addition of this hydrogen atom to one of the nitrogen atoms.

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References

1. M. Chanon, M. Julliard, J. Santamaria, and F. Chanon, *New J. Chem.*, 1992, **16**, 171.
2. M. Julliard, *New J. Chem.*, 1994, **18**, 243.
3. M. Mella, M. Freccero, and A. Albini, *J. Chem. Soc., Chem. Commun.*, 1995, 41.
4. G. B. Shul'pin, M. M. Kats, and G. V. Nizova, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1988, 2653 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1988, **37**, 2395 (Engl. Transl.)].
5. G. B. Shul'pin, M. M. Kats, and P. Lederer, *Zh. Obshch. Khim.*, 1989, **59**, 2742 [*J. Gen. Chem. USSR*, 1989, **59** (Engl. Transl.)].
6. G. B. Shul'pin and G. Süss-Fink, *J. Chem. Soc., Perkin Trans. 2*, 1995, No. 7.
7. G. B. Shul'pin and G. V. Nizova, *React. Kinet. Catal. Lett.*, 1992, **48**, 333.
8. G. V. Nizova and G. B. Shul'pin, *Neftekhimiya* [*Petrochemistry*], 1994, **34**, 364 (in Russian).

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Low-temperature reactions of CO_2 in the presence of iron-titanium intermetallide

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Involving CO_2, which is one of the most easily accessible sources of carbon raw materials, in organic and petrochemical synthesis is being held back by the lack of effective and selective catalytic systems. At present, elaboration of these systems receives much attention.[1,2] In this connection, the development of scientific fundamentals of power-consuming processes of the transformation of CO_2 into fuel compounds or in compounds meant for petrochemical synthesis is of interest.

In this communication we present the results of hydrogenation of CO_2 in the presence of $TiFe_{0.9}Zr_{0.05}Mn_{0.05}$ intermetallide, which is capable of chemisorbing H_2 to form a hydride phase, which reversibly decomposes under relatively mild conditions.[3]

The experiments were carried out in a stainless-steel reactor using a flow-loop type setup (p_{CO_2} = 8 atm, T = 293 to 623 K, a batch of intermetallide was 20 g (5 cm^3)). A specimen with granules of diameter 2—5 mm was used. After preliminary activation of the catalyst in an H_2 flow for 10 h at 373 K, the system was filled with hydrogen, pressure was increased to 100 atm, and the system was kept for 10 h.

The quantity of chemisorbed H_2, determined by manometry based on the pressure drop, was 0.013 mol per g of intermetallide. Hydrogen was displaced with an excess of CO_2, the setup was switched to the circulation conditions, and then the reaction zone was heated to a specified temperature. The turnover frequency of the reaction gas through the layer of intermetallide was 0.25 L $(g\ Cat\ h)^{-1}$.

In the studies on the effect of the temperature on the conversion of CO_2, a fresh sample of the catalyst was taken for each run. The dependence of the accumulation of reaction products on the duration of experiment was studied in three experimental cycles with the same batch of the catalyst. Each cycle included three steps, *viz.*, activation of intermetallide by treating it with H_2 at 373 K, saturation of intermetallide with H_2 (p = 100 atm, T = 293 K, 10 h), and circulation of the gas mixture through the intermetallide layer.

Gaseous and liquid reaction products (CO, hydrocarbons, and H_2O) were analyzed by gas chromatography.

From the data presented in Table 1, one can see that CO and CH_4 are formed even at ambient temperature. Noticeable conversion of CO_2 into gas products

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Table 1. Degree of conversion of CO_2 and composition of the reaction products (the duration of circulation is 40 h)

T/K	Degree of CO_2 conversion	Composition of reaction products		
		CO	CH_4	C_2—C_4
293	1.2	1.0	0.2	—
373	2.0	1.5	0.2	0.3
593	11.5	7.8	1.8	1.9
623	28.4	20.0	6.0	2.4

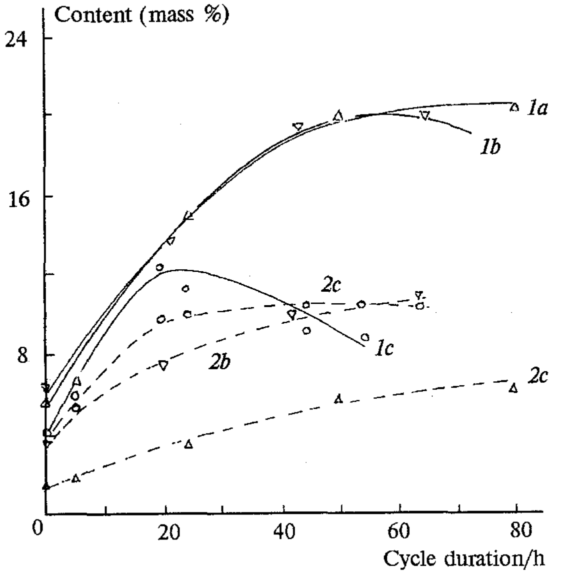

Fig. 1. Dependence of the proportion of CO (*1*) and C_1—C_4 hydrocarbons (*2*) in the gaseous products on the duration of the cycles with one batch of intermetallide: first (*a*), second (*b*), and third (*c*) cycles (T = 623 K, p = 8 atm).

(11—28 % (w/w)) occurs at 593—623 K. In this temperature range, decomposition of the hydride phase of intermetallide and desorption of hydrogen occur.

In the first cycle, CO_2 is mostly converted into CO (80 %) (Fig. 1), and in the subsequent cycles, the proportion of C_1—C_4 hydrocarbons increases. This variation of the composition of the products may be associated with catalytic effect of iron, incorporated in the intermediate, on the synthesis of hydrocarbons from the CO, formed in the reaction, and the desorbed active hydrogen.

The results obtained indicate that the desorption of active hydrogen from the lattice of the iron-titanium intermetallide ensures a noticeable degree of conversion of CO_2 adsorbed on the surface, and this effect is observed even at room temperature. The latter allows iron-titanium alloys to be regarded as promising materials for developing active catalysts of the low-temperature conversion of CO_2.

References

1. E. V. Evdokimova, V. V. Lunin, P. V. Afanasiev, and I. I. Moiseev, *Mendeleev Commun.*, 1993, **1**, 1.
2. I. I. Moiseev, E. V. Evdokimova, V. V. Lunin, P. V. Afanasiev, A. E. Gekhman, and A. R. Gromov, *Dokl. Akad. Nauk*, 1993, **332**, 195 [*Dokl. Chem.*, 1993, **332** (Engl. Transl.)].
3. B. A. Kalachev, A. A. Il'in, V. A. Lavrenko, and Yu. V. Livinskii, *Gidridnye sistemy* [*Hydride Systems*], Metallurgiya, Moscow, 1992, 350 pp. (in Russian).

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New complex of fullerene with an organic donor: $(C_{60})_2 \cdot TPDP \cdot (CS_2)$

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The discovery of superconductivity characterized by high temperatures of the superconducting transition[1] in M_3C_{60} salts (M is an alkali metal) and the discovery of ferromagnetic properties in TDAE $\cdot$ C_{60} salts (see Ref. 2) have awakened considerable interest in studying compounds of C_{60} with organic donors. The use of these donors opens up broad possibilities for the synthesis of substances with various packings of C_{60} in the crystal, which finally determines different properties of these compounds. At present, molecular complexes of fullerene with various donors including S- and Te-containing derivatives of tetrathiafulvalene have been prepared.[3,4]

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