Physical Chemistry

Hydrogen absorption by intermetallics M_2Fe (M = Zr, Hf, Ti) and their effect on the catalytic aromatization of ethane

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The absorption properties of the hydride-forming intermetallics M_2Fe(M = Zr, Hf, Ti) and their effect on the aromatization of ethane over Pt,Ga/HCVM catalyst within the temperature range 400—450 °C are studied. The absorption capacity of the intermetallics under aromatization conditions and their efficiency as hydrogen acceptors are shown to decrease in the order $Zr_2Fe > Ti_2Fe > Hf_2Fe$.

Key words: catalysis, aromatization, ethane, pentasil, hydrogen acceptor, intermetallic compound.

The effect of hydride-forming intermetallics on reactions proceeding with hydrogen evolution was previously investigated for catalytic conversions of hydrocarbons[1—4] and alcohols[5—7] as the example. For the most part, elimination of the H_2 formed in the reaction by intermetallic acceptors promotes a substantial increase of yield of the target products as a consequence of removing thermodynamic limitations of dehydrogenation and suppressing the side processes of hydrocracking. Efficiency of application of the intermetallics is defined by the activity of the catalyst used as well as by their absorption properties. For instance, the removal of hydrogen by Zr_2Fe in the course of ethane aromatization on modified pentasils at 500—550 °C makes it possible to increase the yield of aromatic hydrocarbons from 4—9 to 19—54 mass % depending on the composition of the catalyst. However, phase decomposition of the Zr_2FeH_x into $ZrFe_2H_x$ and ZrH_2 inevitable at $T > 400$ °C irreversibly decreases its absorption capacity,[8] restricting its use as the H_2 acceptor in the reaction. Intermetallics Ti_2Fe and Hf_2Fe are devoid of this disadvantage.[9—11]

The absorption properties of Ti_2Fe and Hf_2Fe intermetallics in comparison with Zr_2Fe as well as their influence on ethane aromatization in the presence of Pt,Ga/NCVM at 400—450 °C are investigated in this work.

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 10, pp. 1726—1729, October, 1994.

Experimental

The catalyst was prepared based on zeolite NCVM (SiO_2/Al_2O_3 = 42, Na_2O < 0.1 %). Modifying admixtures of Ga (1.5 mass %) and Pt (0.5 mass %) were introduced by combined impregnation with aqueous solutions of gallium nitrate and hexacloroplatinic acid.

Prior to use the catalyst was annealed for 5 h in a flow of air at 520 °C followed by treatment with hydrogen for 1.5 h at the same temperature. Intermetallics Ti_2Fe, Zr_2Fe, and Hf_2Fe were prepared by alloying the metals according to the previously described technique.[12]

The H_2 absorption was investigated in a flow-type unit. The initial intermetallic compound (1 cm^3) was introduced into a quartz reactor, heated in the flow of Ar to a preset temperature followed by passing the Ar + H_2 mixture of prescribed composition with the rate 1.2 L h^{-1}. The H_2 concentration at the inlet and outlet of the reactor was registered by GLC.

The reaction was carried out in the same unit. Either a mechanical mixture of 1 cm^3 (0.7 g) of a catalyst with a particle size of 0.25—1.0 mm and 1 cm^3 (1.5—5.0 g) of an intermetallic compound with a particle size of 0.18—0.5 mm or only 1 cm^3 of the catalyst were placed in the reactor. The mixture was heated in the Ar flow to the temperature of the reaction and ethane was passed through with the volume rate of 600 h^{-1}. Products were analyzed by gas liquid chromatography.

Results and Discussion

The data available from literature on the absorption properties of the hydride-forming metals and alloys have been obtained in the static system under high vacuum, with the gases used being carefully purified from microadmixtures. Therefore, it is difficult to expect complete agreement between these data and absorption properties of the intermetallic H_2 acceptors in actual practice of the catalytic dehydrogenation. In this work absorption properties of the intermetallics Zr_2Fe, Hf_2Fe, and Ti_2Fe were investigated under the conditions of a flow-type catalytic system. Tables 1—3 present the main results of the experiments.

The data obtained indicate the high absorption capability of the starting intermetallic compound Zr_2Fe (Table 1). The exothermic process of H_2 absorption by this intermetallic compound without dilution with argon proceeds at a very high speed and warming up of the specimen takes place. A substantial decrease of p_{H_2} in the mixture practically does not influence the volume of the H_2 absorbed. At the same time the ability of the intermetallic compound to absorb H_2 sharply decreases as a result of thermal treatment during regeneration.

Initial intermetallic compound Hf_2Fe is not capable of H_2 absorption under the conditions of a flow-type system obviously owing to the formation of a protective oxide layer on its surface.[13] However, after pre-activation by absorption-desorption cycles in the presence of the alumoplatinic catalyst,[14] its absorption capacity appears to be rather stable both in the absorption experiments and under thermal regeneration (Table 2). The intermetallic compound acquires similar properties after hydrogenation in a vacuum unit followed by thermal treatment of the hydride Hf_2FeH_x formed in the stream of the inert gas (cycle 1'). At the same time the volume of hydrogen required for saturation of Hf_2Fe is more than an order of magnitude smaller in comparison with Zr_2Fe. The increase of p_{H_2} and decrease of the temperature of absorption somewhat enlarges the volume of the H_2 absorbed. Nevertheless this is evidently insufficient for effective use of the given intermetallic compound as an H_2 acceptor in the course of aromatization.

Absorption properties of the Ti_2Fe obtained by heat treatment of the hydride Ti_2FeH_x are quite stable in the absorption-desorption cycles (Table 3). However, a volume of hydrogen absorbed by 1 cm^3 of this intermetallic compound is three times smaller in comparison with Zr_2Fe and is not increased by decreasing the tempera-

Table 1. Absorption properties of Zr_2Fe (T = 500 °C; regeneration in Ar at 600 °C, 1 h)

Absorption—desorption cycle	$p_{H_2} \cdot 10$ /MPa	H_2 absorption /L cm^{-3}
1	1.00	0.375
	0.08	0.330
2	0.05	0.054
3	0.06	0.054

Table 2. Absorption properties of the Hf_2Fe (regeneration in Ar at 600 °C, 1 h)

Absorption—desorption cycle	$p_{H_2} \cdot 10$ /MPa	T/°C	H_2 absorption /L cm^{-3}
1	0.08	500	0.030
1'	0.08	500	0.030
2	0.08	500	0.030
3	0.08	400	0.055
4	0.08	300	0.100
5	0.16	500	0.050
6	0.23	500	0.045
7	0.08	500	0.030

Table 3. Absorption properties of Ti_2Fe ($p_{H_2} = 9 \cdot 10^{-3}$ MPa, regeneration in Ar at 600 °C, 2.5 h)

Absorption—desorption cycle	T/°C	H_2 absorption /L cm^{-3}
1	400	0.123
2	400	0.118
3	300	0.106
4	200	0.100
5	400	0.099

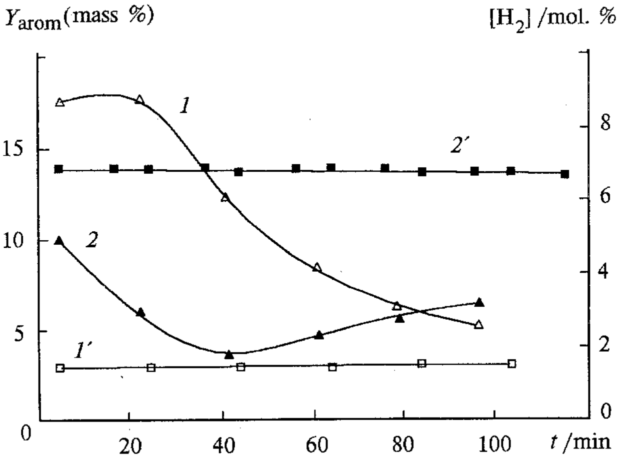

Fig. 1. The yield of aromatic hydrocarbons (*1,1'*) and the hydrogen content in the reaction mixture (*2,2'*) during ethane aromatization over Pt,Ga/NCVM in the presence (*1,2*) and in the absence (*1',2'*) of Zr_2Fe hydrogen acceptor at 430 °C.

ture of absorption. Another disadvantage of this material is the long duration of regeneration needed for recovery of its absorption capacity.

The difference in the absorption properties of the intermetallics in question is reflected in the efficiency of their use as hydrogen acceptors. Figure 1 shows time dependences of the yield of aromatic hydrocarbons AH and the hydrogen content in the reaction mixture during ethane aromatization over either Pt,Ga/NCVM or its composition with Zr_2Fe at 430 °C. Intensive removal of H_2 by the acceptor at the initial stage of reaction is seen to lead to a six-fold rise of the AH yield. As the intermetallic compound is saturated, the H_2 content in the flow grows but the yield of AH is reduced.

Table 4. The effect of intermetallic compounds M_2Fe on ethane aromatization over a Pt,Ga/NCVM catalyst (600 h^{-1})

H_2 acceptor	*X* (%)	*T*/°C	*Y* of AH (mass %)	[H_2] (mol. %)
Absent 3	400	1	3	
	5	430	3	7
	7	450	4	10
	15	500	9	20
	27	550	18	30
Zr_2Fe	10	400	8	2
	21	430	18	3
	27	450	23	4
Hf_2Fe	6	400	4	1
Ti_2Fe	—	400	4	<1
	—	430	16	<1

The high efficiency of Zr_2Fe in the process of the ethane aromatization is observed at 400—500 °C. (Table 4). In presence of Zr_2Fe the maximum yields of AH at these temperatures are higher by factors of 8 and 5.5, correspondingly, in comparison with the same conditions but without removing H_2.

Similar yields of AH can be obtained on the Pt,Ga/NCVM catalyst without the H_2 acceptor when the temperature rises 100—120 °C only.

The highest yield of AH from ethane in the presence of Hf_2Fe and Ti_2Fe at 400 °C is two times smaller than that when Zr_2Fe as hydrogen acceptor is used; the duration of the effect of the intermetallic compound on the reaction is completely different too. So a two-fold decrease in the yield of AH in the presence of Zr_2Fe, Ti_2Fe, and Hf_2Fe is consequently observed at intervals

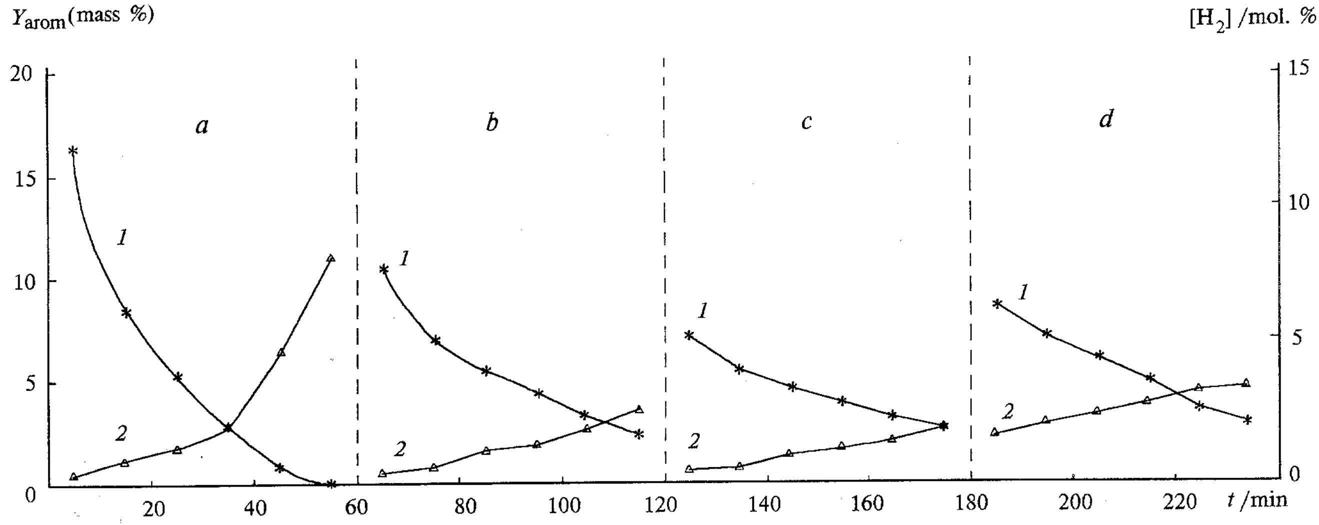

Fig. 2. The yield of the aromatic hydrocarbons (*1*) and the hydrogen content in the reaction mixture (*2*) during ethane aromatization over Pt,Ga/NCVM in the presence of the hydrogen acceptor Ti_2Fe at 430 °C: *a*, initial system, *b,c*, after treatment in Ar at 600 °C for 2.5 h; *d*, after regeneration of catalyst in air at 520 °C for 1 h + treatment in Ar at 600 °C for 2.5 h.

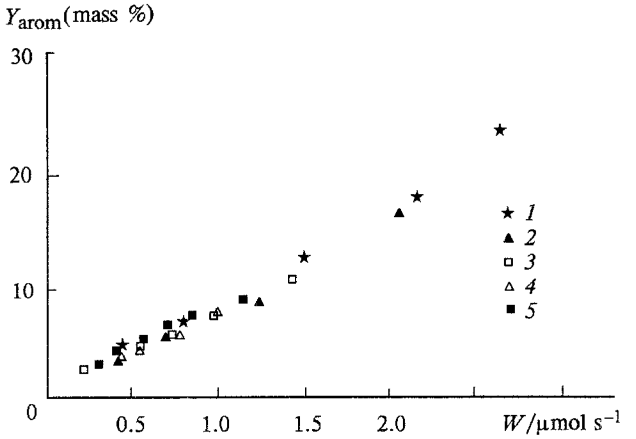

Fig. 3. The dependence of yield of aromatic hydrocarbons on rate of hydrogen absorption by acceptors Zr_2Fe (*1*) and Ti_2Fe in the 1st (*2*), 2nd (*3*), 3rd (*4*), and 4th (*5*) cycles of aromatization-desorption.

of 100, 50, and 30 min after the reaction has been started. Thus Hf_2Fe is hardly effective even at 400 °C and unsuitable as the H_2 acceptor for ethane aromatization because the absorption capacity of this intermetallic compound is reduced with temperature growth (Table 2).

The maximum yield of AH from ethane at 430 °C under removal of H_2 with Ti_2Fe as an acceptor is the same as the yield in the presence of Zr_2Fe (Table 4). However by using Ti_2Fe as the H_2 acceptor the yield of AH is decreased by factor of two during the first 15 min of the reaction (Fig. 2), but in the case of Zr_2Fe it takes an hour (Fig. 1).

Repeated reaction runs after thermal desorption of H_2 from the hydride Ti_2FeH_x lead to a marked decrease in the maximum yield of AH from ethane (Fig. 2, *b*). Further decrease of efficiency of the intermetallic compound in the reaction is observed in the third cycle of aromatization-desorption (Fig. 2, *c*). However even in this cycle an average yield of AH in 1 h is higher than that in the absence of the H_2 acceptor by a factor of 1.5 (Fig. 1). Despite the high stability of Pt,Ga/NCVM in ethane aromatization, it could be supposed that the decrease of the yield of AH is caused by gradual deactivation of the catalyst under deficiency of hydrogen in the reaction medium. Therefore the catalyst has been separated and regenerated in the flow of air at 520 °C for 1 h prior to the next experiment. Nevertheless it has not led to the initial activity of the catalyst-intermetallic compound system being restored. It indicates an irreversible change in absorption properties of Ti_2Fe. The increase of the hydrogen concentration in the reaction flow and the comparatively small yield of AH in this case is likely caused by a decrease of the absorption rate as a result of deactivation of the surface of the intermetallic compound which is rather sensitive to O_2 admixture in the reaction medium.[10] In fact removal of the released hydrogen by the acceptor eliminates thermodynamic restriction of the dehydrogenation of ethane into ethylene. Therefore the yield of AH in the presence of an intermetallic compound is obviously defined by the kinetics of conjugated processes of the aromatization and hydride formation. This is confirmed by a linear dependence of the yield of AH on the rate of H_2 absorption calculated from the data on ethane conversion and the H_2 concentration in the reaction flow (Fig. 3). The correlation observed is retained at different contents of unabsorbed H_2 in the reaction mixture as well as by replacing Ti_2Fe with Zr_2Fe.

Thus the capability of the intermetallic compounds M_2Fe to absorb H_2 under the conditions of aromatization and consequently their efficiency as H_2 acceptors are decreased in the order $Zr_2Fe > Ti_2Fe > Hf_2Fe$. Intermetallic compounds based on Zr and Ti are potential acceptors of H_2. In accordance with published data[8,15] their disadvantages connected with the deterioration of absorption properties either under action of the reaction medium or during absorption-desorbtion cycles can be corrected by introducing oxygen into the composition of the intermetallic compound.

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Received May 5, 1994;
in revised form June 16, 1994