JOURNAL OF CATALYSIS **167,** 210–214 (1997)
ARTICLE NO. CA971560

Isomerization Reaction of 1,1,2,2-Tetrafluoroethane on Chromia—A Study of the Active Sites on the Surface

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Received August 16, 1996; revised November 28, 1996; accepted December 2, 1996

The activation/deactivation processes of chromia occurring during the heterogeneous catalyzed isomerization reaction of 1,1,2,2-tetrafluoroethane were investigated. It was proved that coke formation on acid sites of the solid is mainly responsible for the observed slow decrease in the catalytic activity. Oxygen treatment removes the coke deposits almost completely. Enhanced catalytic activity results from the oxygen posttreatment. By means of CO as well as NH_3 IR and UV–vis spectroscopic measurements, it was shown that a relative increase in the strength of the acid sites took place. Since the active catalyst does not reveal any detectable Brønsted acidity before or after the oxygen treatment, one can conclude that Lewis acid sites alone are responsible for the catalytic cycles of the 1,1,2,2-tetrafluoroethane isomerization reaction. In addition, chromium was formed in higher oxidation states (Cr^{4+} and Cr^{5+}) and was responsible for oxidative reactions during the gas phase as well as for the formation of CO_2 and pentafluoroethane. © 1997 Academic Press

INTRODUCTION

1,1,1,2-Tetrafluoroethane (HFC-134a) is one of the most important CFC alternatives. The industrial synthesis is carried out by heterogeneous catalyzed chlorine–fluorine exchange, starting with trichloroethylene and gaseous HF (1–4). The fluorination reactions of the chloroethylene with HF are accompanied by other halogen exchange reactions, because dismutation, isomerization, and dehydrohalogenation reactions take place. Depending on the reaction conditions, these different reactions can occur as competitive processes which may greatly influence the selectivity of the process. In an earlier contribution, we described the mechanism of the isomerization reaction of CHF_2–CHF_2 (HFC-134) to the asymmetric compound CF_3–CH_2F on chromia (5). By using a fluorocarbon-containing chlorine, as is present in the technical process, the formation of HCl was observed. This adsorbed HCl causes a very complex system of side reactions, which were extensively investigated by employing deuterated compounds (6). Due to the strong tendency to coke formation of some of the intermediates, a pulse technique was exclusively employed for all investigations. Owing to this special experimental technique, the influence of coke on the catalyst activity was more or less suppressed. However, a steady decrease in the catalytic activity was observed with increasing reaction time, which is suggested to be due to the blocking of active sites by coke. On the other hand, Brunet *et al.* (7) reported the behavior of a chromia catalyst in the fluorination reactions of 1,1,1-trifluoro-2-chloroethane with HF forming CF_3–CH_2F. On the basis of TPD and TPO measurements, they found reversible oxidizable chromium species on the chromia surface and a direct relationship between the fluorination activity and the redox activity of the solid.

Depending on the pretreatment of the α-Cr_2O_3, very different sites form on the chromia surface. These sites mainly differ with regard to their oxidation state and coordination number. Oxygen is very strongly adsorbed on chromia surfaces, especially on coordinatively unsaturated Cr^{3+} sites, probably forming Cr^{4+} (8, 9). As Zecchina *et al.* (10) proved, the adsorption of oxygen on chromia leads to partially dissociative adsorbed stages already at room temperature. At higher temperatures the chemisorption of oxygen is assumed to result in the formation of Cr^{5+} and Cr^{6+} sites. Zaki and Knözinger (15) investigated the adsorption of CO on α-chromia containing excess oxygen between 77 and 298 K. By means of IR spectroscopy, they distinguished between chromium cations of different charges and coordination numbers.

Köhler *et al.* (16) detected the formation of CrO_2 as a result of decomposition reactions of chromium (III) nitrate deposited on TiO_2. The CrO_2 formed was reversibly reduced to antiferromagnetic CrOOH. A complete transformation into chromia was observed only at temperatures above 1000 K.

This paper focuses on the formation and characterization of different catalytic sites on α-chromia as well as on their impact on the heterogeneous catalyzed isomerization reaction of CHF_2–CHF_2.

EXPERIMENTAL

The design and construction of the equipment used, as well as the pulse technique employed, have been described

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previously (5, 6). The reactor (inner diameter 5.1 mm) was made of nickel and the other equipment of copper. Posttreatment of the solids by air, oxygen, or hydrogen was carried out by changing the nitrogen carrier gas stream.

The chromia used as a catalyst was synthesized by the volcano reaction of ammonium dichromate, pressed into pellets, and cut and subdivided into corn fractions of 300 to 500 μm. The surface area of the catalyst used here was 47 m^2/g; the bulk density was 1.1 g/ml. All experiments in the pulse reactor were carried out using the same amount of catalyst, namely 700 mg. Each sample was pretreated by calcining in nitrogen for 45 min at 673 K. The chromia prepared in this way was characterized by XRD. X-ray measurements revealed mostly X-ray amorphous parts as well as crystallinic α-Cr_2O_3.

The quantitative analysis of the product gas was performed using a capillary gas chromatograph GC-14A from Shimadzu (column Poraplot u, 25 m). The 1,1,2,2-tetrafluoroethane employed was a product of Fluorochem Limited. For comparative measurements the following compounds were used: 1,1,1,2-tetrafluoroethane (Hoechst), pentafluoroethane (Fluorochem Limited), trifluoroethylene (TFE, Fluorochem Limited), and CrO_2 (Aithaca Chem. Corp.).

The carbon content of the solid samples was determined using an LECO-CHNS 932 analyzer.

The UV–vis spectra were recorded with a spectrometer U3410 (Hitachi) in an integration sphere attachment with barium sulfate as the standard.

IR spectra were recorded using an M 85 Specord Instrument (Carl Zeiss Jena). The self-supporting wafers of the chromia samples (10–20 mg/cm^2) were placed in a quartz IR cell and activated by heating at 673 K under vacuum, in nitrogen, hydrogen, or oxygen atmosphere. In some cases this was followed by posttreatment with 1,1,2,2-tetrafluoroethane at the same temperature until catalytic activity was achieved. In order to characterize the acidic sites of the surface, ammonia was adsorbed at room temperature under a pressure of 4 kPa. Adsorption was followed by evacuation at room temperature to remove physically adsorbed ammonia. Desorption of ammonia was gradually carried out from room temperature up to 573 K. IR spectra were recorded in the range 1800–800 cm^{-1}.

CO adsorption was used for the characterization of the different state of the chromium ions on the surface. After activation, CO was adsorbed at 77 K, followed by evacuation at the same temperature. The IR spectra were recorded in the range 2300–2000 cm^{-1}.

RESULTS AND DISCUSSION

As shown previously (5, 6), before using Cr_2O_3 as a catalyst for the isomerization reaction of CHF_2–CHF_2, the chromia must be activated. In principle, HF can be used as conditioning gas in a similar matter. The same catalytically active sites can be generated with the haloalkane, but very specific activation conditions must be applied. Otherwise, chromium fluoride modifications can be formed with lesser catalytic activity. Therefore, we used only CHF_2–CHF_2 as the conditioning gas.

After reaching a maximum, the catalyst slowly lost its catalytic activity. The changes occurring on the surface of the solid after the activation procedure are given for the purpose of comparison in Fig. 1 (solid dark line). Consequently, the usual behavior of the catalyst activity is determined by two contrary processes. In a first stage the activity increases, probably due to the fluorination of the surface and the formation of active centers on the solid. As fluorination occurs, a destructive mechanism causes a slow decrease in the activity. This is accompanied by a permanent gradual increase in the carbon content of the surface with increasing CHF_2–CHF_2 pulse number. A cleavage of the surface (destruction of the coke layer) should therefore result in enhanced catalytic activity of the chromia used. It is quite common to remove coke layers by exposing them to oxygen. The effect of such an oxygen treatment on the activity is shown in Fig. 1 (open circles) (stages III and IV). As can be seen from the carbon balance (inset), carbon was almost completely removed from the surface due to the oxygen treatment. As the carbon quantity decreased, the isomerization activity of the chromia catalyst increased to a higher level than that of the starting catalyst without this treatment (filled circles). It is somewhat surprising that,

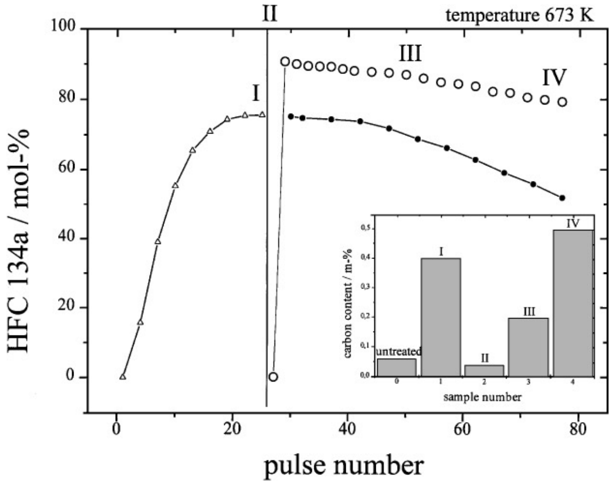

FIG. 1. Concentration of CF_3–CH_2F (HFC-134a) in the organic gas phase depending on the pulse number (673 K, reactant CHF_2–CHF_2 (HFC-134), pulse volume 1 ml_{STP}, contact time 17 s). (Inset) Carbon content in the solid phase stages I–IV. Open triangles, activation period; stage I represents the highest activity of the solid. Filled circles, change in the catalytic activity due to further HFC-134 treatment. Open circles, catalytic activity after a 30 min O_2 treatment (673 K, 10 ml/min_{STP}). Stage II, catalyst immediately after the 30 min O_2 treatment; stage III, 25 pulses HFC-134 after oxygen treatment; stage IV, 50 pulses HFC-134 after oxygen treatment.

TABLE 1

Band Intensities of NH_3 Adsorbed on Chromia after HFC-134 Treatment Depending on the Desorption Temperature

	N_2 673 K		N_2 673 K/5 min HFC-134; 673 K		N_2 673 K/10 min HFC-134; 673 K		N_2 673 K/30 min HFC-134; 673 K		O_2 673 K/2 min HFC-134; 673 K	
Desorption (K)	B	L	B	L	B	L	B	L	B	L
273	0.12	0.13	—	0.13	—	0.14	—	0.09	—	0.14
423	—	0.16	—	0.16	—	0.19	—	0.13	—	0.19
473	—	0.05	—	0.17	—	0.18	—	0.13	—	0.21
523	—	—	—	0.09	—	0.12	—	0.08	—	0.18
573	—	—	—	—	—	—	—	—	—	—

Note. Band at 1440 cm^{-1} characteristic of Brønsted sites (B) and band at 1220 cm^{-1} representative of Lewis sites (L).

after an equivalent number of CHF_2–CHF_2 pulses, the carbon content on the surface is only about half that of the untreated sample (compare stages I and III). This indicates that the strength and distribution of the acidic sites must to some extent be different, although with increasing pulse number the carbon content was once again in the same region as the carbon content before the oxygen treatment. These results lead to the conclusion that the coke deposition occurs at the same centers which are responsible for the catalytic isomerization reactions. Enhanced acidity of the surface was expected as a result of the oxygen treatment. Consequently, the strength and the character of the acidic sites were recorded by IR spectroscopy, by employing gaseous NH_3 as the probe molecule according to the method described under Experimental.

Characteristic data of these measurements are summarized in Table 1 where values for the concentration and strength of the acidity are given in arbitrary units. This means that the intensities of the bands at 1440 cm^{-1} ($\delta_{asNH_4^+}$ representative for Brønsted sites) and at 1220 cm^{-1} (δ_{sNH_3} representative of Lewis sites) were normalized and can therefore be used as relative values. As can be seen in Table 1, the calcined chromia exhibits both Brønsted and Lewis sites. The Brønsted sites are, however, weaker; the band at 1440 cm^{-1} disappeared after heating to 423 K. In principal, one can also assume that the partial formation of other kinds of Brønsted sites would occur if HF were adsorbed strongly on the surface. With the method used here, we did not find any indications of new Brønsted surface sites. Moreover, the Lewis acidity slightly increased at the same time, probably due to the transformation of Brønsted sites into Lewis sites. With increasing temperature, NH_3 desorbed further, and only very strong sites were able to bind the NH_3 molecules on the surface. As a result of the activation with CHF_2–CHF_2 (cf. Table 1, 5 and 10 min HFC treatment) Brønsted sites completely disappeared, whereas enhanced Lewis acidity was found. Not surprisingly, after longer treatment with HFC-134 (here 30 min) the surface acidity decreased, due to coke deposits as discussed before.

As the isomerization activity changed (cf. Fig. 1), Lewis acidic sites seemed to be the catalytic sites for the isomerization reaction of CHF_2–CHF_2. The observed increase in activity of fluorinated chromia after treatment with oxygen is in agreement with this hypothesis; the removal of the coke liberates covered acid sites resulting in enhanced activity. However, in agreement with the already observed increasing catalytic activity in Fig. 1, in this case oxygen posttreatment of those chromia samples should result in a remarkable increase in the detectable acid centers. The acidity of chromia samples was therefore monitored by IR spectroscopic detection of adsorbed ammonia immediately after the oxygen treatment followed by the CHF_2–CHF_2 treatment (stage III in Fig. 1). As can be seen in Table 1, there is in fact an increase in the strength of the acid sites. In addition, the composition of the gas phase was monitored in order to characterize the reactions taking place. As can be seen in Fig. 2, there are two stages of the isomerization reactions when high amounts of carbon dioxide are

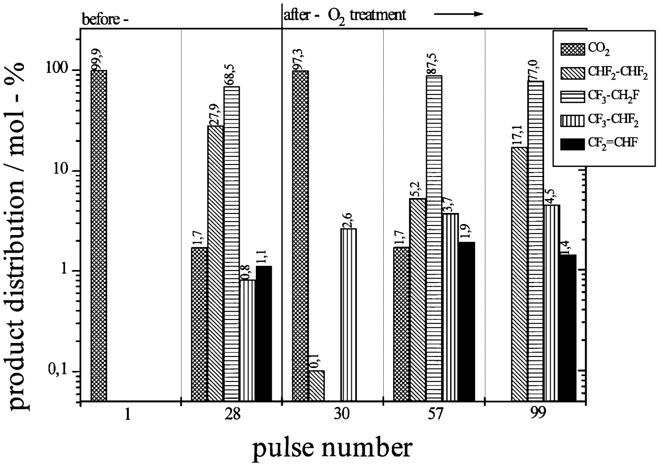

FIG. 2. Product distribution depending on the pulse number (673 K, HFC-134, pulse volume 1 ml_{STP}, contact time 17 s) before and after O_2 treatment (30 min, 673 K, 10 ml/min_{STP}).

formed, just at the first pulse (at the very beginning of the activation process, cf. Fig. 1) and just after the oxygen treatment (pulse 30 in Fig. 1). At both stages, the surface should contain the highest amount of adsorbed oxygen, which is probably responsible for the almost complete oxidation of CHF_2–CHF_2. Besides the formation of CO_2, considerable amounts of additional oxidation products, mainly pentafluoroethane, were observed thus indicating radical reactions due to oxidizing species on the chromia surface. The main goal was to determine whether the oxidation reactions (CO_2 and CF_3–CHF_2 formation from CHF_2–CHF_2) were caused by strongly adsorbed oxygen and/or by chromium in higher oxidation stages.

The oxides, Cr_2O_3 and CrO_2, differ in color, the former being dark green, the latter black. Unfortunately, neither changes in color nor XRD or magnetic measurements revealed any reactions of Cr_2O_3 as a result of oxygen post-treatment. We therefore checked the catalytic behavior of pure CrO_2 in the isomerization reactions of CHF_2–CHF_2. Under the same conditions as those used for Cr_2O_3 the same product distribution was found as has already been described for the oxygen-treated chromia samples, this being indicative of the formation of Cr^{4+} species as a result of the oxygen treatment. Fortunately, Cr_2O_3 exhibits a characteristic spectrum in the visible range. Consequently, diffuse reflection UV–vis measurements were carried out in order to monitor possible changes in the chromia samples. Characteristic results of these investigations are given in Fig. 3. These measurements were not *in situ* experiments but were conducted on different samples. Consequently, the following discussion based on the quantitative values in Fig. 3 must be considered semiquantitative. All normalized spectra exhibit absorption maxima at the wavelengths 460 and 600 nm which are characteristic for octahedrally coordinated Cr^{3+} (*d*–*d* transitions; 460 nm, $A_{2g} \rightarrow T_{1g}$; 600 nm, $A_{2g} \rightarrow T_{2g}$). The spectra differ with regard to their intensities; this can be interpreted in the following way. Both the untreated chromia and the sample activated by CHF_2–CHF_2 and then heated with oxygen (stage II in Fig. 1) exhibit less intense absorption bands. In contrast, CHF_2–CHF_2 conditioned chromia samples (stage I in Fig. 1) reveal much higher absorption coefficients, indicating a significantly higher content of Cr^{3+}. Additionally, chromia was treated in a hydrogen gas stream in order to remove all excess oxygen as well as possible Cr^{4+} species of the solid. As can be seen from Fig. 3, this sample exhibits the highest absorption, in complete agreement with the previous discussion. On the other hand, CrO_2 absorbs in the whole range of this spectrum. The partial formation of Cr^{4+} stages on the surface should therefore be responsible for the observed increase in the background of the absorption lines in Fig. 3. In accordance with this result, the observed formation of oxidized carbon compounds (CF_3–CHF_2 and CO_2) can be explained by the oxidation reactions of CHF_2–CHF_2 , with chromium in higher oxidation states, itself formed by the reaction with oxygen.

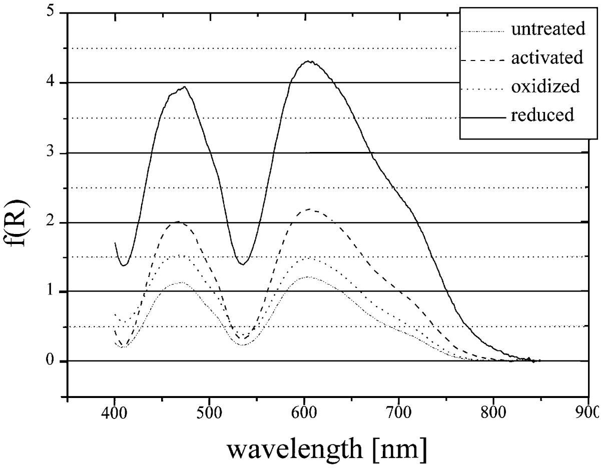

FIG. 3. UV–visible diffuse reflectance spectra of a untreated chromia catalyst, samples in stage I and II (cf. Fig. 1), and a reduced sample with H_2 (773 K, 2 h, 10 ml/min$_{STP}$).

One can distinguish between different oxidation states of chromium by the IR spectroscopic detection of CO absorption (12–15). Consequently, the surface Cr^{n+} states were characterized according to their coordination on the basis of IR spectroscopic detection of CO adsorbed at the surface. Figure 4 shows characteristic results of these measurements, depending on the treatment of the solid samples. The IR spectrum of untreated chromia (Fig. 4a) exhibits a strong band at 2160 cm^{-1} in the range of carbonyl vibrations and a weaker one at 2200 cm^{-1}. According to Zaki *et al.* (15) the band at 2200 cm^{-1} is characteristic of fivefold coordinated Cr^{5+} cations. A weak shoulder at 2180 cm^{-1} (not considered here due to its weakness) suggests a surface complex including Cr^{4+} cations. The band at 2160 cm^{-1} is characteristic of a fivefold coordinated Cr^{3+} complex (15). The H_2-treated sample (Fig. 4b; excess oxygen is removed) reveals bands of similar intensity at 2188 and 2140 cm^{-1}. In accordance with Scarano *et al.* (13, 14), the band at 2188 cm^{-1} is due to threefold coordinated Cr^{3+} surface cations, whereas the band at 2140 cm^{-1} represents physisorbed CO. The sample containing excess oxygen (Fig. 4c) reveals bands at 2200, 2160, and 2140 cm^{-1}. Due to the oxygen treatment of this sample, the intensity of the 2200 cm^{-1} band is stronger than that shown in Fig. 4a, thus explaining the higher content of fivefold coordinated Cr^{5+}. Here too, fivefold coordinated Cr^{3+} is found (2160 cm^{-1}) as well as physisorbed CO (2140 cm^{-1}). The small shoulder at 2180 cm^{-1} might well be due to Cr^{4+} cations on the surface.

A comparison of the IR spectra of the samples containing excess oxygen (Figs. 4a and 4c) with the other two clearly shows the action of oxygen. Under the experimental conditions of the isomerization reaction of CHF_2–CHF_2, oxygen

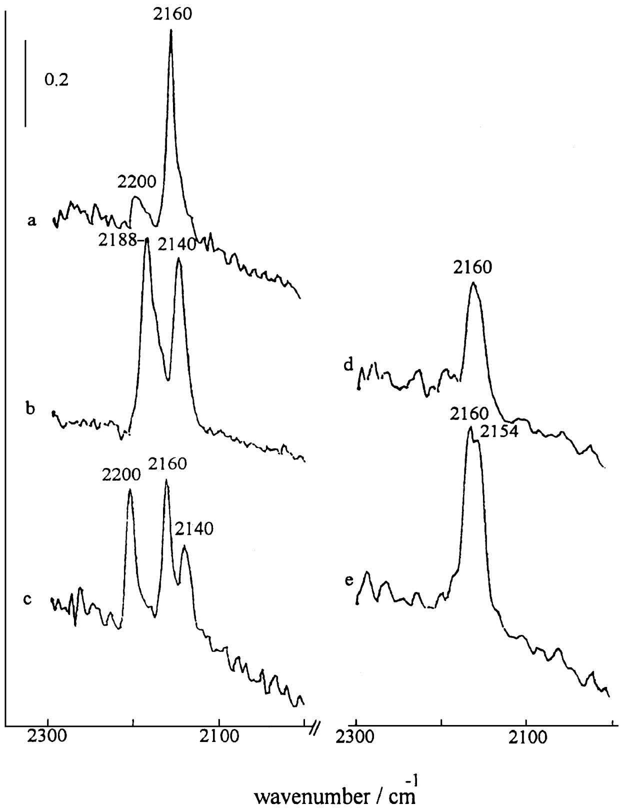

FIG. 4. IR spectra of CO adsorbed on Cr_2O_3 (a–e) at 77 K. Cr_2O_3 (a), evacuated at 673 K; Cr_2O_3 (b), H_2 reduced at 773 K; Cr_2O_3 (c), H_2 reduced after heating in air at 620 K; Cr_2O_3 (d), treated in a HFC-134 atmosphere at 673 K; Cr_2O_3 (e), sample "Cr_2O_3 (c)" followed by heating in HFC-134 at 673 K.

already produces chromium in higher oxidation states on the surface. Subsequently, CHF_2–CHF_2 is oxidized by Cr^{5+} (probably also smaller amounts of Cr^{4+}), thus explaining the observed formation of CF_3–CHF_2 and CO_2 during this reaction stage. Consequently, the characteristic bands for chromium in higher oxidation states disappear (cf. Fig. 4d). Moreover, the CHF_2–CHF_2 treated samples exhibit a slight broadening of the band at 2160 cm^{-1} which results in a new band at 2154 cm^{-1} with longer reaction times. We interpret this band in the following way. The conditioning of chromia consists partly of decomposition reactions of CHF_2–CHF_2 forming gaseous HF. This HF consequently reacts with chromium oxide to form chromium fluoride. Moreover, the isomerization reaction itself also consists of dehydrofluorination followed by a Markovnikov addition reaction (5). Consequently, the chromia sample becomes increasingly fluorinated. The substitution of oxygen by fluorine results in a strengthening of and an increase in the concentration of the acidity of the surface (cf. results given in Table 1). It seems reasonable to explain the new band at 2154 cm^{-1} by CO physisorbed on OH groups (usually with a band at 2140 cm^{-1} on chromium oxide) on surface sites which are strengthened as a result of the fluorination of the surface.

CONCLUSIONS

After the activation procedure the catalytic activity of chromia for the isomerization reaction of CHF_2–CHF_2 decreases slowly, most probably due to coke deposition processes. By using oxygen it is principally possible to remove the carbon deposits at higher temperatures, resulting in increased catalytic activity. Additionally, the oxygen treatment causes the formation of higher oxidized chromium (mainly Cr^{4+} and Cr^{5+}). Although the existence of such chromium in higher oxidation states has been proven, it immediately undergoes redox reactions with the haloalkane, mainly forming CO_2 and CF_3–CHF_2. The observed higher acidity of the catalyst is most probably due to the fluorination of the oxide surface. In addition, a further increase in catalytic activity can be achieved by cleaving coke depositions which mainly cover Lewis acid sites on the surface. Since the oxygen treatment also causes the formation of oxidizing surface sites, undesirable side products are formed, thus diminishing the selectivity of the isomerization reaction.

ACKNOWLEDGMENS

The financial support by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie is gratefully acknowledged. We are obliged to Dr. U. Schedler of the Chemical Institute of Humboldt University, Berlin, for performing UV–vis measurements.

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