rate of ~0.08—0.1 h^{-1} for 2—3 h. After that, the catalytic cycle was considered complete. Then the catalytic system was again subjected to activation by treating the catalyst with H_2 at 100 °C for 10—14 h followed by repeated absorption of H_2 and conduction of the initial cycle under the above-described conditions. In experiments with platinum/alumina catalyst **2**, hydrogen was fed to the system by the traditional method, together with CO_2. The total operation time for catalytic systems **1**, **2**, and **3** was 227, 67, and 277.4 h.

The reaction products were analyzed by gas chromatography in the on-line mode using an LKhM 80-MD chromatograph (see Fig. 1, block *11*). The gas components were identified by adding reference compounds; their concentrations were

Table 1. Main parameters of CO_2 hydrogenation and consumption of bound hydrogen per cycle (catalyst **3**; T = 430 °C; P_0 = 10—12 atm)

Stage	Operation	Sampling time/h	Selectivity of CO formation (%) based on consumption		Conversion of CO_2 (mol.%)	Rate/mmol mol^{-1} h^{-1}		
			of H_2	of CO_2		of H_2 transformation in the reaction products	of molecular H_2 evolution	of CO_2 transformation
1	Treatment with Ar	13	—	—	—	—	—	—
2a	Replacement by CO_2, circulation	13.25	99.6	~100	39	395.6	0.6	393.6
2b	Recycling	14.1	91.2	98	50	125.5	0.9	116.8
2c	The same	14.4	91.7	~100	58	96.9	0.2	84.0
2d	»»	15.1	95.0	~100	72.9	20.5	0.13	39.2
2e	»»	16.1	97.9	~100	75	3.4	0.1	3.2
3a	Cyclohexane dehydrogenation to CO_2	17.1	55.5	91.2	38.1	82.15	10.9	50.0
3b	The same	18.1	27.7	68.1	45.5	97.7	19.5	39.8
3c	Recycling of dehydrogenation products	32.1	4.6	13.1	85.3	46.5	0.5	16.0

calculated by the absolute calibration method. The H_2, CO, CH_4, and CO_2 samples were analyzed using analytical packed column *1* (5 m×4 mm) with the SKT carbon sorbent (0.25—0.5 mm fraction), a heat-conductivity detector, and special-purity grade Ar as the carrier gas. The C_1—C_4 hydrocarbon gases were analyzed on an analytical packed column (2 m×4 mm) with modified α-Al_2O_3 (0.25—0.50 mm fraction) containing 2% of the squalane phase using a flame ionization detector.

The results of chromatographic analysis were used to calculate the amount of CO_2 in the reaction bulk after completion of hydrogenation and the amount of H_2 spent for the formation of CO and C_1—C_4 hydrocarbons. On the basis of these data, the full balance for CO_2 and H_2 was composed and, hence, the degree of CO_2 conversion and the total amount of H_2 consumed for CO_2 transformation and evolved from the intermetallic compound to the reaction bulk was calculated. The procedure for the calculation of the degree of conversion of CO_2 and the amounts of the reaction products formed was described previously.[11,12]

Table 1 presents the main kinetic parameters for the transformation of CO_2 and for the consumption of H_2 for CO_2 hydrogenation in the presence of catalytic mixture **3** in one operation cycle.

The specific surface area of the intermetallic compound was determined by the BET method using an Yravimat-4303 automated weighing unit (Netch) with a sensitivity of 1 μg for samples of up to 1 g at 77 K.

Results and Discussion

The experiments showed that 1 mole of $TiFe_{0.95}Zr_{0.03}Mo_{0.02}$ absorbs 1 mole of H_2. Heating the H_2-saturated intermetallic compound to 135 °C induces evolution of a small amount of H_2, apparently, physically absorbed in the near-surface layers of the structure (Fig. 2).

In the 135—170 °C range, ~0.85 moles of H_2 is evolved. This portion of H_2 can be conventionally referred to as the weakly bound hydrogen (WBH). It can be seen from Fig. 2, *a* that in the 170—184 °C range, the amount of gas again decreases, apparently, due to the change in the crystal structure of the intermetallic compound and absorption of 0.2 moles of H_2 by the catalyst with a new structure.

On further heating to 430 °C, only a small amount of H_2 (<0.05 moles) is evolved. The subsequent prolonged (for up to 24 h) keeping of **1** at 430 °C under Ar induces virtually no H_2 evolution.

Thus, ~0.35 moles of H_2 remains in the structure of 1 mole of the intermetallic compound. In addition, 0.18 moles of H_2 is absorbed by the intermetallic catalyst during circulation of the gas mixture containing H_2 that has evolved from the structure previously.

This portion of H_2 remaining in the intermetallic structure will be conventionally defined as the strongly bound hydrogen (SBH).

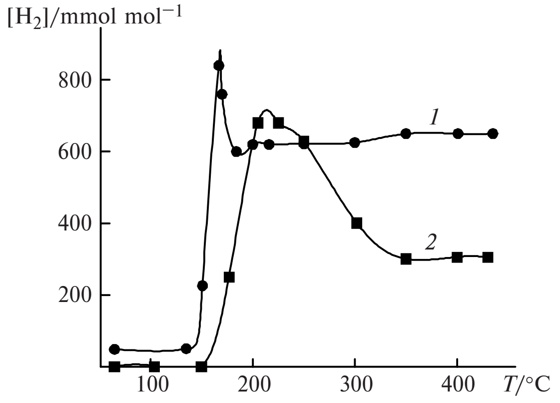


Fig. 2. Thermal desorption of H_2 (P_{init} = 10 atm) from $[TiFe_{0.95}Zr_{0.03}Mo_{0.02}]H_x$ after the primary (*1*) and secondary (*2*) hydrogen absorption runs.

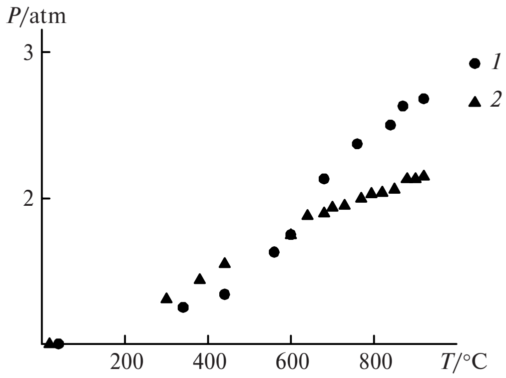


Fig. 3. Gas pressure *vs.* temperature in the reactor loaded by $[IM](H_2)_{0.17}$ (*1*) and the initial intermetallic compound (*2*).

The presence of the SBH was confirmed by separate experiments in which the samples of the initial intermetallic compound and that containing 0.17 moles of H_2 were subjected to high-temperature treatment in an autoclave under Ar (1 atm) with linear temperature programming.

Figure 3 presents the variations of pressure *vs.* temperature for the sample containing 0.17 moles of H_2 and for the initial intermetallic compound. The more intense growth of pressure observed at higher temperatures, starting from ~700 °C, for the system containing the intermetallic compound and 0.17 moles of H_2 relative to that for the initial intermetallic compound was related to the evolution of H_2. The data of chromatographic analysis showed that in the 700—920 °C temperature range, the strongly bound hydrogen is removed almost entirely. Since this temperature range is close to the temperature of H_2 elimination from the TiH_2 phase,[18] it can be suggested that hydrogen that is strongly attached to the intermetallic structure is chemically bound to the Ti atoms.

After the repeated introduction of high-pressure H_2 to the reactor, additional absorption of H_2 takes place (~0.6 moles). Thus, after the repeated absorption, the total content of hydrogen in the intermetallic system approaches again the amount of H_2 absorbed by the fresh intermetallic ($x \approx 1$).

The range of H_2 evolution also changes: desorption of the WBH continues to ~220 °C; as the temperature further increases, the amount of the gas decreases and, after 340 °C, it remains unchanged, which indicates completion of the H_2 evolution.

This change in the total amount of evolved H_2, together with the increase in the temperature of its evolution is, apparently, due to the influence of absorption—desorption cycles on the intermetallic structure.

It is known that during H_2 absorption, the structure of hydrogen-accumulating systems undergoes substantial changes accompanied by mechanical grinding, so called embrittlement.[2,13,15,17] It can be suggested that grinding during thermal desorption gives rise to more extensive active surface of the intermetallic compound, which may favor additional formation of hydride bonds.

The adsorption measurements showed that the initial intermetallic compound does not posses a developed surface, whereas after H_2 absorption and subsequent desorption, the specific surface area of the material is 0.06 ± 0.02 m^2 g^{-1}. It can be noted that this is a fairly high value for a metallic surface.

An increase in the specific surface area of a hydrogen-accumulating system after absorption—desorption procedures has been described previously for a nickel zirconium intermetallic compound.[2]

The secondary treatment with H_2 is, apparently, also accompanied by embrittlement and, as shown in experiments, by additional absorption of some of the H_2 evolved previously. However, in this case, H_2 is absorbed at a higher temperature (see Fig. 2, *b*).

If Ar is replaced by CO_2 after treatment of the catalyst at 430 °C, hydrogenation of CO_2 with the strongly bound hydrogen takes place predominantly to give CO and C_1—C_5 hydrocarbons. Indeed, in the presence of **1**, 60% of carbon dioxide is converted into CO with a selectivity of 80% during the first hour. Virtually complete conversion of CO_2 is attained in the second hour of circulation; however, the selectivity of CO formation decreases to 50% due to an increase in the yield of hydrocarbons. After replacement of the hydrogenation products by fresh CO_2, a much lower degree of CO_2 conversion is observed (22%), the selectivity of CO_2 reduction to CO being very high (98—100%). These data indicate that hydrocarbons might result from the hydrogenation of CO.

In the case of joint supply of H_2 and CO_2 in the presence of catalyst **2** (430 °C, 10 atm), the selectivity of CO formation does not exceed 15—18% for the

Table 2. Rate of CO_2 transformation (ω), selectivity of CO formation (*S*), and composition of hydrogenation products

Catalytic system	*T*/°C	*t**/h	ω_0 /mmol g^{-1} h^{-1}	*S* (%)	Composition of gaseous products (mol.%)			
					CO	C_1	C_2—C_4	H_2
Intermetallic compound **1**	350	—	3.5	98	36.6	0.16	Traces	11.9
	430	0.25	3.3	51	45.5	4.5	3.2	16.7
Intermetallic compound + AlPt (**2**)	430	0.25	3.7	99	99	—	—	0.16
AlPt (**3**)	430	23	0.34	17.7	7.3	16.8	3.6	2.7

* Time required to reach 40—45% degree of CO_2 conversion.

conversion of CO_2 equal to 40% (see Table 2). The major reaction products are C_1—C_4 hydrocarbons, mainly methane (see Table 2).

In the presence of system **3**, the conversion of CO_2 reaches 58%, the selectivity of CO formation being 98—100% at 430 °C (see Table 1).

When catalysts **1** and **3** are used, the CO_2 conversion rapidly decreases during the experiment. However, after replacement of the hydrogenation products by Ar, circulation of Ar, and subsequent replacement of Ar by fresh CO_2, the activity in CO_2 hydrogenation is restored until the SBH is exhausted.

It was found that reduction of CO_2 is accompanied by slow evolution of SBH into the bulk (see Table 1).

As H_2 is accumulated in the gas phase, the selectivity of CO formation diminishes due to more extensive hydrogenation of carbon oxides.

The high selectivity of CO formation is ensured by participation of the SBH in the reaction with CO_2 (Fig. 4); the reduction of CO_2 to hydrocarbons occurs at the cost of gas-phase H_2 and, possibly, carbon deposited on the surface of the heterogeneous system.

It was found that the amount of carbon present on the surface of **1** after 11 h of the gas-phase reaction is 0.14 g, which corresponds to the transformation of 0.012 moles of CO_2. The total amount of converted CO_2 is 0.079 moles, of which 84.8% is converted into CO and C_1—C_5 hydrocarbons, while 15.2% is converted into carbon.

Apparently, the reduction of CO_2 to CO takes place upon stoichiometric reaction of CO_2 with hydride hydrogen atoms connected to the lattice of **1**. Meanwhile, hydrogenation of CO to hydrocarbons involves H_2 from the gas phase. This means that, as the SBH is consumed for the reduction of CO_2, the active sites are continuously restored by the SBH.

It can be seen from the typical kinetic curves for the transformation of CO_2 in the presence of **3** (Fig. 5) that the rate of transformation of CO_2 per operation cycle decreases as the formation of CO goes on. The curve for CO accumulation goes through a maximum, and the dependence of the yield of hydrocarbons on the reaction time is characterized by a weakly pronounced induction period. The yield of hydrocarbons increases as the CO content decreases. Thus, the conclusion about the consecutive character of CO_2 hydrogenation: $CO_2 \rightarrow CO \rightarrow C_1$—$C_4$ is confirmed.

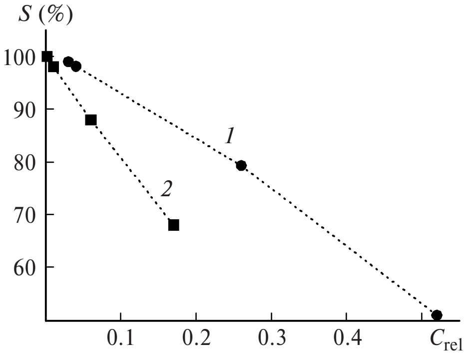


Fig. 4. Effect of the relative concentrations of the molecular and strongly bound hydrogen ($C_{rel} = H_2(molec.)/\Sigma[H_2(molec.) + [H](absorb.)]$) on the selectivity (*S*) of the CO formation at 430 °C and P_{init} = 10 atm in the presence of catalyst **1** (*1*) and **2** (*2*).

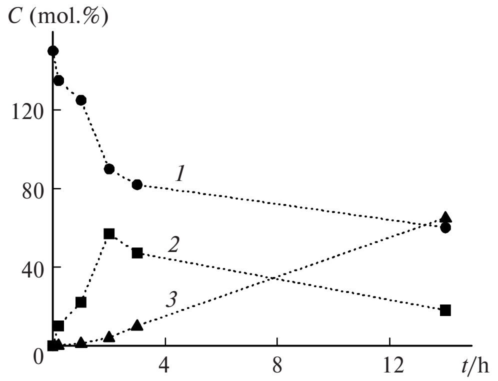


Fig. 5. Kinetics of the consumption of CO_2 and accumulation of hydrogenation products (*C*) in the presence of catalyst **1** at 430 °C and P_{init} = 10 atm: (*1*) CO_2; (*2*) CO; (*3*) C_1—C_4 hydrocarbons.

One of the major components of catalyst **1** is iron. The formation of stable iron carbonyl complexes can retard chemisorption of CO_2 on the active sites of **1**. Diffusion of the strongly bound hydride hydrogen through the lattice of intermetalic **1** toward the surface might be one more factor influencing the decrease in the CO_2 conversion during the reaction (see Fig. 5).

When comparing the catalytic activity of catalysts **1** and **3** in CO_2 hydrogenation with that of the traditional hydrogenation catalyst **2** (see Table 2), one can see that in the presence of the platinum/alumina catalyst, the initial rate of CO_2 reduction is an order of magnitude lower than the initial rate of hydrogenation in the presence of **1** or **3**. Moreover, comparison of the transformation of CO_2 in the presence of systems **1** and **3**, which involves SBH, with the transformation of CO_2 over the platinum/alumina catalyst **2**, which occurs as a result of activation of the adsorbed H_2, shows that the time it takes to reach a 40% degree of conversion of CO_2 over systems **1** and **3** is two orders of magnitude shorter than that on the Pt/Al_2O_3 catalyst.

The experiments on cyclohexane dehydrogenation conjugated with the reduction of CO_2 were carried out with catalysts **1** and **3** in which SBH had been consumed almost completely in the first cycle of the experiment.

It has been found previously[19] that, upon dehydrogenation of cyclohexane in the presence of a mixture of the nickel zirconium intermetallic compound with the platinum/alumina catalyst, the concentration of benzene was substantially greater than the value that could be attained in the presence of traditional catalysts.

In the dehydrogenation of cyclohexane in the CO_2 medium in the presence of system **1** at 430 °C, the

Table 3. Dehydrogenation of cyclohexane (CyH) in the CO_2 medium[a]

Catalytic system	C^b	S^c	Y^d
	%		(mol.%)
Intermetallic compound (**1**)	2.5	68.8	50
Intermetallic compound + AlPt (**2**)	49	92.3	58.5
AlPt (**3**)	97	85.8	25

[a] T = 430 °C, P = 10 atm, supply rate 0.08—0.12 h^{-1}.

[b] Degree of CyH conversion.

[c] Selectivity to benzene.

[d] Amount of H_2 evolved from CyH and consumed for CO_2 hydrogenation.

degree of cyclohexane conversion does not exceed 2.5% (Table 3). When the compound system **3** is used, the degree of cyclohexane conversion reaches 49%, while in the presence of the platinum/alumina catalyst alone, it approaches 97%.

During dehydrogenation of cyclohexane, the concentration of molecular hydrogen in the reaction volume markedly increases (see Table 1). This is accompanied by a substantial increase in the rate of CO_2 hydrogenation in the presence of **3**. However, an increase in the concentration of molecular hydrogen in the reaction bulk decreases the selectivity of CO formation due to extensive hydrogenation of CO_2 to hydrocarbons (see Table 1). Even after termination of cyclohexane supply to the reaction zone, prolonged circulation of the gaseous products over catalysts **1** and **3** results in the transformation of CO_2 and CO into hydrocarbons (see Table 1). However, some hydrogen evolved upon dehydrogenation of cyclohexane is obviously absorbed by the intermetallic compound; as a consequence, after replacement of hydrogenation products by fresh CO_2, the selectivity of CO formation reaches again 99—100%, the carbon dioxide conversion being ~20%.

Cyclohexane dehydrogenation readily occurs in the presence of platinum/alumina catalyst **2**; however, the rate of CO_2 hydrogenation and the selectivity of CO formation are low even for high degrees of cyclohexane conversion (see Table 3). In the presence of intermetallic compound **1** alone, the degree of cyclohexane conversion does not exceed 2.5% (see Table 3). Of the reacted cyclohexane, 40% undergoes hydrogenolysis and only 60% is dehydrogenated to benzene.

Thus, the intermetallic compound $[TiFe_{0.95}Zr_{0.03}Mo_{0.02}]H_x$ contains two types of absorbed hydrogen, one being strongly bound and the other being weakly bound to the intermetallic lattice. The reactivities of these forms of hydrogen in CO_2 hydrogenation are different. The selective reduction of CO_2 into CO for degrees of conversion of up to 60% is attained only when SBH participates in the process. The gas-phase hydrogen is involved predominantly in the reduction of CO to give hydrocarbons.

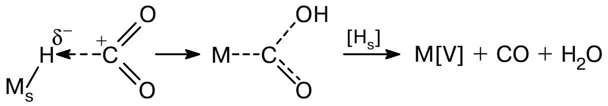
For most of hydrogen-accumulating systems of the ABH_x type, including TiFe, absorption of H_2 is accompanied by the formation of a boundary layer of interstitial solid solutions and hydride phases characterized by a constant composition.[13] It has been noted, however, that absorption of H_2 by this intermetallic compound starts only after the formation of the iron metallic phase; this is attributed to weak catalytic activity of the binary system (TiFe) with respect to the dissociation of hydrogen on its surface.

Modification of the intermetallic compound with a minor amount of Zr and Mo makes it possible to accelerate markedly the process of H_2 absorption with retention of the cubic crystal structure and relatively high absorption capacity.[16,17]

A study by Mössbauer spectroscopy showed that inclusion of hydrogen into the TiFe structure brings about a substantial decrease in the occupancy of the valence level of iron by electrons; this may result in partial transfer of the electron density to the hydrogen atoms linked to the lattice.[13]

Evidently, the high rate of CO_2 reduction and the enhanced selectivity of CO formation are due to chemisorption of CO_2 on the sites containing hydride hydrogen. The subsequent steps may involve destruction of the surface formyl groups (designated by subscript "s") to give CO and water, which is a mechanism postulated in homogeneous catalysis [20] (Scheme 1).

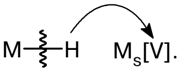
Scheme 1



M is the hydride-forming metal (Ti, Zr)

[V] a hydrogen vacancy

When hydrogen attached to the intermetallic surface has been completely consumed for the reduction of CO_2, a vacancy appears in the coordination sphere of the hydride-forming metal atom; apparently, hydrogen migrates through this vacancy to the surface of the system



This can account for the fact that during the reduction of CO_2, virtually all SBH is involved in the reaction with CO_2.

The decrease in the rate of CO_2 reduction in the reverse water gas shift reaction, which takes place on the surface of nickel catalysts, is due to the strong adsorption of CO, which blocks the active sites.[1,9] The accumulation of CO on the surface of the system might result in the formation of stable iron carbonyl complexes, which hamper the access of CO_2 to the active sites. Treatment of the surface with Ar or fresh CO_2 restores the ability of **1** to reduce CO_2.

In the presence of the catalytic composition **3** consisting of the intermetallic compound and the Pt/Al_2O_3 catalyst, the selectivity of CO formation upon the hydrogenation of CO_2 at 430 °C is markedly higher than that in the presence of either of these catalysts separately at the same temperature. Among other reasons, this synergistic effect can be due to the transfer of hydride hydrogen originated on the surface of the intermetallic compound to the surface of the platinum/alumina catalyst by the spillover mechanism and its participation in the reduction of CO_2. It can also be suggested that the phase transfer of hydrogen is favored by the contact of highly dispersed intermetallic particles arising as a result of embrittlement of **1** with the pellets of the aluminoplatinum catalyst. In the presence of the mixed catalyst, absorption of H_2 starts at a lower temperature than in the presence of either the intermetallic compound alone or catalysts **1** and **2** loaded separately. This points to the possible role of phase transfer of H_2.

The phase transfer of H_2 is observed in hydrogenation reactions over mixed catalytic compositions, in particular, a mixture consisting of the nickel zirconium intermetallic compound and the platinum/alumina catalyst.[19,21] One of the most popular views on the spillover mechanism implies heterophase interaction of heterogeneous systems, resulting in tight contact of the surface layers of the pellets of different catalysts.[22,23]

The synergism in CO_2 hydrogenation conjugated with cyclohexane dehydrogenation in the presence of composition **3** is evidently due to different functions of the system components. The first stage of this process gives molecular hydrogen in a relatively high concentration upon dehydrogenation of cyclohexane, which is catalyzed efficiently by catalyst **2**, and, as a consequence, extensive hydrogenation of CO_2 to CO and light C_1—C_5 hydrocarbons. However, some of the H_2 formed is absorbed from the reaction zone by the intermetallic compound, the H_2 from which has been consumed almost entirely for CO_2 hydrogenation at the preceding stages. The reversibility of absorption at elevated temperatures is also indicated by the data of thermal desorption of H_2 (see Fig. 2).

The formation of active sites containing SBH results in a higher selectivity of CO_2 reduction to give CO after the gaseous products containing a high concentration of molecular hydrogen, obtained upon cyclohexane dehydrogenation, have been replaced by fresh CO_2.

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