## Catalytic conversions of chloroolefins over iron oxide nanoparticles 1. Isomerization of dichlorobutenes in the presence of iron oxide nanopaticles immobilized on silicas with different structures

T. N. Rostovshchikova,<sup>a</sup> V. V. Smirnov,<sup>a</sup> M. V. Tsodikov,<sup>b</sup> O. V. Bukhtenko,<sup>b</sup> Yu. V. Maksimov,<sup>c</sup> O. I. Kiseleva,<sup>a</sup> and D. A. Pankratov<sup>a</sup>

<sup>a</sup>Department of Chemistry, M. V. Lomonosov Moscow State University, 1 Leninskie Gory, 119992 Moscow, Russian Federation. Fax: +7 (095) 932 8846. E-mail: rtn@kinet.chem.msu.ru
<sup>b</sup>A. V. Topchiev Institute of Petrochemical Synthesis, Russian Academy of Sciences, 29 Leninsky prosp., 119991 Moscow, Russian Federation. Fax: +7 (095) 230 2224. E-mail: tsodikov@ips.ac.ru
<sup>c</sup>N. N. Semenov Institute of Chemical Physics, Russian Academy of Sciences, 4 ul. Kosygina, 119991 Moscow, Russian Federation. E-mail: maksimov@chph.ras.ru

The influence of the support nature and electronic state of iron oxide nanoclusters on the catalytic properties of supported systems was studied for dichlorobutene isomerization. A sample with a Fe content of 2.5 wt.% on the activated silica matrix containing Fe<sup>III</sup> and Fe<sup>II</sup> ions in the paramagnetic state exhibits the highest activity. The activity of iron on silica gel enhances with the appearance of magnetically ordered nanoclusters of  $\gamma$ -iron oxide formed at the iron content on the catalyst as high as 15 wt.%. An increase in the catalyst activity is favored by the formation of two states of iron (Fe<sup>III</sup> and Fe<sup>II</sup>) that occurs under the synthesis conditions or during the action of a reactant.

Key words: iron oxide, nanoparticles, supports, dichlorobutene isomerization, structure, catalytic activity.

Iron oxides are widely used as catalysts in the Fischer-Tropsch synthesis, dehydrogenation, alkylation, and other processes.<sup>1,2</sup> They are also active in catalytic reactions involving halogen-containing hydrocarbons<sup>3</sup> in which the catalytic properties of bulky and nanoscale iron oxides differ significantly. Isomerization of dichlorobutenes and benzene alkylation with chloroolefins of the allyl type on bulky iron oxide are accompanied by the formation of a large (up to 30%) amount of oligomerization products characteristics of chain radical conversions of chloroolefins in the presence of peroxide initiators. The same reactions on nanoscale catalysts proceed with much higher rates and enhanced selectivity with respect to the primary alkylation products.<sup>3</sup> The main pathway of the catalytic process in a benzene-chloroolefin system depends on the presence of oxygen. Benzene alkylation with allyl chloride or dichlorobutene occurs only in the presence of oxygen. Removal of the latter favors dichlorobutene isomerization. In the absence of benzene, isomerization also occurs in an oxygen-containing medium. A strong effect of oxygen on the rate and direction of the processes suggests that the iron ions in mixed-valence states are involved in catalysis on nonstoichiometric phases of nanoparticles.<sup>3</sup> The role of structures including two charge states of the iron ions (Fe<sup>II</sup> and Fe<sup>III</sup>) was observed in the Fischer—Tropsch reaction and some other catalytic processes.<sup>4,5</sup>

The nature of the catalyst surface is determined by the size of iron oxide particles and their resistance to reduction and depends strongly on the iron to support ratio and character of particle distribution on the support. For instance, relatively large iron oxide nanoparticles  $(\sim 13-15 \text{ nm})$  obtained at a high (10-15%) iron content on silica gel are reducible with hydrogen on heating to metallic iron.<sup>6</sup> At the same time, fine iron oxide nanoclusters (<5 nm in size), which are formed on the support at a low (down to 5%) iron content, cannot virtually be reduced under similar conditions. This is caused by a stronger interaction between nanoclusters of a smaller size and the support surface. In addition to the particle size, the structure of the support, its surface, and porosity exert a substantial effect on the formation of catalytically active iron species.

Isomerization of dichlorobutenes seems to be convenient to find specific features of the catalyst effects, because this process has previously been studied in detail in

Published in Russian in Izvestiya Akademii Nauk. Seriya Khimicheskaya, No. 6, pp. 1376–1382, June, 2005.

1066-5285/05/5406-1418 © 2005 Springer Science+Business Media, Inc.

the presence of the homo- and heterovalent copper complexes,<sup>7</sup> iron(III) chloride,<sup>8</sup> and nanodimensional metals.<sup>9</sup> The isomerization mechanism in the presence of the supported metal oxides is studied in less detail.<sup>3</sup>

The purpose of this work is to determine the influence of the nature of silica and the ratio of active component to support on the catalytic activity of iron oxides in the isomerization of 3,4-dichlorobut-1-ene (3,4-DCB) to *trans*-1,4-dichlorobut-2-ene (*trans*-1,4-DCB).

```
CH<sub>2</sub>CICHCICH=CH<sub>2</sub> = trans-CH<sub>2</sub>CICH=CHCH<sub>2</sub>CI
```

Silica gel with the standard globular structure and an activated silica matrix (ASM) were chosen as supports. The ASM is prepared by the removal of metal cations from natural vermiculite<sup>4,10</sup> and retains the layer structure typical of mica.

## **Experimental**

Nanoparticles of  $Fe_2O_3$  on the KSK-2 silica gel (specific surface  $S = 340 \text{ m}^2 \text{ g}^{-1}$ ) were prepared<sup>3</sup> by the impregnation of the support with a solution of iron nitrate followed by calcination for 6 h at 400 °C. The iron content in the catalysts was 3, 5, 10, and 15 wt.%. Samples with the 5% iron content including the phases  $Fe_3O_4$  or  $Fe_xO$  (x < 1) along with  $Fe_2O_3$  were obtained by temperature-programmed reduction with hydrogen in an interval of 400—500 °C and continuous *in situ* measurement of magnetization. Reduction was interrupted each time when a new oxide phase was formed.<sup>6</sup> The main characteristics of the catalysts (particle size, specific surface, parameter of Mössbauer spectra) prepared by this method have been described earlier.<sup>3,11</sup>

The activated silica matrix was prepared by two-stage acid etching of vermiculite.<sup>12</sup> At the first stage, vermiculite was treated with dilute hydrochloric acid at 50–60 °C, and the second stage was the treatment with a mixture of 40% sulfuric and concentrated nitric acids taken in a ratio of 40 : 60 (v/v). Thus obtained ASM was characterized by the high specific surface (S =350 m<sup>2</sup> g<sup>-1</sup>) and uniform size distribution of mesopores (~8 nm).<sup>12</sup> The ASM-immobilized iron oxide with a metal content of 2.5 wt.% was prepared by the impregnation of the support with a solution of iron acetylacetonate followed by evacuation and calcination at 400 °C.

Structural studies of the initial catalysts were carried out by X-ray diffraction and Mössbauer spectroscopy. X-ray phase analysis of iron-containing phases was conducted on a DRON-3M diffractometer using filtered Cu-K $\alpha$  radiation. The crystallite size was determined from the broadening of diffraction peaks corrected for structure anisotropy. Mössbauer absorption spectra were measured on MS1101E (MNPP "MosTek," Russia and Haldor, Germany) electrodynamic-type spectrometers at room temperature. Sources of  $\gamma$ -radiation were <sup>57</sup>Co sources in the matrix of metallic chromium or rhodium with activity lower than 1.1 GBq. Chemical shifts were determined relatively to  $\alpha$ -Fe. Spectra were processed by the standard leastsquares method assuming the Lorentzian line shape.

Reagents and solvents were dried and distilled, and purity was monitored by chromatography. Isomerization of 3,4-DCB was carried out in sealed glass tubes with stirring in an interval of 60-120 °C in the presence of oxygen. A tube was loaded with a weighed sample of the catalyst with the specified metal content and a measured amount of 3,4-DCB or its solution in dichloroethane with the reactant to solvent ratio varying from 1 : 1 to 1 : 9. All experiments were conducted under conditions when the process rate was independent of the stirring velocity.

The composition of the reaction mixture was analyzed on a Kristall Lyuks-4000 chromatograph with a flame-ionization detector on a column packed with the SE-30 stationary phase using the temperature-programmed regime of the column in an interval of 50–150 °C. According to the data of chromatographic analysis, the main product of 3,4-DCB isomerization was *trans*-1,4-DCB. The yield of the *cis*-isomer did not exceed 2%. At high conversions, the reaction products contained up to 1% by-products: chloroprene and higher-boiling substances.

The specific catalytic activity was calculated as the number of moles of *trans*-1,4-DCB per mole of iron per hour using the maximum rate of the process determined from a slope of the curve of *trans*-1,4-DCB accumulation.

In the absence of an induction period (a low-rate region) in the kinetic curves, the results were processed in the coordinates of a reversible first-order reaction  $\ln[(A_{\infty} - A_0)/(A_{\infty} - A)] - t$ , where  $A_{\infty}$  and  $A_0$  are the equilibrium and initial concentrations of *trans*-1,4-DCB, and A is its current concentration. Equilibrium concentrations  $A_{\infty}$  at different temperatures were calculated from the known equilibrium constants of isomerization.<sup>13</sup> The content of *trans*-1,4-DCB in the initial mixture ( $A_0$ ) was determined by chromatography; this value usually did not exceed 1%. The accuracy of determination of isomerization rate constants was 15%.

## **Results and Discussion**

Iron oxide nanoparticles immobilized on silicas. The X-ray diffraction patterns of the samples supported on the KSK-2 silica gel with the iron content 10 and 15 wt.% contain a broad halo corresponding to an amorphous to X-ray phase and broadened reflections from the  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> nanoclusters (d = 0.2762, 0.2714, 0.2528, 0.2292, and 0.2209 nm) with sizes of 13 and 15 nm, respectively. The spectra of the catalysts based on KSK-2 with the iron content 3 and 5 wt.% exhibit very weak reflections, most likely, from the same clusters along with the broad halo. The ASM-supported catalyst with the iron content 2.5 wt.% is amorphous to X-rays.

The parameters of the Mössbauer spectra of the studied catalysts are presented in Table 1. As follows from the data presented, the lines of magnetic HFS are the most intense in the spectra of the KSK-2-supported catalyst samples. The presented parameters of components 1 and 2 (Fe<sup>III</sup>(magn.)) correspond to the spectra of nanoclusters of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> (hematite) with the rhombohedral lattice and mean size >10 nm.<sup>14</sup> This agrees with the data on X-ray diffraction. The presence of two HFS components from Fe<sup>III</sup>(magn.) (1 and 2) in the spectra of the samples containing 5 and 10 wt.% iron indicates that the system contains two dimensional modes of hematite nanoclusters.

Fe	Component	$\delta \pm 0.03$	$\Delta \pm 0.03$	Г±0.03	$H_{\rm in} \pm 0.1/{\rm T}$	Relative
(wt.%)			$\rm mm~s^{-1}$			content (±5%)
			KS	K-2		
5	Fe <sup>III</sup> (magn.), 1;	0.35	-0.22	0.39	50.4	48
	Fe <sup>III</sup> (magn.), 2;	0.22	-0.26	0.74	47.8	15
	Fe <sup>III</sup> (paramagn.)	0.30	0.70	0.53	_	37
10	Fe <sup>III</sup> (magn.), 1;	0.38	-0.21	0.32	50.9	69
	Fe <sup>III</sup> (magn.), 2;	0.33	-0.23	0.46	49.3	24
	Fe <sup>III</sup> (paramagn.);	0.29	0.74	0.64	_	5
	singlet	0.54	_	0.68	_	2
15	Fe <sup>III</sup> (magn.), 1;	0.38	-0.21	0.43	50.4	48
	Fe <sup>III</sup> (magn.), 3;	0.32	-0.06	0.73	44.9	14
	Fe <sup>III</sup> (magn.), 4;	0.39	-0.05	1.13	39.0	13
	Fe <sup>III</sup> (paramagn.);	0.31	0.68	1.12	_	23
	singlet	0.58	_	0.32	_	2
			AS	M		
2.5*	Fe <sup>III</sup> (paramagn.);	0.36	0.88	0.60	_	85
	Fe <sup>II</sup> (paramagn.)	1.19	2.07	0.56	_	15
After	Fe <sup>III</sup> (paramagn.);	0.35	0.76	0.68	_	70
reaction	Fe <sup>II</sup> (paramagn.)	1.18	1.96	0.33	_	30

**Table 1.** Parameters of the Mössbauer spectra of the starting catalysts at room temperature ( $\delta$  is the isomeric shift,  $\Delta$  is the quadrupole shift in the spectra with magnetic splitting or quadrupole splitting in the spectra with paramagnetic components,  $\Gamma$  is the linewidth, and  $H_{in}$  is the internal field on the iron nucleus)

\* In the starting catalyst.

Narrower lines and a higher internal field on the iron nucleus ( $\Gamma \approx 0.3 - 0.4 \text{ mm s}^{-1}$ ,  $H_{\text{in}} \approx 50 - 51 \text{ T}$ ) for component 1 can be assigned to larger particles with a rather narrow size distribution. The parameters of the second mode with  $\Gamma \approx 0.5 - 0.7$  mm s<sup>-1</sup> and  $H_{in} \approx 48 - 49$  T characterize smaller clusters with a broader size distribution of particles. Since this component is absent from the spectrum of the sample with the iron content 15 wt.%, we can assume that of hematite clusters of the same size with the parameters  $H_{in} \approx 50.4 \text{ T}$  and  $\Gamma \approx 0.4 \text{ mm s}^{-1}$  prevail. Along with component 1 from the magnetic hematite clusters, the spectrum of the sample with 15 wt.% Fe exhibits distinctly two HFS components: 3 (Fe<sup>III</sup>(magn.)) and 4 (Fe<sup>III</sup>(magn.)). The spectra with these parameters characterize magnetically ordered defect clusters of  $\gamma$ -oxide with the spinel structure and average size of  $\sim 10$  nm.<sup>15</sup> The spectra of all the KSK-2-supported iron samples contain the component Fe<sup>III</sup>(paramagn.) corresponding to the Fe<sup>III</sup> ions in the high-spin state in the octahedral oxygen environment. Probably, this spectral component characterizes very small ( $\leq 5-6$  nm) clusters of  $\gamma$ - or  $\alpha$ -iron oxide with superparamagnetic properties.<sup>16</sup> The data in Table 1 show that the contribution of the Fe<sup>III</sup>(magn.) components decreases and, correspondingly, the relative fraction of small clusters increases with a decrease in the iron content. Finally, weak single lines in the spectra of the samples containing 10 and 15 wt.% iron can be attributed (by the isomeric shift value) to

superparamagnetic magnetite nanoclusters with a size of ~6 nm.  $^{17-19}$ 

Unlike the spectra of the catalysts with KSK-2 as a carrier, the spectrum of the iron sample on the ASM support contains only paramagnetic signals from the Fe<sup>III</sup> and Fe<sup>II</sup> ions in the high-spin state. The presence of the paramagnetic signal from the Fe<sup>III</sup> ion measured at room temperature agrees with the X-ray diffraction data, because it cannot be excluded that this signal corresponds to very small clusters of  $\gamma$ -iron oxide amorphous to X-rays. Weak ferrimagnetism has previously<sup>4</sup> been observed in similar systems by an analysis of the data on magnetic susceptibility.

**Catalytic properties of iron oxides supported on silica gel.** The kinetic curves of *trans*-1,4-DCB accumulation for the KSK-2-based catalysts with different compositions at different catalyst and reactant concentrations in a temperature interval of 80–110 °C are shown in Figs 1 and 2. In some cases, the rate of *trans*-1,4-DCB formation increased after the induction period had elapsed. An estimate of the induction time was made by analyzing the kinetic curves and taking the time needed to achieve the maximum isomerization rate (Table 2). As follows from the data in Fig. 1 and Table 2, the induction time increases for the samples with a low content of the catalyst active phase and with a decrease in the catalyst amount in the reaction mixture. The induction time decreases with an increase in the iron content and temperature increase.



**Fig. 1.** Kinetic curves of *trans*-1,4-DCB accumulation on the KSK-2-supported iron oxide with a Fe content of 15 (*I*), 10 (2, 2'), and 5 wt.% (3); T = 100 (1-3) and 110 °C (2'); catalyst weight 0.003 (*I*), 0.005 (2, 2'), and 0.010 g (3);  $V_{3,4-\text{DCB}} = 0.1 \text{ mL}.$ 



**Fig. 2.** Kinetic curves of *trans*-1,4-DCB accumulation on the KSK-2-supported iron oxide (3 wt.% Fe) under different conditions: 90 °C, 0.6 mL of a 3,4-DCB—dichloroethane (1 : 9) mixture (1); 80 °C, 0.6 mL of a 3,4-DCB—dichloroethane (1 : 9) mixture (2); 90 °C, 0.6 mL of a 3,4-DCB—dichloroethane (1 : 1) mixture (3); 80 °C, 0.6 mL of 3,4-DCB (4). The catalyst weight is 0.004 g.

In the presence of the catalyst containing 15 wt.% iron, no induction period is observed and a high initial rate of the process is achieved (see Fig. 1). However, further the

**Table 2.** Duration of the induction period of 3,4-DCB isomerization ( $\tau$ ) at different iron contents in the catalysts supported on KSK-2 at 100 °C and different catalyst amounts

Fe (wt.%)	Catalyst weight/g	τ <u>+</u> 5/min
3	0.015	25
5	0.010	12
10	0.005	7
10	0.0025	10
10	0.0015	15



**Fig. 3.** Kinetic curves of *trans*-1,4-DCB accumulation at 90 (1), 100 (2), and 110 °C (3) on the catalyst supported on KSK-2 with a Fe content of 10 wt.% in the coordinates  $\ln y - t$  ( $y = (A_{\infty} - A_0)/(A_{\infty} - A)$ ).

isomerization rate decreases sharply, and the system does not achieve the equilibrium yield of *trans*-1,4-DCB, being 77% at 100 °C.<sup>13</sup> This is probably related to the fast catalyst deactivation due to the formation of iron(II) chloride, which is inactive in isomerization.<sup>3</sup> When 3,4-DCB is diluted with the polar chloroorganic solvent (dichloroethane), the induction period also decreases and disappears completely in excess solvent (see Fig. 2).

Thus, the isomerization of 3,4-DCB is a complex process, which cannot be described, in the general case, by simple kinetic equations. Only under certain conditions (at the iron content in the catalyst >10 wt.%, iron content in the reaction mixture >0.08 mol L<sup>-1</sup>, and temperature >90 °C) almost without induction period, the reversible reaction formally obeys a kinetic equation of the first order with respect to 3,4-DCB. This is indicated by the linearized kinetic curves shown in Fig. 3. The apparent rate constants of the forward and backward reactions along with the known equilibrium constants<sup>13</sup> at different temperatures are given in Table 3. Under these conditions,

**Table 3.** Equilibrium constants  $(K_{eq})^{13}$  and apparent rate constants of the forward and backward reactions of 3,4-DCB isomerization to *trans*-1,4-DCB ( $k_1$  and  $k_{-1}$ , respectively) at different temperatures for the KSK-2-supported catalyst with the Fe content 10 wt.%

<i>T</i> /°C	K <sub>eq</sub>	$(k_1 + k_{-1}) \cdot 10^4$	$k_1 \cdot 10^4$	$k_{-1} \cdot 10^4$
			s <sup>-1</sup>	
120	2.70	18.0 <u>+</u> 2.0	13.0 <u>+</u> 1.0	5.0 <u>+</u> 1.0
110	3.00	9.0 <u>+</u> 1.0	7.0 <u>+</u> 0.5	2.0 <u>+</u> 0.5
100	3.33	7.0 <u>+</u> 1.0	5.5 <u>+</u> 0.5	1.5 <u>+</u> 0.5
90	3.85	4.0 <u>+</u> 0.6	3.2 <u>+</u> 0.3	0.8 <u>+</u> 0.3
90*	—	12.0 <u>+</u> 1.0	9.5 <u>+</u> 0.5	2.5 <u>+</u> 0.5

\* In dichloroethane.





Fig. 4. Specific catalytic activity  $(A_{sp})$  vs. iron content for the catalysts supported on KSK-2 at 100 °C.

the apparent activation energy of the forward reaction is  $53\pm10$  kJ mol<sup>-1</sup>, and that of the backward reaction is  $69\pm12$  kJ mol<sup>-1</sup>.

The plot of the specific catalytic activity vs. iron content in the catalyst is shown in Fig. 4. The specific activity increases from 90 to 230 moles of 1,4-DCB (mol Fe)<sup>-1</sup> h<sup>-1</sup> with an increase in the iron content from 3 to 15 wt.% (see Fig. 4). However, it follows from the data of X-ray diffraction and Mössbauer spectroscopy that the fraction of large (>10 nm) nanoclusters increases with an increase in the iron content  $\geq 10$  wt.%. Therefore, with the increase in the iron content a decrease rather than an increase in the specific activity can be expected. An enhancement of the catalytic activity with an increase in the iron content can be explained by a change in the composition of the catalyst oxide phase found by Mössbauer spectroscopy. In particular, the starting catalyst can contain the catalytically more active  $Fe_3O_4$  clusters<sup>3</sup> or cubic  $\gamma$ -iron oxide with the spinel structure, which can be reduced with reactants to form mixed-charge states.<sup>20</sup>

To establish the effect of the charge state of a metal on the activity of the system, the rate of 3,4-DCB isomerization was determined in the presence of the catalysts containing other oxides in addition to iron(III) oxide:  $Fe_3O_4$ or Fe<sub>x</sub>O (the parameters of the Mössbauer spectra of the samples have been presented earlier<sup>3</sup>). The data obtained are shown in Fig. 5. As can be seen, the catalyst containing  $Fe_3O_4$  is the most active. At the same time, the presence of wustite  $Fe_xO$ , whose lattice contains mainly  $Fe^{II}$ ions, does not increase the catalytic activity. It can be concluded that an active phase of the catalyst based on magnetite, whose structure simultaneously contains the Fe<sup>II</sup> and Fe<sup>III</sup> ions, is formed by the action of reactants and/or solvent during the induction period. This result confirms the assumption that an increase in the activity with an increase in the iron oxide content on the support can be caused by the formation of mixed-charge states already in the starting catalyst or by the action of reactants, for example, involving  $\gamma$ -iron oxide.

As shown (see Table 2), the duration of the induction time increases with a decrease in the iron content in the



**Fig. 5.** Kinetic curves of *trans*-1,4-DCB accumulation at 100 °C on the iron oxides supported on KSK-2 (5 wt.% Fe) with different degrees of reduction:  $Fe_3O_4$  (1),  $Fe_2O_3$  (2), and  $Fe_xO$  (3) (0.01 g of catalyst, 0.1 mL of 3,4-DCB).

catalyst. Fine iron oxide nanoparticles ( $\leq 5-6$  nm), prevailing at low Fe contents on KSK-2 (3 and 5 wt.%), are capable of strong interacting with the support. Under these conditions, the formation of a catalytically active structure is energetically unfavorable, and the formation of the active catalyst surface requires a long time. Larger iron oxide particles (>10 nm) in the catalysts with 10 and 15 wt.% Fe are easily reduced with reactants and, hence, the catalytically active structure is formed more rapidly. If the catalyst contains iron ions in two oxidation states as in magnetite already in the initial state, no induction period is observed.

For larger iron oxide nanoparticles carried by KSK-2 (10 and 15 wt.% Fe), the reaction with chloroolefins can proceed until the complete conversion of iron(III) oxide to iron(II) chloride is achieved.<sup>3</sup> As a result, the catalysts with high iron contents are not catalytically active when used repeatedly.

Catalytic properties of iron oxides supported on the activated silica matrix. For the ASM-supported iron oxide, the samples with a low iron content (2.5 wt.%) have a high catalytic activity. Already at 80 °C, the reaction occurs without an induction period, and the equilibrium yield of trans-1,4-DCB equal to ~80% is achieved within 10-15 min. Meanwhile, such a high yield is not achieved even within several hours for the KSK-2-supported catalyst with a similar iron content (3 wt.%) (see Fig. 2, curve 4). For the both supported systems, the dilution of the reaction mixture with dichloroethane enhances the process rate and reduces the induction period. The kinetic curves of trans-1,4-DCB accumulation at 60 °C in the presence of dichloroethane for two supported catalysts (3 wt.% Fe on KSK-2 and 2.5 wt.% Fe on ASM) are presented in Fig. 6. As can be seen, the presence of the iron oxide supported on the ASM decreases the induction time. The activity of iron oxide on the ASM estimated from regions of the maximum rate at different temperatures is presented in Table 4. A comparison of these data



**Fig. 6.** Kinetic curves of *trans*-1,4-DCB accumulation at 60 °C in the presence of the iron oxide supported on ASM (2.5 wt.% Fe, 0.005 g of catalyst, 0.6 mL of a 3,4-DCB—dichloroethane (1 : 9) mixture) (1) and KSK-2 (3 wt.% Fe, 0.004 g of catalyst, 0.6 mL of a 3,4-DCB—dichloroethane (1 : 9) mixture) (2).

**Table 4.** Maximum isomerization rate (V) and specific catalytic activity  $(A_{sp})$  of iron oxide immobilized on the ASM in the isomerization of 3,4-DCB at different temperatures

<i>T</i> ∕°C	$V/{ m mol}\ { m L}^{-1}\ { m h}^{-1}$	$A_{\rm sp}$ /mole of 1,4-DCB (mol Fe) <sup>-1</sup> h <sup>-1</sup>
60	0.68	180
70	1.05	280
80	1.73	470

with the results for the catalysts on silica gel (see Fig. 4) shows that even at a lower temperature (80 °C) the ASM-supported catalyst is approximately twofold more active than the most efficient catalyst on KSK-2 as a carrier with the 15% iron content. The rate constants of the forward and backward reactions, which were estimated from the kinetic data, in the presence of iron oxide on the ASM at 90 °C were  $5.7 \cdot 10^{-4}$  and  $2.1 \cdot 10^{-4}$  s<sup>-1</sup>, respectively. These values approximately twofold exceed the isomerization rate constants obtained for the catalysts with the optimum composition prepared using a KSK support (see Table 3).

The ASM-immobilized iron oxide is also superior to the catalyst obtained using KSK-2 by stability to reduction. As can be seen from the data in Table 1, after the ASM-supported iron oxide was used in isomerization (on heating the reaction mixture for several hours at 80 °C), the Mössbauer spectra retain signals from the Fe<sup>III</sup> and Fe<sup>II</sup> ions. The parameters of these signals are close to those observed for the starting sample, and the relative fraction of the reduced form increases approximately twofold in the spent catalyst. An enhanced stability of the ASM-immobilized Fe<sup>III</sup> oxide to complete reduction compared to the iron oxides on KSK-2 is related, probably, to the strong interaction of the metal ion with layer silica. The presence of structural defects in particles amorphous to X-rays (lamellas) of silica favors the reduction of some  $Fe^{III}$  ions to  $Fe^{II}$ , and a possible electron transfer between them provides a high catalyst activity in redox steps of the reaction.<sup>20</sup>

Thus, with the use of the activated silica matrix for stabilization of iron oxide nanoparticles a more active catalyst can be formed. Reasons for high activity of the catalysts immobilized on silicas remain unclear. The data of this work confirmed that chloroolefin isomerization assuming the C—Cl bond cleavage is, most likely, a complex multistep process involving both oxidation—reduction and acid sites of the catalyst *via* different routes.<sup>3,7–9</sup> Evidently, the support nature, particle size, and simultaneous presence of two charge iron states in the catalyst are key factors determining the optimum properties of the catalyst.

The authors are grateful to P. A. Chernavskii for synthesis of the catalysts by temperature-programmed reduction and to G. V. Murav´eva for their X-ray diffraction study.

This work was financially supported by the Russian Foundation for Basic Research (Project Nos 01-03-32783, 03-03-33104, and 03-03-32029).

## References

- 1. H. Hayashi, L. Z. Chen, T. Tago, M. Kishida, and K. Wakabayshi, *Appl. Catal. A: Gen.*, 2002, **231**, 81.
- 2. C. Kurts, Y. Arita, W. Weiss, W. Ranke, and R. Schlögl, *Topics in Catal.*, 2001, **14**, 111.
- T. N. Rostovshchikova, O. I. Kiseleva, G. Yu. Yurkov, S. P. Gubin, D. A. Pankratov, Yu. D. Perfil'ev, V. V. Smirnov, P. A. Chernavskii, and G. V. Pankina, *Vestn. Mosk. Gos. Univ., Ser. 2. Khim.*, 2001, **42**, 318 [*Vestn. Mosk. Univ., Ser. Khim.*, 2001, **42** (Engl. Transl.)].
- M. V. Tsodikov, Ya. R. Katsobashvili, E. V. Slivinskii, Yu. V. Maksimov, V. V. Matveev, I. P. Suzdalev, O. G. Ellert, and G. F. Ivanova, *Izv. Akad. Nauk SSSR. Ser. Khim.*, 1986, 2666 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1986, **35**, 2443 (Engl. Transl.)].
- Yu. V. Maksimov, M. V. Tsodikov, M. A. Perederii, I. P. Suzdalev, A. I. Nekhaev, V. T. Popov, and O. V. Bukhtenko, *Izv. Akad. Nauk. Ser. Khim.*, 1997, 86 [*Russ. Chem. Bull.*, 1997, 46, 81 (Engl. Transl.)].
- P. A. Chernavskii, V. V. Kiselev, and V. V. Lunin, *Zh. Fiz. Khim.*, 1992, 66, 2712 [*Russ. J. Phys. Chem.*, 1992, 66 (Engl. Transl.)].
- T. N. Rostovshchikova, V. V. Smirnov, and A. I. Kokorin, J. Mol. Catal. A: Chem., 1998, 129, 141.
- 8. T. N. Rostovshchikova, V. V. Smirnov, and E. N. Golubeva, *Khim. Fiz.* [*Chemical Physics*], 1998, **17**, 63 (in Russian).
- L. I. Trakhtenberg, G. N. Gerasimov, V. K. Potapov, T. N. Rostovshchikova, V. V. Smirnov, and V. Yu. Zufman, Vestn. Mosk. Gos. Univ., Ser. 2. Khim., 2001, 42, 325 [Vestn. Mosk. Univ., Ser. Khim., 2001, 42 (Engl. Transl.)].

- V. V. Matveev, Yu. V. Maksimov, I. P. Suzdalev, M. V. Tsodikov, and I. A. Litvinov, *Hyperfine Interact.*, 1990, 56, 1707.
- P. A. Chernavskii, G. V. Pankina, and V. V. Lunin, *Zh. Fiz. Khim.*, 1996, **70**, 1016 [*Russ. J. Phys. Chem.*, 1996, **70** (Engl. Transl.)].
- M. V. Tsodikov, Doct. Sci. (Chem.) Thesis, A. V. Topchiev Institute of Petrochemical Synthesis, Russian Academy of Sciences, Moscow, 1992 (in Russian).
- E. M. Asatryan, N. L. Saakyan, I. V. Gul'neva, and G. T. Martirosyan, Arm. Khim. Zh., 1986, 39, 584 (in Russian).
- 14. I. P. Suzdalev, Dinamicheskie effekty v gamma-rezonansnoi spektroskopii [Dynamic Effects in Gamma-Resonance Spectroscopy], Atomizdat, Moscow, 1979, 192 pp. (in Russian).

- Yu. V. Maksimov, M. V. Tsodikov, O. G. Ellert, O. V. Bukhtenko, and V. V. Matveev, *J. Catal.*, 1994, **148**, 119.
- Yu. V. Maksimov, M. V. Tsodikov, E. A. Trusova, I. P. Suzdalev, and J. A. Navio, *Catal. Lett.*, 2001, 72, 11.
- 17. F. Menil, J. Phys. Chem. Sol., 1985, 46, 763.
- S. Morup, H. Topsoe, and J. Lipka, J. Phys. (Paris), 1976, 37, C6-287.
- S. J. Oh, D. C. Cook, and H. E. Townsend, *Hyperfine Interact.*, 1998, **112**, 59.
- O. S. Morozova, Yu. V. Maksimov, D. P. Shashkin, P. A. Shirjaev, V. A. Zhorin, and O. V. Krylov, *Appl. Catal.*, 1991, 78, 227.

Received December 30, 2003; in revised form April 6, 2005