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Structure Characterization and Catalytic Properties of Cr_2O_3 Doped with MgO Supported on MgF_2

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A characterization of double oxide systems containing Cr_2O_3 doped with MgO and supported on MgF_2 was carried out. The catalysts were prepared by impregnation and co-impregnation methods and characterized by the Brunauer–Emmett–Teller method, EPR, and temperature programmed reduction. The results proved the interactions between supported oxides and the presence of spinel-like phase after treatment at 400°C. Magnesium oxide clearly influences the catalytic activity as well as selectivity of chromium catalysts supported on MgF_2 . The $\text{MgO-Cr}_2\text{O}_3/\text{MgF}_2$ systems were active and selective in the reaction of CO oxidation at the room temperature and in the dehydrogenation of cyclohexene.

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1. Introduction

The industrial importance of chromium-based catalysts has generated much interest in their physicochemical properties. The catalysts have been applied in polymerization, hydrogenation and dehydrogenation of hydrocarbons, dehydration and dehydrogenation of alcohols to produce aldehydes, ketones and alkenes, dehydrocyclization of paraffins, water gas shift reaction and decomposition and fluorination of chlorinated volatile compounds [1–3].

With bivalent cations Cr_2O_3 creates spinels or perovskites [4], which are characterized by a particularly high selectivity in oxidation and reduction reactions [5].

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Until now, little attention has been devoted to MgO–Cr₂O₃ systems. Earlier works revealed that in the unsupported mixture of magnesium and chromium oxides, both these oxides react with each other at elevated temperatures to form a spinel [6, 7]. Usually supported spinels are better catalysts. In our research we examined the transformation of MgO and Cr₂O₃ with different chromium concentrations supported on MgF₂ and its influence on catalytic activity. The catalysts were tested in two important reactions: CO oxidation at room temperature which is used for elimination of poisonous CO, and in cyclohexene dehydrogenation — a method of synthesis of such valuable product as benzene.

2. Experimental

2.1. Catalysts preparation

Magnesium fluoride was obtained by adding small amounts of MgCO₃ · Mg(OH)₂ to aqueous solution of hydrofluoric acid until neutralization, then the mixture was acidified by the introduction of a few additional drops of the acid. The precipitate was aged at room temperature for some days, dried for 24 hours at 105°C and calcined at 400°C for 4 h. After the calcination, MgF₂ (denoted as F-4) was ground to obtain 0.2–0.5 mm grain size.

The Mg₂/F-4 and Cr_x/F-4 catalysts were obtained by impregnation of MgF₂ with aqueous solutions of Mg(NO₃)₂ · H₂O and Cr(NO₃)₃ · 9H₂O, respectively. The Mg₂Cr_x/F-4 catalysts were prepared by the conventional co-impregnation method with the aqueous solutions of Mg(NO₃)₂ · H₂O and Cr(NO₃)₃ · 9H₂O. After impregnations all the catalysts were dried in air at 120°C for 24 h and then calcined at 400°C for 4 h.

2.2. Surface area and pore volume measurements

The low-temperature adsorption of nitrogen was performed with an ASAP 2010 Micromeritics instrument. Specific surface area was determined using the Brunauer–Emmett–Teller (BET) method and pore size distribution was established on the basis of the Barrett–Joyner–Harenda (BJH) method, using a desorption isotherm.

2.3. TPR studies

The temperature programmed reduction (TPR) experiments were carried out with an ASAP ChemiSorb 2705 (Micromeritics). A portion of 100 mg of the catalyst was reduced in a mixture of 10 vol.% H₂ in Ar at a total flow rate of 30 cm³/min (standard temperature and pressure, STP), and at 10°C/min heating rate up to a final temperature of 700°C.

2.4. EPR studies

The catalysts for EPR experiments were oxidized at 400°C and partially reduced by vacuum treatment at room temperature or at 250°C and sealed.

EPR measurements were carried out on a Radiopan SE/X 2742 spectrometer (X-band) with cylindrical TM_{110} resonator and 100 kHz magnetic field modulation. EPR spectra were recorded at room temperature. The g -factors describing the EPR line positions in the magnetic field were calculated as $g = 71.4484\nu/B$, where ν is the resonance frequency (in GHz) measured by HP 5340A frequency counter, and B is the magnetic field (in mT) determined from field markers generated by the NMR magnetometer.

2.5. Catalytic activity

The catalytic properties of the samples were determined in the reaction of cyclohexene dehydrogenation and carbon monoxide oxidation. In the reaction of cyclohexene dehydrogenation the samples were pre-treated in the reactor at 370°C for 0.5 h in a stream of helium. The catalyst weight was 0.3 g and the pulse method was applied (pulse volume 0.2 μ l). Products of the reactions were analyzed using a Carlo Erba 6000 gas chromatograph equipped with 2 m long column filled with propylene carbonate and the FID detector.

The catalysts activity in the oxidation of carbon monoxide was tested by the continuous method. The conditions of the catalytic tests were as follows: reaction temperature — room temperature, catalyst weight — 0.1 g, gas mixture: 2% CO in air (flow rate 50 ml/min). Reaction products were analyzed using a Carlo Erba 6000 gas chromatograph equipped with RT-Msieve 13X PLOT column (30 m) and TCD detector.

3. Results and discussion

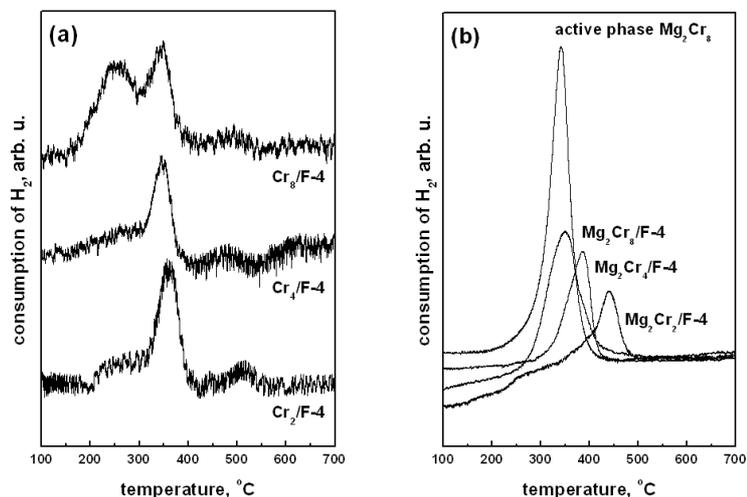
Table lists the chemical composition, BET surface areas, and pore volumes of the samples studied. In the case of catalysts a significant decrease in surface area and pore volume compared with MgF_2 is observed. Especially strong decrease is noted when MgO is supported on MgF_2 . The chromium oxides cause a smaller decrease in surface area which depends on chromium loading. In the binary oxide systems it comes also to decrease in the surface area and it is the most for catalyst containing both 2 wt.% of Mg and 2 wt.% Cr compared with MgF_2 .

The important results were obtained from the TPR experiments. MgF_2 supports coated with magnesium oxide did not show any reduction effect in the range of examined temperatures. However, the presence of chromium oxides caused the appearance of typical reduction profiles [8]. The reduction profiles of mono- and binary phases supported on MgF_2 are shown in Fig. 1. For samples with Cr only changes in TPR profiles are registered as the concentration of Cr increased. For the samples with the lowest Cr content, the reduction at $\approx 360^\circ\text{C}$ is dominant with small signals at $\approx 250^\circ\text{C}$ and $\approx 510^\circ\text{C}$. Low-temperature reduction peak is particularly intensive when the Cr concentration increases, however the high temperature reduction peak does not change (apart from small shift towards

TABLE

Characterization of the catalysts.

Catalysts	Content of active component		Surface area [m ² /g]	Pore volume [cm ³ /g]	Average pore diameter [Å]
	Mg [wt.%]	Cr [wt.%]			
F-4	–	–	46.3	0.218	151
Mg ₂ /F-4	2	–	23.1	0.081	152
Cr ₂ /F-4	–	2	41.2	0.203	197
Cr ₄ /F-4	–	4	37.9	–	–
Cr ₈ /F-4	–	8	33.9	–	–
Mg ₂ Cr ₂ /F-4	2	2	26.9	–	–
Mg ₂ Cr ₄ /F-4	2	4	36.2	–	–
Mg ₂ Cr ₈ /F-4	2	8	32.8	0.136	155

Fig. 1. TPR profiles of Cr_x/F-4 (a) and Mg₂Cr_x/F-4 (b) catalysts calcined at 400°C.

lower temperature). According to [9], where Cr₂O₃/Al₂O₃ was studied, the low-temperature reduction is connected with the presence of Cr⁶⁺ in the form of CrO₃. The presence of Cr⁶⁺ in the chromium preparations supported on MgF₂ was earlier registered [10]. The main reduction maximum is attributed to the reduction of Cr³⁺ to Cr²⁺. The appearance of high-temperature signal at 490–510°C, irrespective of the amount of supported chromium, could be connected with the reaction between Cr₂O₃ and coordinately unsaturated Mg²⁺ cations from MgF₂ which led to spinel-like compounds. In the case of binary oxide catalysts (Fig. 1b) only one reduction peak is observed. When the Cr concentration increased, this maximum shifted towards lower temperatures. This peak occurred in the range of

temperature typical of Cr_2O_3 reduction [9]. The other difference between mono- and binary oxide systems is the shift of maximum of Cr^{3+} reduction as the concentration of Cr_2O_3 increases: for chromium systems it is only $\approx 10^\circ\text{C}$, and for magnesium-chromium it exceeds 90°C . The higher temperature reduction of the binary oxide systems is connected with interactions between MgO and Cr_2O_3 and formation of new amorphous phase. The phase consists probably of MgCr_2O_4 spinel diluted with Cr_2O_3 .

Based on the TPR- H_2 measurements we affirmed that in chromium and magnesium-chromium catalysts supported on magnesium fluoride the predominant phase was Cr_2O_3 . However, in the case of samples non-doped with magnesium it came to the partial oxidation of Cr^{3+} to Cr^{6+} [10]. Such a change of oxidation stage is not observed in the presence of magnesium ions.

Figure 2 shows the room temperature EPR spectra of chromium and magnesium-chromium catalysts. The spectra are loading-dependent and consist of at least two signals of various intensity. EPR spectrum of the sample $\text{Cr}_{2,\text{RT}}/\text{F-4}$ with the low chromium loading (2%) shows a weak broad line centred at $g = 1.96$ with the line width $\Delta B_{\text{pp}} = 80$ mT indicating a strong dipolar interaction among the Cr^{3+} ions. Superimposed on it there is a sharp signal around $g = 1.9$. This signal is composed of two narrow isotropic lines with $g_0 = 1.983$ and $g_0 = 1.971$. In agreement with previous paper [11, 12] the sharp axially symmetric signals (often referred to as the γ -signals) are usually attributed to isolated, mononuclear Cr^{5+} ($3d^1$, $S = 1/2$) species and are interpreted as due to a pseudotetrahedral CrO_4^{3-} species with $g_{\perp} = 1.985$ and $g_{\parallel} = 1.906$ and a square pyramidal species with $g_{\perp} = 1.973$ – 1.976 and $g_{\parallel} = 1.955$ – 1.957 [11]. The signal due to Cr^{5+} disappeared for the sample with the higher Cr content (8%) and evacuated at room temperature and at 250°C (the samples $\text{Cr}_{8,\text{RT}}/\text{F-4}$ and $\text{Cr}_{8,250}/\text{F-4}$, respectively). For

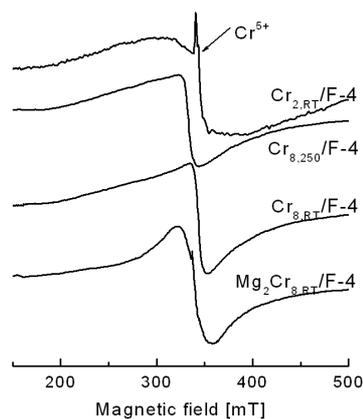


Fig. 2. Room temperature EPR spectra of $\text{Cr}_x/\text{F-4}$ and $\text{Mg}_2\text{Cr}_8/\text{F-4}$ catalysts after vacuum treatment at 250°C and at room temperature (RT) recorded at 9.39 GHz.

these catalysts only an asymmetric broad line with $g = 1.96$ and $\Delta B_{pp} = 18$ mT was detected. This signal is assigned to Cr^{3+} ($3d^3$, $S = 3/2$) in Cr_2O_3 -like clusters (usually denoted as β -signal) on the surface of the catalyst [13]. The decrease in the broad ΔB_{pp} line width with the Cr loading in going from Cr_2 to Cr_8 is due to exchange coupling between the Cr^{3+} ions which results in an exchange narrowing of the resonance line. Thus, the decrease in the ΔB_{pp} with increasing chromium content can suggest an increase in the particle size of Cr_2O_3 on the surface.

Similarly, the complex spectra were observed for the calcined under oxygen at 400°C and evacuated $\text{Mg}_2\text{Cr}_8/\text{F-4}$ catalysts. A broad line of the 360 mT width at $g = 1.975$ and a sharp peak superimposed on it was detected. The width of the broad line increases from $\text{Cr}_{8,\text{RT}}/\text{F-4}$ to $\text{Mg}_2\text{Cr}_{8,\text{RT}}/\text{F-4}$ due to weakening of the exchange coupling between Cr^{3+} ions. Probably it is the result of reaction between MgO and Cr_2O_3 leading to a new spinel-like phase presented earlier when TPR- H_2 profiles were discussed.

The catalytic activity of all samples was examined in the following reactions: dehydrogenation of cyclohexene and CO oxidation.

In the dehydrogenation of saturated hydrocarbon (cyclohexane) the catalysts studied did not show any activity, however they were active in the dehydrogenation of cyclohexene. This reaction is often accompanied by secondary reaction of hydrogenation. The activities of preparations calcined at 400°C in the dehydrogenation reaction are shown in Fig. 3a. The MgF_2 doped with magnesium oxide only were not active. The introduction of chromium oxide led to an increase in catalytic activity. In the case of mixed catalysts $\text{Mg}_2\text{Cr}_x/\text{F-4}$, the activity increased with the amount of chromium oxide introduced on the support, achieving the highest values from among samples examined. The activities of non-doped preparations were smaller and they decreased somewhat with increase in chromium concentration. The tested samples catalyzed the dehydrogenation reaction only.

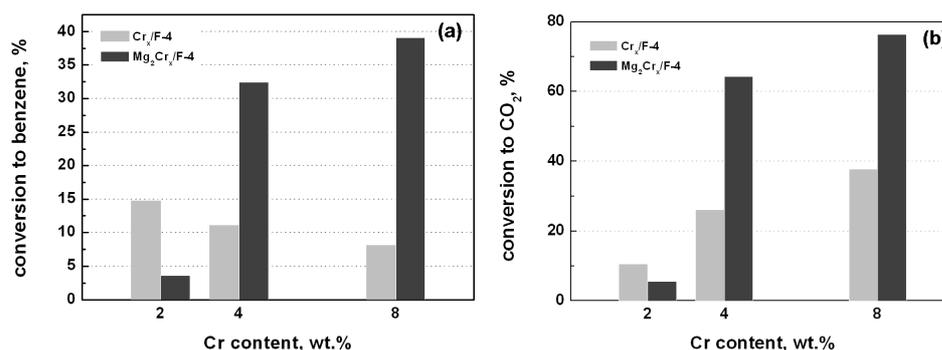


Fig. 3. Activity of $\text{Cr}_x/\text{F-4}$ and $\text{Mg}_2\text{Cr}_x/\text{F-4}$ catalysts calcined at 400°C in the reaction of cyclohexene dehydrogenation (a) and CO oxidation (b).

All catalysts prepared were also examined in CO oxidation reaction (Fig. 3b). The support itself and doped with MgO did not catalyze this reaction. The activity appeared only after the introduction of chromium oxide phases. Especially active were the mixed catalysts $\text{Mg}_2\text{Cr}_x/\text{F-4}$ with the 4 wt.% content of chromium and more.

In both reactions studied the catalytic activity is connected with chromium presence. Introduction of magnesium ions enhances the activity. It has been established by TPR- H_2 and EPR methods that MgO and Cr_2O_3 react and probably a spinel phase arises. The existence of this phase results in the observed enhancement of catalytic activity.

4. Conclusions

1. EPR spectra showed the presence of two different chromium species in the catalysts calcined in O_2 at 400°C , e.g. Cr^{3+} species in the Cr_2O_3 crystalline and dispersed Cr^{5+} species.
2. The interactions between MgO and Cr_2O_3 supported on MgF_2 lead to the spinel-like phase.
3. The presence of the spinel phase influences significantly the catalytic activity and selectivity of chromium catalysts.
4. The special advantage of $\text{MgO-Cr}_2\text{O}_3/\text{MgF}_2$ systems is the high catalytic activity in the reaction of CO oxidation at room temperature, as well as the selectivity in the reaction of dehydrogenation of cyclohexene.

Acknowledgments

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