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Structure and catalytic activity of double oxide system: Cu–Cr–O supported on MgF2

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Abstract

Two series of chromium–copper catalysts were prepared: co-impregnated and consecutively impregnated. On the basis of XPS, IR, EPR, X-ray investigations, and catalytic tests, a conclusion was drawn, that on the surface of each sample, an interaction between copper and chromium ions occurred, leading to an electron transfer from chromium to copper. As a result, Cr^{6+} and Cu^{1+} centres were formed. These sites were responsible for the catalytic activity of studied samples. The order of active phase deposition determined the properties of consecutively impregnated catalysts. The best performance was found for consecutively impregnated copper–chromium catalysts, which showed the highest influence of copper–chromium interaction on the properties of such systems. The surface structures of particular catalysts were proposed. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: CuO; Cr_2O_3; Copper–chromium electron transfer; Double oxide system; Catalysis; Oxide monolayer catalysts

1. Introduction

In catalytic studies, much attention has been paid to systems containing two different oxide phases deposited on the support [1–3] because the interaction between the two components may lead to changes in the surface structure, hence, to the modification of their catalytic properties as compared to systems containing such oxides separately. During the thermal treatment, many phenomena originating from the oxide–oxide and oxide–support interactions may take place resulting in the formation of different products:

1. each oxide deposited on the surface as a separate phase;
2. one of the oxides dispersed over the other one in form of a monolayer or small crystallites;
3. interacting oxides form surface compounds; or
4. one or both oxides dissolved in the surface layer of the support.

The type of interaction between supported oxides and the structure of the material formed depend on the chemical and crystallochemical properties of each of them, their surface free energy, preparation method, and calcination temperature. For example, in the supported bi-

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nary $CuO–Cr_2O_3$ systems [4,5], the presence of Cr_2O_3 was reported to substantially improve the performance of copper in the dehydrogenation reaction, since it helps to prolong the activity and stability of copper catalysts. However, the mechanism of interaction between chromium oxide and copper oxide has so far not been fully explained. Some authors suggest [6,7] the formation of CuO and $CuCr_2O_4$ clusters on the surface of such systems, while others report that Cr_2O_3 particles act as a barrier between copper crystallites, preventing their sintering. Authors of Ref. [1] indicate that Cr_2O_3 is not only the promoter of copper structure, but the interaction between copper and chromium is also important [1]. It should be noted, that an electron transfer from one oxide to the other one is possible. It will result in the appearance of contact potential which may change the surface chemical potential of oxides, hence, modify the properties of the system [3].

Since copper catalysts are applied in dehydrogenation reactions and in some oxidation processes [8], while chromium systems are used in hydrogenation, dehydrogenation, and polymerization of hydrocarbons [9], deposition of both oxides on the support can produce catalysts of new quality. Thus, we considered it interesting to follow the changes in the surface structure of the system containing CuO and Cr_2O_3 depending on the preparation method, and make an attempt to correlate the appearing surface species with catalytic activity. Magnesium fluoride was used as a support because:

1. it is chemically inert and, therefore, the supported oxides could react only with each other, but not with the support;
2. it is thermally stable and resistant to annealing in air;
3. the point of zero charge of MgF_2 surface corresponds to pH ~ 7, thus, the surface does not contain any acidic or basic sites, and the unwanted parasitic reactions can be avoided; and
4. as the support contains no oxygen atoms, all oxygen atoms taking part in the catalytic reaction must originate from the supported transition metal oxides.

MgF_2 was used earlier as a support for several transition metal oxides [10–14].

2. Experimental

2.1. Preparation of catalysts

Two series of catalysts were prepared: co-impregnated (C) and consecutively impregnated (P).

The samples of C series were obtained by mixing MgF_2 powder of 0.25–0.5 mm grain size (preheated at 673 K for 5 h) with an aqueous solution of chromium nitrate and copper nitrate. The amount of solution taken was sufficient for incipient wetness to be observed. Samples were then dried first at 333 K, next at 378 K for 24 h, and finally calcinated at 673 K for 4 h. The solution used for impregnation contained the amount of chromium and copper nitrates corresponding to the surface coverage with: 0.1, 0.2, 0.3, 0.5, and 1.0 monolayer of each component. Although the supported oxide in the preparations was present in form of molecularly dispersed species, surface clusters, and small microcrystallites, the expression of the total amount of supported oxide in terms of the percentage of ideally dispersed monolayer seems to describe best the quantitative relations. Thus, the samples were labelled with the symbols C-MFCuCr$_x$, where x means the monolayer fraction of each active component.

The P series catalysts were obtained by consecutive introduction of the active components onto the previously calcinated MgF_2. For P-MFCrCu$_x$, magnesium fluoride powder was placed in an aqueous solution of chromium nitrate, then NH_4OH (10%) was added under continuous stirring to deposit on the surface $[Cr(NH_3)_6](NO_3)_3$ complexes, insoluble in water. After drying (378 K for 24 h), the samples were subsequently impregnated with an aqueous solution of copper nitrate. The preparations were

then evaporated and dried first at 333 K, then at 378 K for 24 h, and finally calcinated at 673 K for 4 h. The P-MFCuCr$_x$ samples were obtained in the same way, but with the reverse order of introduction of precursor nitrate solutions. The catalysts will be labelled with the symbols P-MFCrCu$_x$ and P-MFCuCr$_x$, where x means the fraction of monolayer of each active component and the CuCr, or CrCu order is consistent with the order of deposition of active phase precursor.

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 instrument.

2.3. Quantitative determination of Cr^{6+} ions content in the samples

One gram portions of each type of samples containing 1.0 monolayer of active phase were placed in small flasks containing 10 cm^3 H_2O. The samples were then heated for 4 h at 323 K under frequent stirring. Obtained solutions were next placed in graduated flasks of 50 cm^3. A drop of concentrated NH_4OH was added to prevent polymerization of H_2CrO_4 to $H_2Cr_2O_7$, and the flasks were filled with distilled water to graduation. The absorption measurements were then performed using HP 8452A Diode Array Spectrophotometer in the UV range ($\lambda = 373$ nm, $\epsilon = 1.4 \times 10^3$). From the equation:

$$A = ecl,$$

the amount of Cr^{6+} ions was determined. The results are shown in Table 4.

2.4. Infrared spectra

The IR spectra were recorded using a Bruker IFS 113V spectrophotometer. For the experiments in the range of 1100–650 cm^{-1}, the samples were prepared by pelleting the catalysts with KBr. The spectra in the ranges 1800–1300 cm^{-1} and 4000–3000 cm^{-1} were registered using samples prepared in the form of self-supporting thin wafers which were placed in vacuum cell equipped with NaCl windows. The wafers were oxidized in oxygen at 673 K for 4 h, then outgassed under a pressure of 10^{-3} Pa at room temperature, and their IR spectra were recorded. Pyridine was then introduced into the cell at 473 K, the cell was outgassed for 3 min at this temperature, cooled to room temperature, and the IR spectra of adsorbed pyridine were recorded.

2.5. X-ray diffraction

The XRD diffraction patterns were obtained with the use of Philips diffraction equipment in conjunction with PW-1050/70 goniometer employing CuK$_\alpha$ radiation and nickel filter. The obtained diffractograms were reprocessed with Philips APD computer program. The obtained data were compared with ASTM cards data.

2.6. XPS spectra

The XPS spectra were recorded with a VG Scientific ESCA-3 photoelectron spectrometer using AlK$\alpha_{1,2}$ radiation (1486.6 eV) from X-ray source operating at 13 kV and 10 mA. Working pressure was lower than 5×10^{-7} Pa. All spectra were recorded at a photoelectron take-off angle of 45°. Binding energies were referred to the C 1s peak from the carbon surface deposit at 248.8 eV. Data processing consisted of calibration of the peak position against the C 1s line, Shirley's background and K$\alpha_{3,4}$ band removal together with routines for the analysis of composite spectra and their fitting with single peaks, doublets or multiplets.

Spectra were decomposed into symmetric Gaussian-20%–Lorentzian peaks.

The relative element content (N) was calculated from the formula including λ described according to Ref. [15]:

$$N = FI_A E_A^{0.25} \sigma_A^{-1} \exp\left(d_C \lambda_{C,A}^{-1}\right),$$

where F contains all instrumental factors (including transmission function T) and is assumed to be constant for the measurements, I_A is the intensity of the line A measured, E_A is the kinetic energy of the A level, σ_A is the elemental cross-section for photoionization [16], λ_A is A-level electrons' inelastic mean free path in the adventitious carbon deposit and d_C is the thickness of the carbon deposit [17]. The λ and T values were obtained using the Penn approximation [17].

In this study, the Scofield's cross-sections were used only for C 1s ($\sigma = 1.0$) and O 1s ($\sigma = 2.93$) lines. In the case of all other XPS and Auger lines, the sensitivity factors obtained from the element-oxygen intensity ratio in simple oxides were determined and applied instead of A in the element content calculations.

XPS spectra in the region of C 1s, O 1s, Cr 2p, Cu 2p, F 1s, Mg 1s and Mg-Auger bands were recorded. Bands of Cu 2p and Cr 2p were fitted with multiplets observed in the spectra of simple oxides.

The measured values of binding energies of electrons (BE) for all elements agree well with the reference data [18]. Oxidation numbers of elements in almost all cases could be easily obtained. The only exception was copper for its low content and too low intensity of LMM Cu-Auger spectra to be registered. The oxygen band was composite, as expected for different values of O 1s binding energy in oxides and hydroxides of the contributory metals.

2.7. EPR spectra

EPR spectra were recorded on a Radiopan SE/X-2542 spectrometer in the X-Band. The catalysts were placed in a quartz tube of 3-mm i.d. The same tube was used for thermal processing of the samples under vacuum, for EPR measurements at room temperature and at 77 K. The samples were heated in oxygen at 673 K or 873 K for 2 h, then degassed by evacuation at room temperature. Some samples were reduced by hydrogen admitted for 3 h at 773 K and removed by evacuation at room temperature. Some samples were reduced by vacuum at room temperature for 0.5 h.

2.8. Catalytic activity

Catalytic properties of the samples were determined by pulse method in such reactions as: 2-propanol decomposition, cyclohexane and cyclohexene dehydrogenation, and dehydrogenation of cumene. Before measurements, the samples were pretreated in the reactor at 573 K for 1 h in the stream of helium. Then, the temperature of the reactor was adjusted to the desired value and pulses of the given reagent were injected into the stream of helium, serving as a carrier gas. The conditions of catalytic tests were as follows: 2-propanol decomposition: reaction temperature = 523 K, catalyst weight = 0.01 g, pulse volume = 0.1 μl; cyclohexane and cyclohexene dehydrogenation: reaction temperature = 643 K, catalyst weight = 0.1 g, pulse volume = 0.2 μl; cumene dehydrogenation: reaction temperature = 643 K, catalyst weight = 0.1 g, pulse volume = 0.2 μl. Products of the reactions were analysed using Carlo Erba 6000 gas chromatograph with 1-m long column filled with emulphor 0 and flame ionisation detector.

The catalytic tests in the hydrogenation of nitrobenzene to aniline were performed in a flow reactor at 623 K. A mixture of nitrobenzene and hydrogen was passed through the microreactor over 0.1 g of catalyst at a flow rate of 0.004 cm^3/min. The products of the reaction were collected in a receiver at 273 K and analysed chromatographically using a column filled with Apiezon L and a catharometer as the detector.

3. Results and discussion

3.1. Surface area

In Table 1, the characteristics of particular catalysts and their surface areas are given. For

Table 1
Characteristics of the samples

Sample	Surface coverage monolayer	Surface area (m^2/g)
C-MFCuCr$_{0.1}$	0.1	26
C-MFCuCr$_{0.2}$	0.2	29
C-MFCuCr$_{0.3}$	0.3	33
C-MFCuCr$_{0.5}$	0.5	30
C-MFCuCr$_{1.0}$	1.0	32
P-MFCuCr$_{0.1}$	0.1	26
P-MFCuCr$_{0.2}$	0.2	27
P-MFCuCr$_{0.3}$	0.3	28
P-MFCuCr$_{0.5}$	0.5	26
P-MFCuCr$_{1.0}$	1.0	25
P-MFCrCu$_{0.1}$	0.1	26
P-MFCrCu$_{0.2}$	0.2	30
P-MFCrCu$_{0.3}$	0.3	38
P-MFCrCu$_{0.5}$	0.5	37
P-MFCrCu$_{1.0}$	1.0	29
MFCr$_{1.0}$	1.0	30
MFCu$_{1.0}$	1.0	27

every series of samples, the surface area increased with active phase loading and attained a maximum at 0.3–0.5 monolayer of active phase. The highest growth of the surface area was observed in the case of P-MFCrCu samples, while for P-MFCuCr and C-MFCrCu catalysts, the changes of the surface area were small.

3.2. X-ray study

In Fig. 1, the results of XRD experiments are presented. For MFCu samples, apart from the lines characteristic of magnesium fluoride, the presence of lines originating from crystalline CuO phase was detected. Similarly, in the case of MFCr, the additional lines characteristic of crystalline Cr_2O_3 were recorded. This is not the case of preparations containing both CuO and Cr_2O_3 supported on MgF_2. While for the co-impregnated samples, only some of the lines characteristic of CuO and Cr_2O_3 were recorded, in the diffractograms of consecutive impregnated samples P-MFCrCu and P-MFCuCr, apart from the lines originating from CuO and Cr_2O_3, there were also lines of another phase. Using the computer analysis of diffractograms, the interfacial distances and *hkl* indexes were calculated, which in correlation with peaks intensities, allowed to identify this phase to be $CuCrO_4$.

XRD data obtained for co-impregnated samples (only some of the lines characteristic of CuO and Cr_2O_3 phase were visible) indicates that the deposited active phase is composed of very small and well-dispersed crystallites. Contrary, in consecutively impregnated samples, the active phase is in the form of CuO and Cr_2O_3 crystallites and also $CuCrO_4$ crystallites. The lack of the shifts of the lines characteristic of magnesium fluoride in the studied samples indicates, that the deposited copper and chromium compounds are located on its surface and did not form the solid solution.

3.3. XPS results

The differences in the structure of the surface of particular preparations were confirmed by XPS results summarised in Tables 2 and 3. XPS spectrum of the samples containing only chromium ions supported at the surface of MgF_2 revealed the presence of two types of chromium ions, characterized by the Cr 2p peaks at 577.0 eV and 578.8 eV. Binding energies of Cr 2p electrons in the range of 576–577 eV are characteristic of chromites, and those in the range of 578–579 eV of chromates. It could be thus concluded, that these samples contained at the surface Cr^{3+} and Cr^{6+} ions in the environment similar to that in $MgCr_2O_4$ and $MgCrO_4$.

It is interesting to note that the spectra of all samples show the presence of two peaks of O 1s electrons, the difference between the values of binding energies of these peaks being of the order of 1–2 eV. This is the order of magnitude of the difference between the value of binding energy of O 1s electrons in hydroxyl groups and in oxygen of oxide lattice. It has been shown earlier [11], that in the process of deposition, the surface of MgF_2 becomes hydroxylated by exchange of F^- ions with OH^- ions, whose surface concentration remained constant independently of the surface coverage with transition

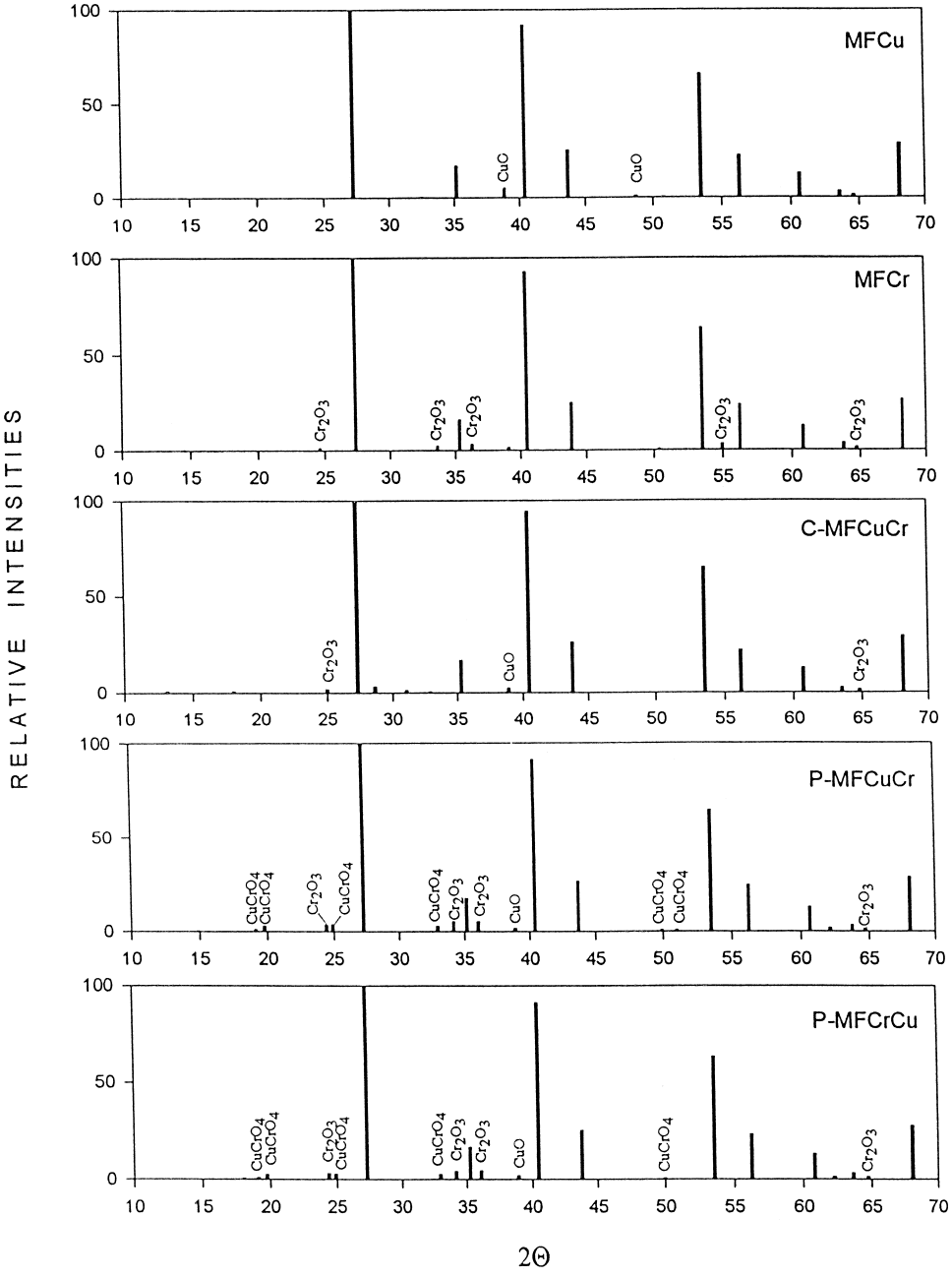

Fig. 1. Results of X-ray diffraction.

metal ions. Thus, the appearance of the peak of O 1s electrons of higher binding energy value may be interpreted as due to the hydroxylation of MgF_2 surface, the peak of lower binding energy value being related to the deposition of Cr or Cu.

The spectra of the samples obtained by co-impregnation of chromium and copper ions from their mixed solution showed the presence of the only one peaks of Cr 2p electrons at 575.1 eV, assigned to Cr^{3+} in the lattice of Cr_2O_3. No peaks corresponding to Cu 2p electrons could

Table 2
XPS Data

Element	Sample			
	$MFCr_{1.0}$	C-$MFCrCu_{1.0}$	P-$MFCrCu_{1.0}$	P-$MFCuCr_{1.0}$
Mg	0.28	0.29	0.28	0.30
F	0.57	0.49	0.53	0.56
O	0.13	0.21	0.16	0.11
Cr	0.030	0.010	0.019	0.021
Cu	–	–	0.017	0.006

Surface composition (relative atomic content).

be detected in the spectrum. It may be thus concluded, that the clusters of Cr_2O_3 were formed as the outermost layer, screening the copper ions which apparently precipitated at the surface of MgF_2 first.

Preparations obtained by consecutive impregnation of the surface of MgF_2 first with chromium ions and then with copper ions had the XPS spectrum in the range of binding energies of Cr 2p electrons similar to the spectrum of the sample impregnated only with Cr ions. The Cr 2p peak had the binding energy 576.7 eV, which can be assigned to Cr^{3+} ions, either in Cr_2O_3 modified by additives or in a mixed oxide with Mg^{2+} ions. A peak was present in the range of binding energies of Cu 2p electrons, at 932.1 eV characteristic of Cu^{1+} ions in Cu_2O or metallic copper. The surface concentrations of the two elements were of the same order.

This was not the case when deposition of copper ions was carried out first, followed by that of Cr ions. There was also one peak of Cu 2p electrons at the same binding energy, indicating the presence of Cu^{1+} ions, but its intensity was much lower. Apparently, the Cu ions were hidden below the layer of chromium oxides, which was composed of chromium ions in two types of environments. The peak of 577.5 eV could be assigned to a mixed oxide clusters of Cr^{3+} ions of the $MCrO_2$ type, where M might be, e.g., Cu^{1+}, and the peak at 579.5 eV indicated the presence of Cr^{6+} ions in CrO_3 or $CuCrO_4$ structures. The presence of the latter was confirmed by XRD experiments. Interaction between copper ions present at the surface of MgF_2 and chromium ions forming the outermost layer might maintain the chromium ions at their highest oxidation state and copper ions at the lower oxidation state.

Concluding the surface of the samples impregnated only with chromium ions contained Cr^{3+} and Cr^{6+} ions, while on that obtained by co-impregnation, mainly Cr^{3+} ions in Cr_2O_3 clusters were exposed. At the surface of P-MFCuCr samples, mainly Cr^{6+} ions were present, while for P-MFCrCu, both Cr^{3+} and Cu^{1+} clusters were exposed.

3.4. Quantitative analysis

The presence of Cr^{6+} was also confirmed by the results of quantitative analysis (Table 4). These data indicated the increase of percentage content of Cr^{6+} ions relative to the total amount of chromium introduced in binary catalysts when compared with Cr_2O_3/MgF_2. Another important conclusion that can be drawn from these data, is that consecutive impregnated samples contained more Cr^{6+} complexes than the co-impregnated ones.

Table 3
Binding energies (eV)

Electric level	Sample			
	$MFCr_{1.0}$	C-$MFCrCu_{1.0}$	P-$MFCrCu_{1.0}$	P-$MFCuCr_{1.0}$
Mg 1s	1304.2	1304.3	1304.5	1304.2
F 1s	685.5	685.5	685.5	685.5
O 1s	528.7	528.9	529.4	530.0
	529.3	530.8	530.9	531.3
Cr 2p	577.0	575.1	576.7	577.5
	578.8			579.5
Cu 2p	–	–	932.1	932.1

Table 4
The percentage mole of Cr^{6+} ions relative to the total amount of chromium deposited on the samples

Symbol	Cr^{6+} (mol%)
$MFCr_{1.0}$	8
C-$MFCuCr_{1.0}$	18
P-$MFCrCu_{1.0}$	30.5
P-$MFCuCr_{1.0}$	26

3.5. IR study

It has been proposed from Raman [19] and IR [20] spectroscopic studies that the surface structure of supported metal oxides under ambient conditions, where the catalysts contain adsorbed water, resemble the metal oxide species in aqueous solution. Upon dehydration, not only does desorption of adsorbed water take place, but decomposition of the hydrated metal oxide clusters also occurs, which results in the formation of dehydrated surface metal oxides species on the support surface [21]. A dependence has been established between the valence state of the metal ion and the frequency of the stretching M=O vibration in the Raman and IR spectrum [22–24]. These vibrations give rise to bands in the 1000–900 cm^{-1} range, the higher being the frequency of the band, the higher is the positive charge of the metal ion. Bands in the range 900–700 cm^{-1} assigned to M–O–M and O–M–O vibrations [25] are indicative of the presence of polymeric oxide species.

The IR spectrum of the sample MFCr containing only deposited chromium ions reveals the presence of only the broad band at 942 cm^{-1}. The absence of bands in the 900–800 cm^{-1} range which are due to the O–Cr–O bond of polymeric species indicates either the isolated nature of chromate species or the presence of CrO_2 chain moieties [26]. The appearance of Raman band in this range in the case of CrO_3/MgO samples has been attributed to the presence of defected $MgCrO_4$ structure [27]. Formation of such highly dispersed phase in our CrO_3/MgF_2 samples would not be visible in the X-ray diffractograms. The latter indicates the presence of Cr_2O_3 phase, whose IR bands appear in the frequency range below 600 cm^{-1} [28].

The IR spectra of both coimpregnated and consecutively impregnated mixed oxide samples reveal the presence of bands at 1008, 970, 952–942, 908, 880, 830, and 750 cm^{-1}. The bands at 1008 and 880 cm^{-1} are attributed to the symmetric stretching modes of terminal Cr=O bond and bridging O–Cr–O bonds for polymeric hexavalent chromium oxide species, respectively [26]. The asymmetric stretching mode of Cr=O bond may be discerned at 1030 cm^{-1} in agreement with earlier observations [27]. The band around 950 cm^{-1} increases in intensity with increasing chromium content and is much more intense for consecutively impregnated than coimpregnated samples, being shifted to 952 cm^{-1}. A tentative assignment of this band to the presence of defected $CuCrO_4$ structure may be proposed, in agreement with the results of X-ray analysis.

The origin of the band at 750 cm^{-1} recorded for the copper–chromium samples is not clear. Such band has been observed in $[CuF_4O_2]$ structures [29–31]. In the range not presented in this work (below 650 cm^{-1}), the band at 504 cm^{-1} was recorded characteristic of copper complexes in oxygen ligands surrounding. On the other hand, the band at 750 cm^{-1} is not observed in the case of the $MFCu_1$ sample, where it should have the highest intensity (Fig. 2).

The low transmission above 1000 cm^{-1} in the spectrum of C-MFCuCr samples can be a consequence of the high dispersion of active phase. This is confirmed by XRD studies, which indicates the presence of highly dispersed small crystallites of deposited active phase in C-MFCuCr preparations.

The above data confirm the coexistence of various copper and chromium species on the surface of $CuO,Cr_2O_3/MgF_2$ preparations. The presence of Cr_2O_3, 'chromate-like' structures and Cu^{2+} species in two different coorditional environments (oxidic and fluoric-oxidic) was found. IR results have also shown the presence of other compounds, which could be copper–chromium spinel structures.

Deposition of chromium and copper compounds on the surface of magnesium fluoride could cause the changes in the hydroxyl cover of the support. Thus, it was important to analyse the IR spectra in the ranges of OH stretching vibrations. On the surface of pure MgF_2, three bands at: ~3770, 3620, and 3400 cm^{-1} [10]

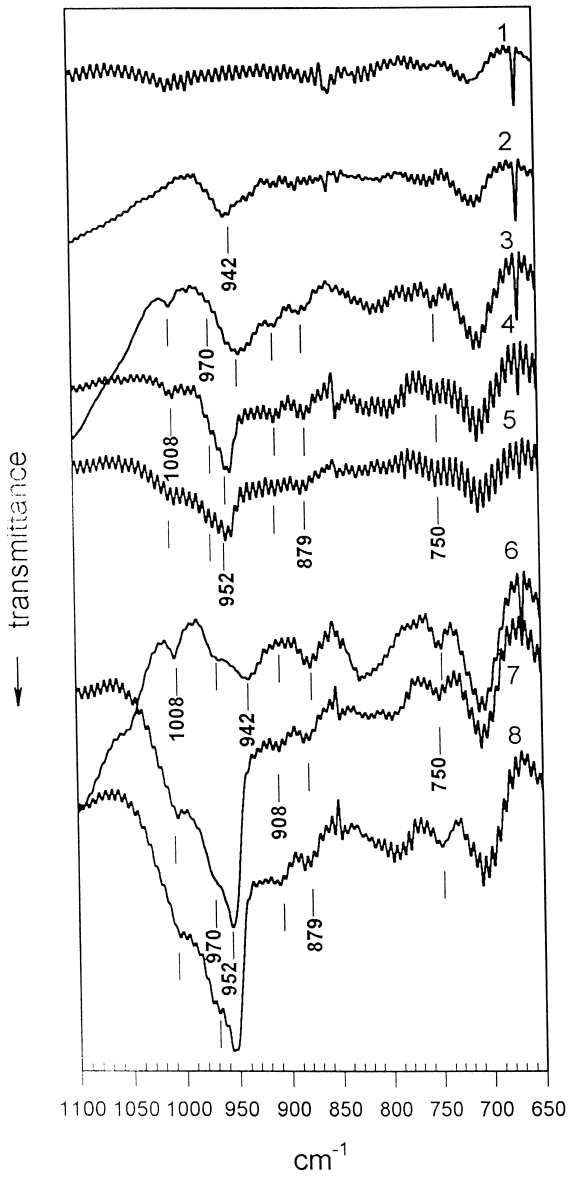

Fig. 2. IR spectra of: (1) $MFCu_1$, (2) $MFCr_1$, (3) C-$MFCuCr_{0.5}$, (4) P-$MFCrCu_{0.5}$, (5) P-$MFCuCr_{0.5}$, (6) C-$MFCuCr_{1.0}$, (7) P-$MFCrCu_{1.0}$, and (8) P-$MFCuCr_{1.0}$.

corresponding to various OH groups, originating from adsorption of water, were detected (spectrum 1, Fig. 3). Introduction of copper and chromium compounds resulted in appearance of additional bands at 3590, 3522, and 3245 cm^{-1} in the case of MFCu samples (spectrum 2) and at 3522 and 3245 cm^{-1} for MFCr preparations (spectrum 3). The bands present at 3590 and 3522 cm^{-1} are attributed to OH groups bonded to coordinatively unsaturated copper or chromium surface ions. However, the band at 3245 cm^{-1} originates from the vibrations of bonded water molecules. In the case of co-impregnated samples (spectrum 4), the spectrum was similar to that obtained for MFCu sample. The only difference was an additional band at 3685 cm^{-1}. For consecutively impregnated samples, a series of bands were recorded in the range 3750–3500 cm^{-1}, with better separated bands in the spectra of P-MFCuCr preparations (spectrum 5). One should note, that in the case of consecutively impregnated samples, the bands observed in the range 3700–3650 cm^{-1} were not recorded for C-MFCuCr preparations. Since

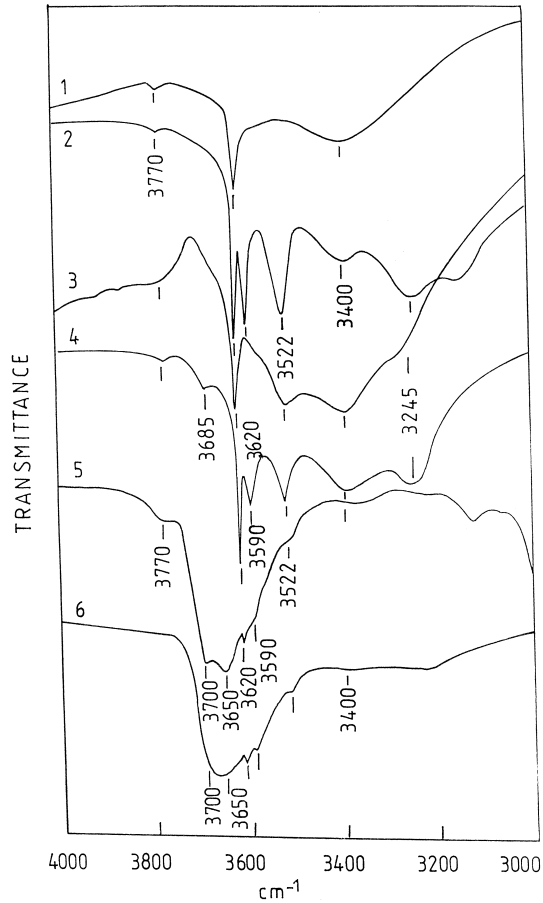

Fig. 3. IR spectra of: (1) MgF_2, (2) $MFCu_1$, (3) $MFCr_1$, (4) C-$MFCuCr_{1.0}$, (5) P-$MFCuCr_{1.0}$, and (6) P-$MFCrCu_{1.0}$.

XRD and XPS studies have shown the presence of copper–chromium spinel structures in the consecutively impregnated samples, thus, the bands in the range 3700–3650 cm^{-1} can be attributed to OH groups bonded to such structures.

It is worth noting, that introduction of a monolayer of active components does not affect the intensity of bands attributed to OH groups bonded to Mg^{2+} ions. Deposition of transition metal ions onto the surface of the support could occur as a result of three different processes: simple adsorption, ionic exchange, or substitution. Unaffected intensity of the bands attributed to OH groups bonded to MgF_2 surface indicates, that the deposition proceeds via simple adsorption. Similar situation was observed for the V_2O_5/MgF_2 and WO_3/MgF_2 catalysts [10–14]. Magnesium fluoride OH groups are not enough acidic or basic to react with the active phase precursor, and thus, they remain unchanged after deposition of the active phase.

In the spectra of all samples after pyridine adsorption, no bands characteristic of pyridinium ions were observed. This indicated the lack of Brønsted acid sites on the samples. However, in the case of every studied preparations, the bands typical of pyridine adsorbed on Lewis acid sites were recorded. This indicates that some Lewis acid sites were present on the surface of the studied samples.

3.6. EPR experiments

The EPR spectra of co-impregnated and both consecutively impregnated catalysts were similar. For the samples that were not reduced (spectrum 3, Fig. 4), the lines were characterized by parameters $g = 2.404$ and $g = 2.074$ typical of CuO complexes with Cu^{2+} ions in tetragonally distorted octahedral $[CuO_6]$ clusters [32], similarly as for CuO/MgF_2 catalysts (spectrum 1, Fig. 4). However, no lines characteristic of Cr^{3+} complexes were detected. Contrary to this, for the Cr_2O_3/MgF_2 catalysts, the

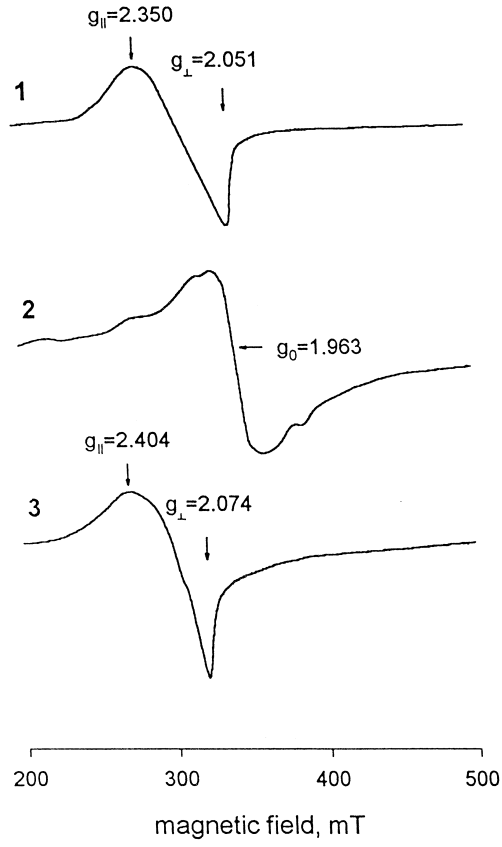

Fig. 4. EPR spectra of: (1) $MFCu_{1.0}$, (2) $MFCr_{1.0}$, and (3) P-$MFCuCr_{1.0}$ calcinated in oxygen at 673 K.

spectrum composed of two lines: a broad one with $\Delta B_{pp} = 24$ mT and a narrow one, with $\Delta B_{pp} = 9.8$ mT and $g_0 = 1.963$ (spectrum 2, Fig. 4) was registered. These lines were identified as originating from Cr^{3+} ions in various ligand surroundings H_2O, OH^-, or O^{2-} [32]. However, similar signal originating from Cr^{3+} complexes was recorded for binary samples after their reduction under hydrogen flow (spectrum 1, Fig. 5). The lack of the signal attributed to Cr^{3+} complexes in binary not-reduced catalysts and its appearance after reduction evidence the presence of a large contribution of chromium in higher oxidation state. The EPR spectra of the softly reduced binary samples (0.5 h of vacuum treatment) confirmed this conclusion (spectrum 2, Fig. 5), as a narrow intensive signal characterized by $g_0 = 1.977$ was observed which originates from the Cr^{5+} ions.

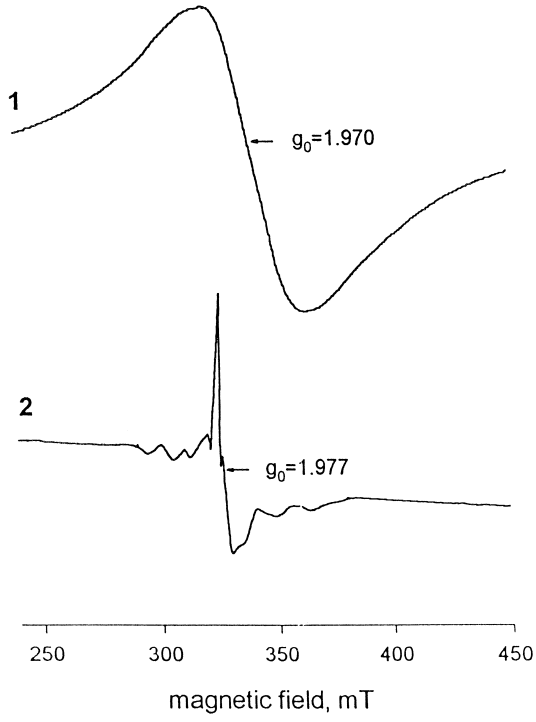

Fig. 5. EPR spectra of P-MFCuCr$_{1.0}$ sample (1) reduced at 773 K in hydrogen, and (2) reduced at RT by vacuum for 0.5 h.

The above results indicated that an interaction between copper and chromium ions operates in catalysts containing both CuO and Cr_2O_3 supported on MgF_2. The increase of the amount of chromium ions in higher oxidation state relative to Cr_2O_3/MgF_2 samples could be explained as a result of an electron transfer between chromium and copper ions. Such an electron transfer led to the formation of Cu^0, Cu^{1+} and Cr^{6+} ions. The necessary conditions for such a transfer to occur are:

$$E^0\,Cu^{2+}/Cu^0 > E^0\,Cr^{6+}/Cr^{3+}$$
$$E^0\,Cu^{2+}/Cu^{1+} > E^0\,Cr^{6+}/Cr^{3+},$$

where E^0 is the standard redox potential [33]. Since E^0 $Cu^{2+}/Cu^0 = 0.34$ V, E^0 $Cu^{2+}/Cu^{1+} = 0.167$ V, and E^0 $Cr^{6+}/Cr^{3+} = -0.12$ V [34], the condition is fulfilled and the transfer should take place.

3.6.1. Surface structure of CuO,Cr_2O_3/MgF_2 catalysts

3.6.1.1. Co-impregnated samples C-MFCrCu. The XRD examination of these samples indicates that both copper and chromium ions are in highly dispersed state. There may be two ways of the deposition of copper and chromium ions at the surface of the MgF_2 support. One way consists in adsorption of the oxy-ions through the oxygen ligands at the coordinatively unsaturated Mg^{2+} ions (XPS and IR data excluded the deposition of the active phase through ionic exchange or substitution of surface OH groups). The second possibility consists in the interaction of Cu^{2+} and Cr^{3+} ions with the coordinatively unsaturated surface F^- anions, incorporating them into the coordination sphere when the first surface layer is formed. The high dispersion is confirmed by the low transmission above 1000 cm^{-1} in the IR spectrum of C-MFCrCu samples and is also in line with the conclusions emerging from the EPR spectra. The latter are namely similar to those of CuO and reveal no lines which could be attributed to chromium ions. Results of the chemical analysis of samples 'as prepared' indicates that in the course of preparation, chromium ions were partially oxidized to the hexavalent state. Indeed, the 1008 and 880 cm^{-1} in the IR spectra may be taken as an indication of the presence of polymeric hexavalent chromium oxide species. At this point, studies of the behaviour of hexavalent chromium oxide species, highly dispersed at the surface of different supports, should be reminded [35] which showed that on heating in mildly reducing atmosphere, they are consecutively reduced to Cr^{5+}, Cr^{4+}, and finally to Cr^{3+} ions. Indeed, our EPR data show that Cr^{5+} ions appear in the C-MFCrCu samples when they are reduced in mild conditions, but transform to Cr^{3+} ions in strongly reducing atmosphere. This is the reason

why XPS spectra registered in UHV conditions reveal the presence of Cr^{3+} ions only.

3.6.1.2. Consecutively impregnated samples of P-MFCrCu and P-MFCuCr series. The X-ray diffraction patterns of both series of samples are very similar and indicate that the two components deposited at the surface of MgF_2 have reacted in the course of the preparation of the catalysts and have formed microcrystallites of copper chromate. This conclusion is confirmed by the results of chemical analysis which show that these samples contain large proportion of hexavalent chromium ions. Comparison of the amount of Cr^{6+} ions in the consecutively impregnated samples, containing both chromium and copper ions with the amount of theses ions present in the sample containing only chromium ions deposited on the surface of MgF_2, leads to the conclusion that the presence of copper ions mediates the oxidation of chromium ions to the hexavalent state, which may be stabilized by the formation of surface copper chromate phase. Results of XPS studies seem to indicate, however, that the redox properties differ depending on the order of deposition of the two components at the MgF_2 surface. Samples of the P-MFCrCu series contain the highest amount of Cr^{6+} as detected by chemical analysis, but the value of the binding energy of Cr 2p electrons as measured in the XPS spectrum corresponds to that of Cr^{3+} ions, and the binding energy of Cu 2p electrons—to Cu^{1+} ions. It is noteworthy that in these samples, both Cr and Cu ions are visible at the surface in the XPS spectra in practically 1:1 proportion, which may be taken as an indication that indeed, a compound of the formula $CuCrO_x$ is present at the surface of the support. The apparent contradiction between the results of chemical analysis and of XPS determination could be understood if it is assumed that samples of this series are most sensitive to the changes of the redox potential of the gas phase and are easily oxidized in the course of the pretreatment in air, but equally easily reduced when exposed to UHV in the ESCA spectrometer. At variance with these results, in the case of P-MFCuCr series, the presence of a large excess of chromium as compared to copper is seen in the XPS spectra, and chromium ions in two valence states can be recognized. A hypothesis could be advanced that microcrystallites of copper chromate, detected by XRD technique, are formed in the first stage of the deposition of chromium onto the surface, already covered by copper ions, are then covered by an overlayer of chromium oxide species. The latter undergo a slower reduction in the UHV of the spectrometer.

3.7. Catalytic activity

Catalytic dehydrogenation of primary and secondary alcohols to corresponding aldehydes and ketones, respectively, is an important industrial process; therefore, extensive studies of activity and selectivity of various catalysts in this reaction have been carried out. Most of them are oxides, which often show activity in dehydrogenation and dehydration. It has been found that dehydration is catalyzed by acid sites, whereas dehydrogenation, by redox or basic sites. Therefore, addition of small amounts of a strong basic oxide, which poisons acidic centres, suppresses dehydration activity and increases dehydrogenation. Many oxides catalyze the dehydrogenation of alcohols, particularly selective being oxides of zinc, copper, chromium, iron, and their combination. It is generally assumed that copper oxide is reduced to cuprous oxide or metallic copper, which is the active phase, whereas chromium oxide serves as a structural promoter [1,36–38]. One of the catalysts used as active in dehydrogenation of alkanes is a supported chromium oxide catalyst. It is usually doped with alkali metal ions to decrease the surface acidity. The nature of the active sites in these catalysts has been debated for a long time and Cr^{3+} or Cr^{2+} ions have been proposed to play this role. The importance of the presence of some Cr^{6+} ions to catalyze the coke combustion has been suggested.

Fig. 6 presents the activity of the five series of catalysts in the dehydrogenation of 2-propanol to acetone, as recalculated per unit surface area. The reaction along the second possible passway, i.e., dehydration to propene was negligible, which is related to the complete absence of acid sites at the surface of MgF_2 support, as revealed by the adsorption of pyridine described earlier. The highest activity was shown by consecutively impregnated copper–chromium samples P-MFCuCr, maximum conversion of about 60% being observed. High activity was attained already at small surface coverage and remained practically independent of coverage on its further increase. Pure support showed practically no activity. Among other catalysts, P-MFCrCu exhibited considerable activity, similar to that of C-MFCuCr. Much smaller activity was observed with MFCr samples, whereas the MFCu samples were rather inactive. It was reported [12] that on the surface of chromia supported on magnesium fluoride,

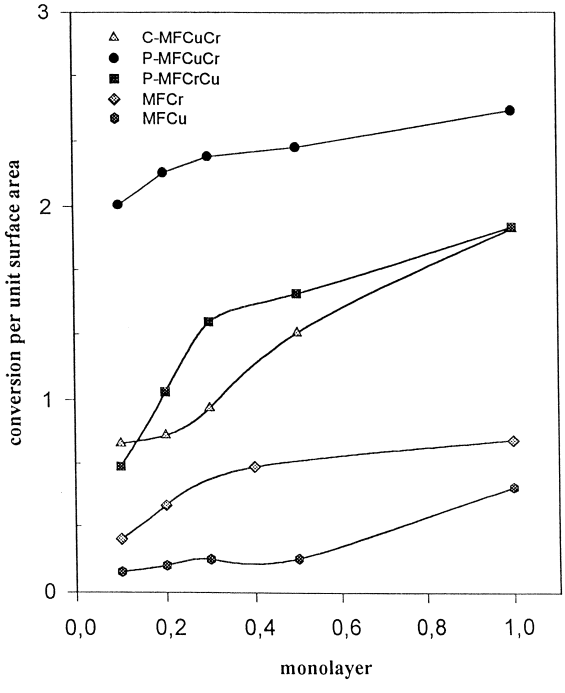

Fig. 6. Catalytic activity of Cr_2O_3/MgF_2, CuO/MgF_2 and $CuO,Cr_2O_3/MgF_2$ catalysts in the reaction of 2-propanol decomposition towards acetone.

some Cr^{6+} centres were present whose amount increased to a small degree with increasing surface coverage. Thus, the activity of Cr_2O_3/MgF_2 catalysts increased slightly with the growth of monolayer fraction. In the case of the CuO/support catalysts, it is known that on the surface of such systems, some amount of Cu^0 or Cu^{1+} centres responsible for the activity in propanol-2 dehydrogenation appear, despite the oxidative conditions of pretreatment [39]. Considerably higher activity of supported binary oxide catalysts relative to that of monooxidic samples should be related to increased number of centres active in this process. Depending on the preparation method (the order of deposition of the active phase), mainly Cr^{6+}(P-MFCuCr), Cu^{1+}(P-MFCrCu), or Cr^{3+}(C-MFCuCr) were exposed on the surface of the mixed-oxide samples. In the case of P-MFCuCr catalysts, high activity was found already for the samples with low coverage of the surface. This could be explained by the way of formation of the surface layer, in which chromium ions were located over the previously deposited copper species, which enhance the formation of surface Cr^{6+} complexes. The number of such centres only slightly increased with surface coverage, because on its increase, more and more Cr^{3+} ions are deposited besides the Cr^{6+} sites. For P-MFCrCu catalysts, copper precursor was deposited as the second active component and as a result of chromium–copper interaction, Cu^{1+} species were available on the surface. The higher the coverage of active components, the higher the number of surface Cu^{1+} species. In the case of coimpregnated samples C-MFCuCr, where only Cr^{3+} complexes were detected on their surface, the activity was considerably lower than that of other binary catalysts. Only in the case of C-MFCuCr$_{1.0}$ that the activity increased to the level of P-MFCrCu$_{1.0}$ sample. Such behaviour of the samples indicated that in this case, another type of sites must be responsible for the catalytic activity in propanol-2 decomposition. Such sites could be surface O^- or OH groups. This was confirmed by the XPS study

which revealed almost twice as high the amount of oxygen atoms on the surface of the C-MFCuCr samples relative to other catalysts (Table 3). They were the atoms of the lattice of the crystallites of active components or OH groups present at their surface.

Fig. 7 summarizes the results of the determination of catalytic activity of the five series of preparations in dehydrogenation of cumene to α-methylstyrene. Similarly as in dehydrogenation of 2-propanol, the most active were samples of consecutively impregnated copper–chromium preparations P-MFCuCr, very high activity being attained already at the surface coverage of 0.1 monolayer. Other preparations, containing both Cu and Cr oxides were also active, whereas lowest activity was exhibited by preparations containing only Cu-oxide. Similarly, in dehydrogenation of cyclohexane (Fig. 8) and hydrogenation of nitrobenzene (Fig. 9), preparations impregnated with both metal ions were active, most active being always the consecu-

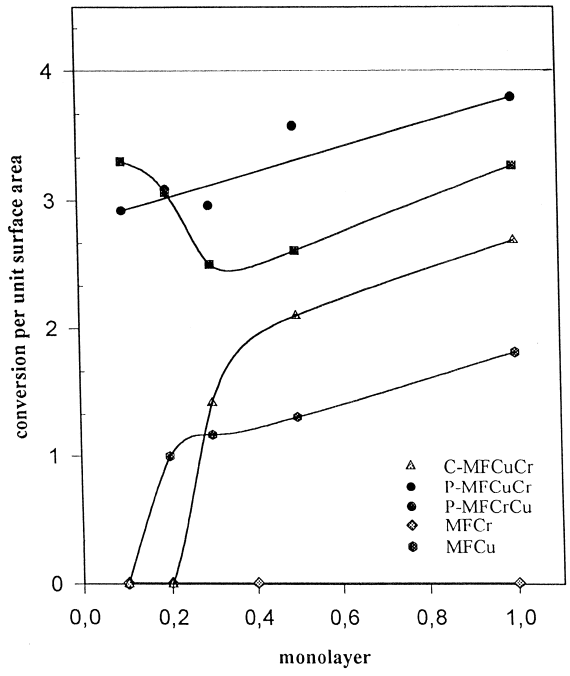

Fig. 8. Catalytic activity of Cr_2O_3/MgF_2, CuO/MgF_2 and $CuO,Cr_2O_3/MgF_2$ catalysts in the reaction of cyclohexane dehydrogenation towards benzene.

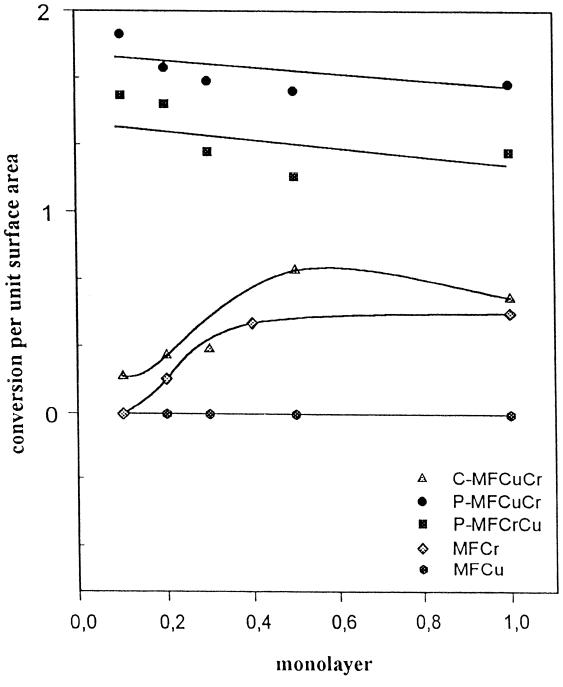

Fig. 7. Catalytic activity of Cr_2O_3/MgF_2, CuO/MgF_2 and $CuO,Cr_2O_3/MgF_2$ catalysts in the reaction of cumene dehydrogenation towards α-methylstyrene.

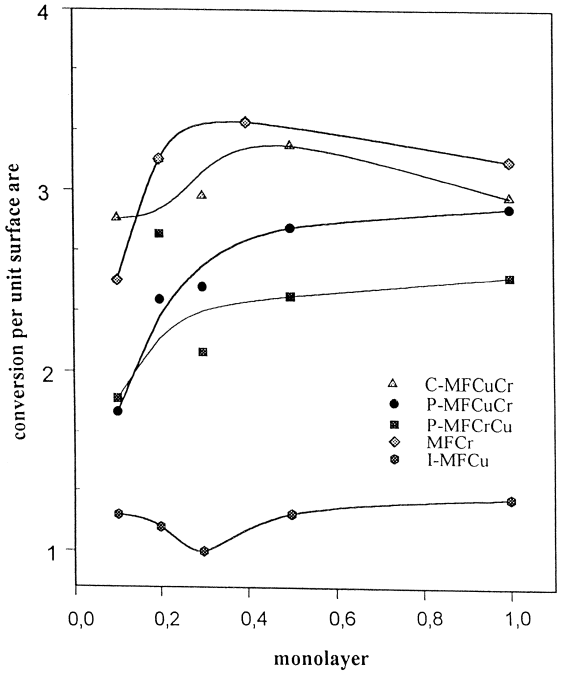

Fig. 9. Catalytic activity of Cr_2O_3/MgF_2, CuO/MgF_2 and $CuO,Cr_2O_3/MgF_2$ catalysts in the reaction of nitrobenzene hydrogenation towards aniline.

tively impregnated P-MFCuCr preparation. The preparations containing only one metal oxide were inactive. A different behaviour was observed in the case of dehydrogenation of cyclohexene (Fig. 10), where the preparations containing only chromium proved to be most active. In the case of all preparations, the activity increased with coverage and attained a plateau at the coverage of 0.5 monolayer. Thus, it could be concluded that Cr^{3+} complexes were responsible for the activity in this reaction. The same conclusion could be drawn on the basis of the shape of the activity curve obtained for the consecutively impregnated samples. This is consistent with the results of earlier studies of chromia catalysts which indicated, that Cr^{3+} centres are involved in dehydrogenation reactions [40,41].

Analysis of the catalytic behaviour leads to several general conclusions. In the three dehydrogenation reactions studied, i.e., 2-propanol → acetone, cumene → α-methylstyrene, and cyclohexane → benzene, supported pure copper oxide catalysts are inactive, whereas supported pure chromium oxide catalysts show an activity increasing with surface coverage. This may be taken as an indication that in the case of catalysts described here, surface chromium ions play the role of active sites in the dehydrogenation. Conversely, in hydrogenation of nitrobenzene, the supported pure chromium oxide catalysts turned out to be completely inactive and supported pure copper oxide catalysts showed considerable activity indicating that surface copper ions are involved in this reaction. In both cases, deposition of the second oxide component at the surface of the support resulted in an important increase of activity. In the case of the dehydrogenation of 2-propanol and cumene, the addition of copper oxide to chromium oxide containing catalysts raised the activity by more than one order of magnitude. Studies of the surface structure of these preparations showed that the surface is covered by copper chromate and Cr_2O_3. It contains considerable amount of Cr^{6+} ions, stabilized by the presence of copper ions in the copper chromate matrix. Because of the presence of Cr_2O_3, the surface contains also Cr^{3+} ions, which are resistant to oxidation in the course of pretreatment.

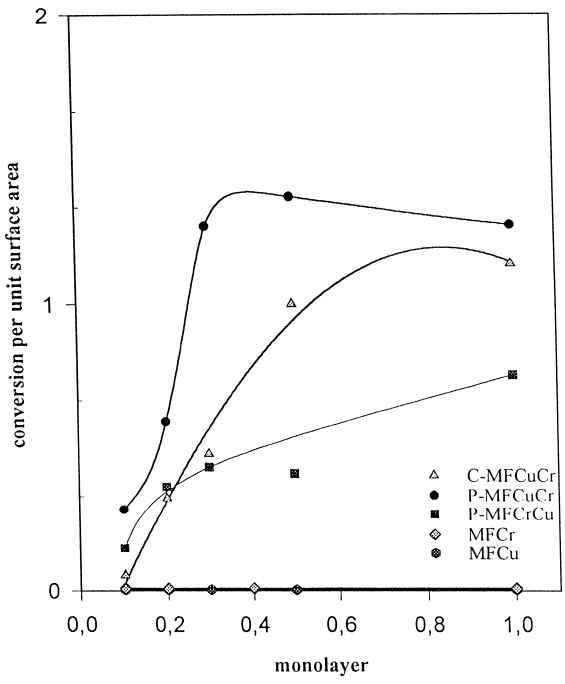

Fig. 10. Catalytic activity of Cr_2O_3/MgF_2, CuO/MgF_2 and $CuO,Cr_2O_3/MgF_2$ catalysts in the reaction of cyclohexene dehydrogenation towards benzene.

4. Conclusions

Preparations containing both copper and chromium oxides deposited on the surface of MgF_2 support showed that in dehydrogenation of 2-propanol and cumene, the catalytic activity is one order of magnitude higher than preparations containing only the single oxides. The surface was covered by highly dispersed copper chromate and Cr_2O_3 crystallites. The presence of the first facilitates the redox processes, the presence of the second stabilizes at the surface the Cr^{3+} ions. Since the redox potential of the copper ions system is much higher than that of chromium ions system, there is a tendency for a

transfer of electrons to form Cr^{6+} and Cu^{1+} ions, playing the role of active sites in catalytic dehydrogenation reactions.

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