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Properties of the Cr_2O_3/MgF_2 system – catalytical aspect

M. Wojciechowska [1] and S. Łomnicki

Faculty of Chemistry, A. Mickiewicz University, Poznań, Poland

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The influence of Cr_2O_3 on properties of the Cr_2O_3/MgF_2 catalysts obtained by impregnation and precipitation–deposition is described. The IR technique enabled monitoring of changes in the structure of the MgF_2 surface after introducing chromium ions. Tetrahedral chromium complexes as well as structures of Cr_2O_3 type were observed. The deposited species generated the Lewis and Brønsted acidity which in turn was responsible for the catalytic activity in the reactions of 2-propanol decomposition, butene double bond isomerization, cumene cracking, dehydrogenation of cyclohexane and decomposition of methyl alcohol.

Keywords: chromium oxides; catalytic reactivity; reactive centers; IR

1. Introduction

Catalysts based on chromium oxide have found wide applications in numerous industrial processes: naphtha reforming, butadiene manufacturing, automotive exhaust gas purification and the production of polyethylene [1–3]. The quality of the produced catalysts essentially depends on choosing the appropriate support. So far, oxides like Al_2O_3 [4–7], SiO_2 [3–6,8] or TiO_2 [4,5] were used as supports for chromium oxide. The properties of Cr_2O_3 are modified by interaction with a support. For instance, chromium oxides supported on alumina or titania interact strongly with these supports, while the interaction with SiO_2 is weak [3]. In spite of many works devoted to the chromium oxide/oxidic support systems, the nature of the interaction between the support and the active phase is not clear yet. Thus, in order to distinguish between different chromium–oxygen polyhedra formed on the surface of the catalysts for its various loadings with the active phase, we decided to examine chromium–oxygen species supported on a non-oxidic support. Magnesium fluoride was used as a support regarding the fact that, when it was used as a support for transition metal oxides [9–13], it generated new acid–base and redox active sites in various reactions.

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[1] To whom correspondence should be addressed.

The aim of this work was to characterize the influence of the chromium–oxygen species on catalytic properties of the Cr_2O_3/MgF_2 samples prepared by the impregnation method and the precipitation–deposition method. On the basis of the IR study we tried to determine the centers responsible for the activity of examined preparations.

2. Experimental

2.1. PREPARATION OF CATALYSTS

Two series of Cr_2O_3/MgF_2 samples were prepared: one by impregnation (I) and the other by precipitation–deposition (P).

Preparations of series I were obtained by mixing a MgF_2 powder of 0.25–0.5 mm grain size, previously heated at 673 K for 5 h and cooled to room temperature, with an aqueous solution of $Cr(NO_3)_3$. The amount of solution taken was sufficient for incipient wetness to be observed. The preparations were then dried, first at 325 K under frequent stirring, then at 375 K for 24 h and finally heated at 673 K for 4 h. The solutions taken for impregnation contained the amounts of chromium nitrate that corresponded to the surface coverage of MgF_2 equal to: 0.1, 0.2, 0.4, 0.1 and 2.0 monolayer of Cr_2O_3.

Preparations of the P series were obtained by precipitation from an aqueous solution of $Cr(NO_3)_3$ of known concentration onto suspended particles of freshly precipitated magnesium fluoride [9]. The suspension was then evaporated till it was dry. By using solutions of chromium nitrate of different concentrations we obtained samples characterized by Cr / Mg atomic ratios between 0.01 and 0.25. Then the preparations were dried at 383 K for 24 h and finally heated at 673 K for 4 h.

The samples were hereafter denoted with the symbols I-$MFCr_x$ or P-$MFCr_x$, where I refers to the impregnated series and P to the precipitated–deposited series, and x is equal to the Cr / Mg atomic ratio expressed as a per cent.

2.2. SURFACE AREA

The surface area was determined by the BET method from the adsorption isotherms of nitrogen at liquid nitrogen temperature with the help of a Sartorius Gravimat.

2.3. INFRARED SPECTRA

The IR spectra were determined using a Bruker IFS 113V spectrometer in the range 650–1100 cm^{-1} and in the range of OH groups as well as in the range of stretching and deformation frequencies of adsorbed pyridine. For examination within the range of free lattice vibrations, samples were prepared by pelletizing the catalysts with KBr. Experimental procedure in the range 1400–4000 cm^{-1} was similar to that described in ref. [11].

2.4. CATALYTIC ACTIVITY

The catalytic properties of the samples were determined with the pulse microreactor technique in reactions of 2-propanol decomposition at 523 K, butene double bond isomerization at 573 K, cumene cracking at 673 K, dehydrogenation of cyclohexane at 607 K and decomposition of methyl alcohol at 423 K.

The conditions of catalytic measurements for the first four reactions were similar to those described previously [12,14].

The products of methyl alcohol decomposition reaction were analyzed with a Carlo Erba 6000 gas-phase chromatograph on a 4 mm × 3 m stainless-steel column packed with SE-30 at 425 K.

3. Results and discussion

3.1. SURFACE AREA

The results characterizing the Cr_2O_3/MgF_2 preparations and their surface areas are shown in table 1. These data indicate, that the impregnation of magnesium fluoride with aqueous solution of chromium nitrate did not affect its surface area, which remained constant for all the preparations of the impregnated series (series I). In the case of the precipitated–deposited samples (series P) with a lower chromium loading (the Cr/Mg atomic ratio = 0.01–0.10) the values of the surface areas of the catalysts differed only in a small range, while introduction of higher amounts of chromium caused significant enlargement of the surface area. For the P-$MFCr_{25}$ preparation it was 3.5 times higher than for the pure MgF_2. It could be

Table 1
Characteristics of Cr_2O_3/MgF_2 preparations

	Impregnated samples					
	MF	I-$MFCr_{0.1}$	I-$MFCr_{0.2}$	I-$MFCr_{0.4}$	I-$MFCr_{1.5}$	I-$MFCr_{2.5}$
atomic ratio Cr/Mg	0.000	0.001	0.002	0.004	0.015	0.025
MgF_2 surface coverage with Cr (monolayer)	0.0	0.1	0.2	0.4	1.0	2.0
surface area (m^2/g)	30	30	29	29	30	30
	Precipitated deposited samples					
	MF	P-$MFCr_1$	P-$MFCr_5$	P-$MFCr_{10}$	P-$MFCr_{18}$	P-$MFCr_{25}$
atomic ratio Cr/Mg	0.0	0.01	0.05	0.10	0.18	0.25
surface area (m^2/g)	30	29	27	28	38	105

accounted for by assuming that the large amounts of nitrates contained in this preparation induced the rapid emanation of gases during the thermal treatment, giving the "fluffing" effect. This phenomenon positively influenced the microporous system.

3.2. INFRARED SPECTRA

The IR spectra of both series I and P preparations in the range of 650–1100 cm^{-1} are presented in figs. 1A and 1B, respectively. In these spectra some other bands besides those due to pure MgF_2 were observed: ~ 890, ~ 910, ~ 950 and 1007 cm^{-1}. On the basis of the literature data these bands could be assigned to the chromium species. Thus, the bands at ~ 890 and ~ 910 cm^{-1} originated from the "chromate-like" structures, while the band at ~ 950 cm^{-1} was characteristic for Cr_2O_3 [15]. The band at 1007 cm^{-1} originated from the chromium structures with Cr^{5+} ion [15]. The analysis of the spectra of the impregnated preparations indicated that the intensity of the bands at 889, 908 and 950 cm^{-1} increased with increasing surface coverage with chromium ions (spectra 1–3, fig. 1A). However, in the case of series P preparations, the intensity of these first two bands initially

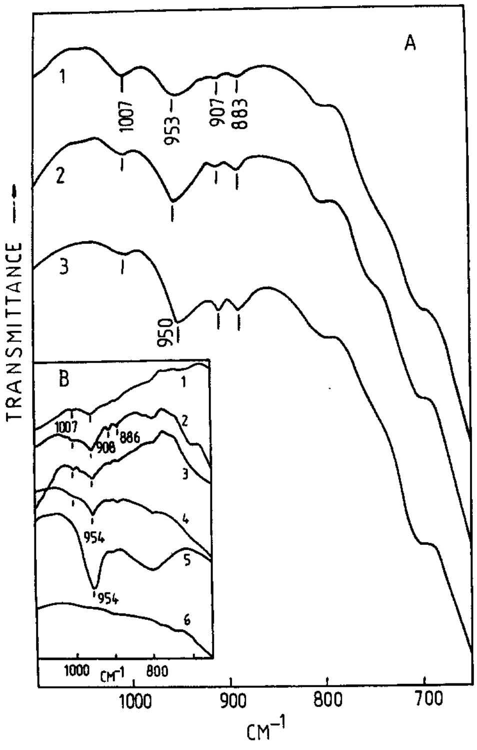

Fig. 1. IR spectra of Cr_2O_3/MgF_2 preparations. (A) Series I: (1) I-MFCr$_{0.2}$, (2) I-MFCr$_{1.5}$, (3) I-MFCr$_3$; (B) series P: (1) P-MFCr$_1$, (2) P-MFCr$_5$, (3) P-MFCr$_{10}$, (4) P-MFCr$_{18}$, (5) P-MFCr$_{25}$, (6) MgF_2.

increased reaching a maximum for the P-$MFCr_5$ preparation (spectrum 2, fig. 1B). With further augmentation of the chromium amounts in the catalysts there was an increase of the band at 954 cm^{-1}, while the other two decreased. The above data indicated that at low MgF_2 surface coverage with chromium ions both the "chromate-like" structures and Cr_2O_3 were formed, however, at higher loading with chromium mainly Cr_2O_3 was produced. In the case of preparations characterized by Cr/Mg atomic ratio $\leqslant 0.18$ a band at 1007 cm^{-1} attributed to $Cr^{5+}=O$ groups was also observed.

An X-ray analysis of the Cr_2O_3/MgF_2 preparations revealed only the presence of MgF_2 and Cr_2O_3. The lines characteristic for other chromium links were not observed. The lack of differences in crystal structure and framework distances in MgF_2 after introduction of chromium compounds excluded the formation of solid solutions and indicated that chromium species were located on the MgF_2 surface.

On the basis of the above data it could be thought, that the MgF_2 surface was covered partly with $[CrO_4]$ isolated tetrahedral species and partly with the layer of the Cr_2O_3 structures. The presence of both Cr_2O_3 and chromium ions in higher oxidation state was confirmed by the EPR study [16].

Introduction of chromium ions onto the MgF_2 surface must have modified the structure of the surface hydroxyl groups of pure magnesium fluoride. Hence, it was very interesting to observe these changes in IR spectroscopy, in the region of the stretching vibrations of OH groups. On the surface of MgF_2 three kinds of OH groups were present [9]: $\sim$3400, 3620 and 3770 cm^{-1} – spectrum 1, fig. 2. Introduction of the chromium nitrate onto calcined MgF_2 caused the appearance of a new

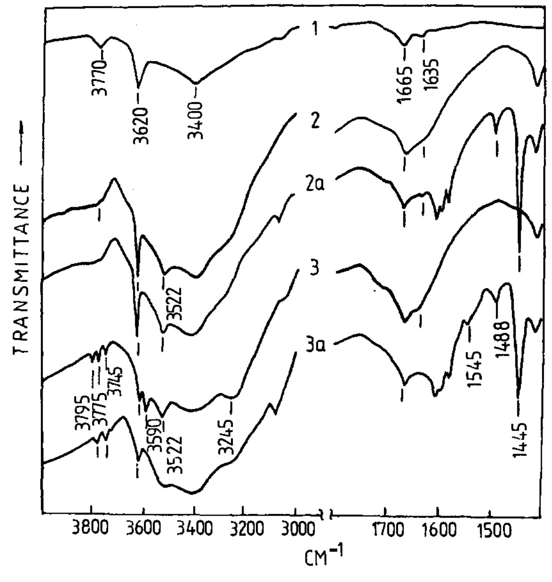

Fig. 2. IR spectra of MgF_2 (1), I-$MFCr_{1.5}$ (2), P-$MFCr_5$ (3) before pyridine adsorption and I-$MFCr_{1.5}$ (2a), P-$MFCr_5$ (3a) after pyridine adsorption.

band at 3522 cm^{-1} as well as a distinct widening and deepening of the band at $\sim$ 3770 cm^{-1} (spectrum 2, fig. 2). However, on the precipitated–deposited preparation, P-$MFCr_5$, bands appeared at: 3245, 3522, 3590, 3745 and 3795 cm^{-1} (spectrum 3, fig. 2). The OH groups attributed to these bands should be related to the chromium species formed on the surface of the catalysts. The band at 3245 cm^{-1} originated from H_2O molecules linked with Cr_2O_3 [17,18]. The widening of the band at 3770 cm^{-1} on the impregnated catalysts evidenced the appearance of brand new OH groups on the surface, similarly as for the precipitated–deposited preparation.

Simultaneously with the bands of the isolated OH groups and OH groups linked by the hydrogen bond, the bands originating from the adsorbed water, 1665 and 1667 cm^{-1}, were also observed on the examined preparations. After introduction of chromium nitrate these bands increased significantly. Introduction of pyridine vapours (Py) and the performance of the IR spectra revealed that the preparations possessed acidic properties (spectrum 2a, 3a, fig. 2). The evidence of the presence of Lewis acid sites was the band at 1445 cm^{-1}, however, the band at 1545 cm^{-1} indicated the presence of Brønsted acid sites. On the surface of the I-$MFCr_{1.5}$ preparation only the band at 1445 cm^{-1} was noticed, while on the $MFCr_5$ preparation both Lewis and Brønsted acidity were detected. Introduction of the Py vapours caused also a decay of the bands at 3590 and 3795 cm^{-1}. It should be believed that the hydroxyls attributed to these bands had acidic character. One should notice, that the OH groups present on the surface of pure MgF_2 did not reveal acidic properties – they did not interact with pyridine. Thus the appearance of the protonic centers could be explained by only the presence of the hydroxyl groups linked with tetrahedral chromium. This resulted from the OH group charge value bound with such a chromium, calculated in the same way like for the MoO_3/MgF_2 preparations [9]. However, the Lewis acidity could originate from coordinatively unsaturated chromium ions in the $[CrO_4]$ and $[CrO_6]$ complexes. These chromium–oxygen structures on the surface of MgF_2 were discussed elsewhere [16].

3.3. CATALYTIC ACTIVITY

Fig. 3 (curves 1 and 2) presents the catalytic activity of series P preparations in the reaction of 2-propanol decomposition. The 2-propanol elimination reaction can proceed in two directions: dehydrogenation (to acetone) and dehydration (to propene). The dehydration reaction proceeds in the presence of acidic sites, even of weak strength, while the dehydrogenation reaction requires the presence of strong basic or redox sites.

P series preparations tested in the reaction of 2-propanol decomposition (curve 1, fig. 3) showed activity towards acetone. The values of the conversion expressed per m^2 increased with increasing amount of introduced chromium, and, after it reached maximum for the $MFCr_{18}$ preparation, it dropped significantly. There was also observed the conversion towards propene (curve 2, fig. 3). Thus, on the surface

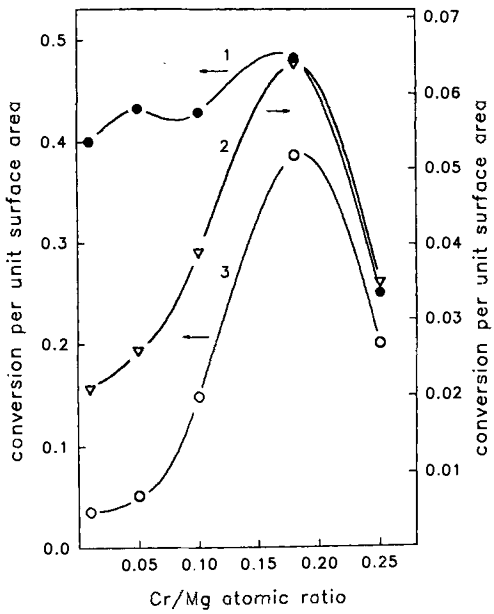

Fig. 3. Catalytic activity of the precipitated–deposited preparations for 2-propanol decomposition: acetone (1), propylene (2) and dehydrogenation of cyclohexane (3) as a function of the Cr / Mg atomic ratio.

of the Cr_2O_3/MgF_2 preparations, apart from the strong basic or redox sites, some acidic sites were also found.

Another reaction studied was isomerization of the double bond of butenes. This reaction proceeds on the acidic sites of medium strength as well as on the basic sites. Catalysts with the Cr / Mg atomic ratio between 0.01 and 0.18 showed increasing activity with rising chromium loading (curve 1, fig. 4). Above the Cr / Mg atomic ratio 0.18, the conversion per m^2 decreased, which indicated that, with the enhancement of the chromium amounts, neither increase in the surface concentration of the acidic sites nor their strengthening occurred. The value of the cis-butene-2/ trans-butene-2 ratio was close to one, which suggested, that the isomerization of butene-1 reaction proceeded on the acidic sites through butyl carbocation [19]. Pure magnesium fluoride was completely inactive in this reaction, though, introduction of chromium ions resulted in appearance of new acid sites, active in the isomerization reaction of butenes. These were acidic centers of medium strength, and the amount of such centers was the highest for the $MFCr_{18}$ preparation.

The results of the dehydrogenation reaction of cyclohexane towards benzene enabled us to determine the redox properties of the examined catalysts. The results obtained for the P series preparations are presented in fig. 3 (curve 3). The $MFCr_{18}$ preparation exhibited the highest conversion per m^2. The active sites in this reaction could be expected to be chromium ions, whose surface concentration was the highest for this preparation.

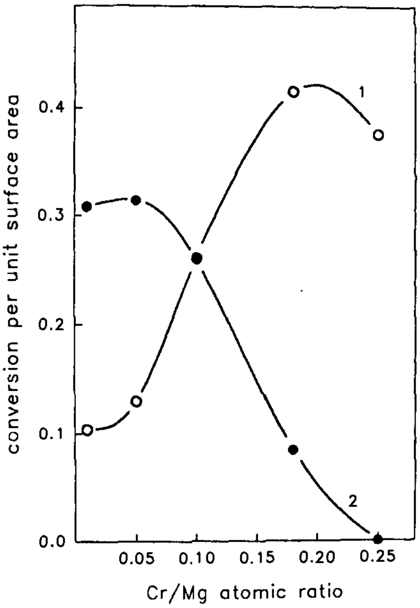

Fig. 4. Catalytic activity of the precipitated–deposited preparations for 1-butene isomerization (1) and cumene cracking (2) as a function of the Cr/Mg atomic ratio.

The redox character of the studied preparations was confirmed by the decomposition reaction of methyl alcohol. This reaction can proceed on the redox sites towards methyl formate and formaldehyde or towards dimethyl ether on the Brønsted acidic sites [20]. The obtained results are given in fig. 5. The $MFCr_{18}$ preparation appeared to be the most active towards methyl formate formation (curve 1, fig. 5). The activities of other preparations were significantly lower. Also observed was some activity towards the formaldehyde and dimethyl ether formation (curves 2 and 3, fig. 5).

The above mentioned catalysts were additionally tested in the reaction of cumene cracking. The transformation of cumene can proceed on the protonic centers towards benzene or on the one-electron-accepting centers towards α-methylstyrene [21]. In the presence of the Cr_2O_3/MgF_2 catalysts the cumene cracking reaction led to the formation of α-methylstyrene (curve 2, fig. 4). The P-$MFCr_1$ and P-$MFCr_5$ preparations showed the highest activity per m^2. Further augmentation of the chromium amounts resulted in a distinct drop of activity. It should be believed, that the acceptor sites engaged in the formation of α-methylstyrene were the one-electron-accepting centers capable of extracting a hydrogen anion from a hydrocarbon molecule.

The Cr_2O_3/MgF_2 preparations were also examined in the isomerization reaction of cyclohexene. In this case, the lack of the strong acidic sites resulted in the inactivity of both series P and I preparations.

All the catalytic experiments were repeated for the preparations of series I. The

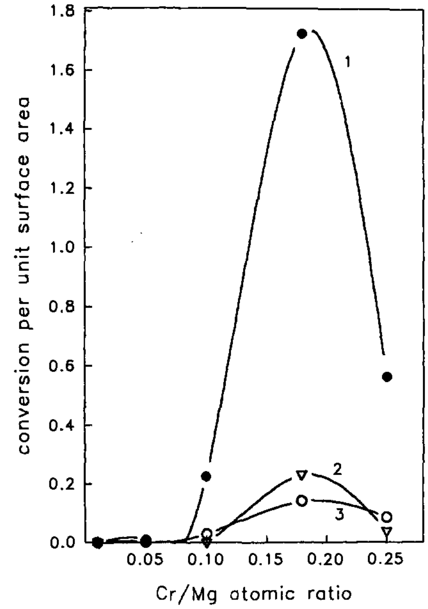

Fig. 5. Catalytic activity of the precipitated–deposited preparations for methyl alcohol decomposition: methyl formate (1), dimethyl ether (2), formaldehyde (3) as a function of the Cr / Mg atomic ratio.

results obtained for the 2-propanol decomposition reaction are shown in fig. 6. The enlargement of the MgF_2 surface coverage with chromium ions caused a significant increase of the acetone content in the reaction products (curve 1, fig. 6), and production of small amounts of propene (curve 2, fig. 6). Thus, it can be concluded, that on the surface of the examined preparations the basic or redox sites and some amount of acidic sites were formed.

The second reaction studied was isomerization of 1-butene (curve 2, fig. 7). The catalytic activity was found to grow up with the increasing surface coverage of MgF_2 with chromium ions. Thus, introduction of chromium species onto the moulded support caused the appearance of the acidic sites of medium strength.

The next studied reaction was cumene cracking. The amount of the formed α-methylstyrene at first developed fast and then reached an almost stable level (curve 1, fig. 7). This fact testified to the involvement of the chromium species in the formation of one-electron-accepting centers on the surface of the examined preparations.

The impregnated preparations were also tested in the cyclohexane dehydrogenation reaction (curve 3, fig. 7). The obtained activity for these preparations indicated the presence of the some redox centers on their surface.

The above data led to the conclusion, that the deposition of chromium oxide on the MgF_2 surface caused a strong change of its catalytic properties. In the case of the decomposition reaction of 2-propanol, isomerization reaction of 1-butene and dehydrogenation of cyclohexane we observed a gradual increase of the activity

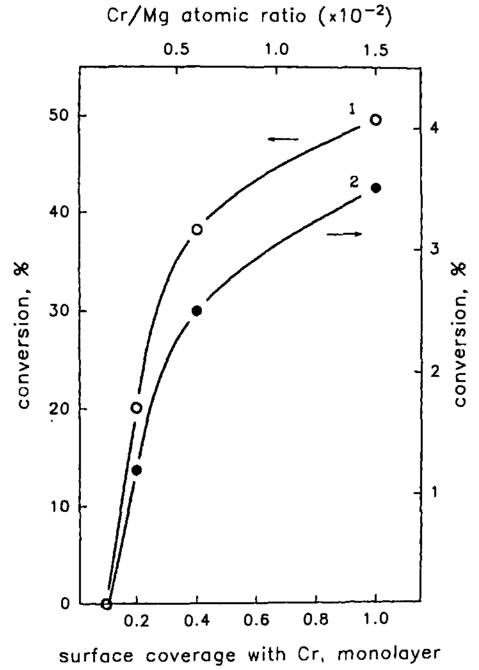

Fig. 6. Catalytic activity of the impregnated preparations for 2-propanol decomposition: acetone (1), propylene (2) as a function of surface coverage with Cr.

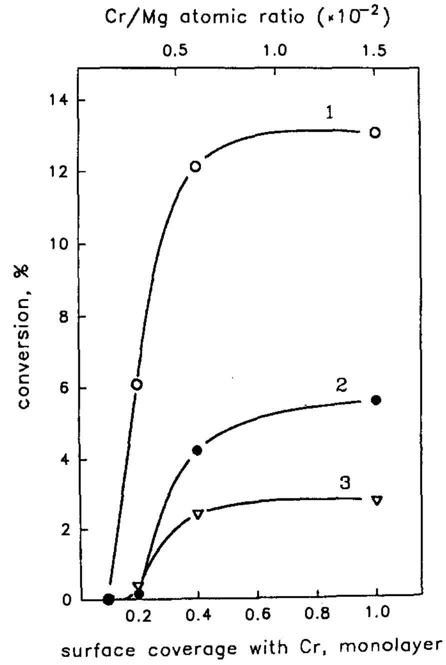

Fig. 7. Catalytic activity of the impregnated preparations for cumene cracking (1), 1-butene isomerisation (2) and dehydrogenation of cyclohexane (3) as a function of surface coverage with Cr.

with the enhancement surface coverage with the chromium species for the preparations of both series I and P. Such behavior was observed for the Cr / Mg atomic ratio between 0.01 and 0.18 (the drop of the activity for the P-$MFCr_{25}$ preparation was explained by the decrease of the concentration of surface chromium due to the growth of the surface area of this preparation). In the cumene cracking reaction with the enlargement of chromium loadings the amounts of produced α-methylstyrene increased initially (series I preparations) reaching a plateau for the 0.5 and 1.0 monolayer, and then a decrease of the activity was observed (the P series preparations). This indicates, that chromium–oxygen species formed on the surface of the support were responsible for the activity in a particular reaction. Accordingly, the coordinatively unsaturated ions, mainly chromium ions in the tetrahedral complexes and chromium ions in octahedral surrounding in the Cr_2O_3 type structures, were responsible for the proceeding of the reactions with the engagement of the acidic sites i.e.: the butene isomerization reaction and the decomposition of 2-propanol alcohol towards propene. In the reactions which require the redox centers (the decomposition reaction of 2-propanol towards acetone, the dehydrogenation of cyclohexane and the dehydrogenation reaction of methyl alcohol towards methyl formate) chromium ions in lower oxidation state were involved i.e.: Cr^{3+} ions. Namely, it was found in our IR study, that the amount of Cr^{3+} ions in the form of $[CrO_6]$ complexes grew up with the increase of chromium coverage. Simultaneously with the rising number of the latter, the increase of the activity was observed for the above mentioned reactions. However, in the case of the cumene cracking reaction towards α-methylstyrene, which requires the presence of one-electron-accepting centers, mainly Cr^{6+} ions were involved. This conclusion is in accordance with the IR study, which revealed the highest amount of the $[CrO_4]$ structures for the preparations with low chromium coverage – the activity towards α-methylstyrene formation decreased with the enhancement of surface coverage with chromium above Cr / Mg atomic ratio = 0.05.

4. Conclusions

The $[CrO_4]$ isolated tetrahedral species and the $[CrO_6]$ structures of the Cr_2O_3 type were found to form on the surface of the Cr_2O_3/MgF_2 preparations. Formation of such structures caused the appearance of both Lewis and Brønsted acidity on the precipitated–deposited preparations, and the Lewis acidity on the impregnated preparations. The origin of the redox sites was the $[CrO_6]$ structures, however, for the one-electron-accepting centers the $[CrO_4]$ complexes were responsible. The Lewis acidity should be related with the coordinatively unsaturated chromium ions, while the Brønsted centers were accompanied with the OH groups in the chromium–oxygen polyhedrons. The presence of the above mentioned structures on the surface of MgF_2 resulted in the appearance of the activity, mainly in the redox reactions.

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