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Catalytic properties of Cr_2O_3 doped with MgO supported on MgF_2 and Al_2O_3

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Catalytic properties of Cr_2O_3 supported on MgF_2 or Al_2O_3 have been modified by magnesium oxide. The catalysts have been obtained by the co-impregnation method and characterised by: BET, XRD and TPR. As follows from the results, the oxides supported on magnesium fluorine react with each other already at 400 °C, leading to formation of an amorphous spinel-like phase. On the Al_2O_3 support such an $MgCr_2O_4$ spinel has appeared at much higher temperatures. The addition of magnesium oxide has a significant effect on the activity and selectivity of the catalysts studied in the CO oxidation reaction at room temperature and in the reaction of cyclohexane dehydrogenation. The magnesium–chromium catalysts supported on MgF_2 have been found to show much higher activity and selectivity than the analogous systems supported on Al_2O_3.

KEY WORDS: magnesium–chromium oxide catalysts; MgF_2; Al_2O_3; $MgCr_2O_4$ spinel; XRD; TPR.

1. Introduction

The industrial importance of chromia-based catalysts has generated much interest in their physicochemical properties. They have been applied in the reactions of polymerization, hydrogenation and dehydrogenation of hydrocarbons, dehydration and dehydrogenation of alcohols to produce aldehydes, ketones and alkenes, dehydrocyclization of paraffins, water gas shift reaction, the automotive exhaust purification [1] and for the deep oxidation and decomposition and fluorination of chlorinated volatile compounds [2–4].

Chromium oxides have also been used as components of mixed catalysts. For instance in the system with V_2O_5 [5] or nickel [6] they are known to form catalysts active in the reactions of oxidation and reduction, which has been attributed to changes in their semiconducting properties.

With divalent cations, Cr_2O_3 forms spinel or perovskite type compounds [7] showing particularly high selectivity in the reactions of oxidation and reduction [8,9]. Such a divalent cation can be magnesium but hitherto not much attention has been paid to the system MgO–Cr_2O_3. Earlier works have shown that in an unsupported mixture of MgO and Cr_2O_3 the two components react forming a spinel [10,11]. The reaction can occur already at 400 °C. Unfortunately, no information has been available on the behaviour of the oxides deposited on a support. It has been generally recognised that the properties of chromium oxide species strongly depend on the support and the surface concentration of chromium oxide [3]. Therefore, a study has been undertaken of the catalysts of different concentration of chromium supported on MgF_2 or Al_2O_3. The former support has not been hitherto applied for this phase. Al_2O_3 is a widely known and commonly used support of acid-base nature. The application of magnesium fluoride as a support has been limited although its structure, chemical and catalytic properties have been well recognised [12]. It is characterised by almost chemically inert surface and good thermal stability up to ~500 °C [13], it has a mesoporous structure and its surface area reaches ~45 m^2/g, after calcination at 400 °C.

Earlier attempts at using MgF_2 supported systems have brought about active and selective catalysts for the NO reduction in the presence of CO [14,15] and hydrocarbons [16,17] as reducing agents, CO oxidation [18], hydrodesulfurization of thiophene [19,20] and hydrodechlorination of chlorofluorocarbons [21,22].

The aim of the study presented was to establish the effect of dotting of chromium (III) oxide with magnesium oxide, both supported on MgF_2 or Al_2O_3, on the surface properties of this system and its catalytic activity in the reactions of cyclohexane dehydrogenation and CO oxidation.

2. Experimental

2.1. Catalysts preparation

Magnesium fluoride was obtained by adding small amounts of $MgCO_3 \times Mg(OH)_2$ to aqueous solution of hydrofluoric acid until neutralisation, then the mixture was acidified by introduction of a few additional drops of the acid. The precipitate was aged at room tempera-

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ture for some days, then dried for 24 h at 105 °C and calcined at 400 °C for 4 h. After the calcination, MgF_2 (denoted as F-4) was ground to obtain 0.2–0.5 mm grain size.

To get Al_2O_3 as a support, aluminium isopropoxide ($Al[OCH(CH_3)_2]_3$) was heated until melting. After cooling to 60 °C the same volume of 2-propanol was added. Then the mixture was poured into distilled water on stirring till precipitation of $Al(OH)_3$. The obtained precipitate was filtered off and dried at 105 °C. Dry $Al(OH)_3$ was calcined for 4 h at 400 and 950 °C (the respective samples are denoted as A-4 and A-9) respectively, and then ground to obtain 0.2–0.5 mm grain size.

The Mg_2/F-4 and Cr_x/F-4 catalysts were obtained by impregnation from aqueous solutions of $Mg(NO_3)_2 \times H_2O$ and $Cr(NO_3)_3 \times 9H_2O$, respectively, onto MgF_2 powder of 0.25–0.50 mm grain size (preheated at 400 °C for 4 h). The Mg_2Cr_x/F-4 catalysts were prepared by the conventional co-impregnation method from the aqueous solutions of $Mg(NO_3)_2 \times H_2O$ and $Cr(NO_3)_3 \times 9H_2O$. After impregnations, all the catalysts were dried in air at 120 °C for 24 h and then calcined at 400 °C for 4 h.

The catalysts Mg_2/Al_2O_3, Cr_x/Al_2O_3 and Mg_2Cr_x/Al_2O_3 were obtained in the same way as these supported on MgF_2. The catalysts supported on Al_2O_3 were calcined at two different temperatures: 400 and 950 °C.

2.2. XRD

X-ray examination was carried out with an M-62 diffractometer working with a HZG-3 powder goniometer, employing CuKα radiation.

2.3. 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 BET method and the pore size distribution was established on the basis of the BJH method, using a desorption isotherm.

2.4. TPR studies

The temperature programmed reduction experiments were carried out with an ASAP ChemiSorb 2705 (Micromeritics). A portion of 100 mg of the catalyst or 15–20 mg of oxides were reduced in a mixture of 10 vol.% H_2 in Ar at a flow rate of 30 cm^3/min (STP), and at 10 °C/min heating rate up to a final temperature of 700 °C.

2.5. Catalytic activity

The catalytic properties of the samples were determined by the pulse method in the reaction of cyclohexene dehydrogenation. Before measurements, 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 volume was 0.2 μl. Products of the reactions were analysed using a Carlo Erba 6000 gas chromatograph equipped with a 2 m long column filled with propylene carbonate and a FID detector. The catalyst activity in the oxidation of carbon monoxide was tested by the continuous method. The conditions of the catalytic tests were as follows: room temperature, catalyst weight – 0.1 g, gas mixture: 2% CO in air (flow rate 50 ml/min). Reaction products were analysed using a Carlo Erba 6000 gas chromatograph equipped with a RT-Msieve 13X PLOT column (30 m) and a TCD detector.

3. Results

3.1. Surface area

Table 1 gives the chemical composition, BET surface areas and pore volumes of the samples studied. When MgO is supported on MgF_2 a significant decrease in the surface area and pore volume is observed. Chromium oxides supported on magnesium fluoride cause smaller changes depending on the oxide loading: the higher the loading the lower the surface area. In binary oxide systems the decrease in the surface area is also observed, especially for the catalyst containing both 2%wt of Mg and Cr.

The BET surface area of Al_2O_3 depends on the calcination temperature. After calcination at 950 °C the surface decreases over twice in comparison with that of the support calcined at 400 °C. Contrary to MgF_2, introduction of MgO on alumina has practically no effect on the surface area. Some differences occur after introduction of chromium oxide. The surface area of the samples calcined at 400 °C increases markedly with increasing Cr loading, except for the mixed catalyst of the highest loading, while the surface are of those calcined at 950 °C decreases with increasing Cr loading, except for Mg_2Cr_8/A-9.

3.2. XRD

The crystallinity of the samples investigated was determined by XRD. From among the supports, magnesium fluoride revealed very high crystallinity as reported in [13]. Weak and broad signals recorded for aluminium oxide indicated a low degree of crystallinity, particularly after calcination at 400 °C. Introduction of MgO alone on the support (MgF_2 or Al_2O_3) did not cause the appearance of new crystalline phases. Only when a larger amount of chromium was introduced onto MgF_2, some new peaks corresponding to Cr_2O_3 appeared (figure 1). No peaks characteristic of crystal compound formation as a result of the interaction between magnesium and chromium oxides were observed.

The situation was quite different when chromium oxide phases were introduced on Al_2O_3. After calcination of chromium and magnesium–chromium catalysts at 400 °C no additional crystalline phase was detected. The diffraction patterns of the samples calcined at 950 °C revealed peaks corresponding to Cr_2O_3 (Cr_8/A-9). In the double catalysts (Mg_2Cr_8/A-9) in the presence of magnesium, Cr_2O_3 signals diminished considerably and trace amounts of $MgCr_2O_4$ spinel could be detected. The presence of magnesium oxide influenced the chromium phase supported on Al_2O_3, lowering its crystallinity.

3.3. *TPR-H_2*

Important information was obtained from the TPR experiments. MgF_2 and Al_2O_3 supports coated with magnesium oxide did not show any reduction effect in the range of the temperatures studied. Only the presence of chromium oxides caused an appearance of typical reduction profiles. The reduction profiles of mono- and double-oxide phases supported on MgF_2 are shown in figure 2. For samples with Cr, changes in the TPR profiles appear with increasing concentration of Cr_2O_3. For the samples with the lowest Cr content, the reduction at ~360 °C is dominant with small signals at ~250 and ~510 °C. The low-temperature reduction peak is particularly intensive when the Cr concentration is higher, however, the high temperature reduction peak (apart from a small shift towards lower temperatures) did not change. According to [23], this low-temperature reduction is connected with the presence of Cr^{+6} in CrO_3. The presence of Cr^{+6} in the chromium preparations supported on MgF_2 was detected earlier [24]. The main reduction maximum is attributed to the reduction of Cr^{3+} to Cr^{2+}. The appearance of a high-temperature signal at (490–510 °C), irrespective of the amount of chromium supported, could be related to the reaction between Cr_2O_3 and co-ordinately unsaturated Mg^{2+} cations from MgF_2 surface, leading to formation of the spinel – like compounds. In the reduction profiles of binary oxide catalysts (figure 2b) only one reduction peak is observed. When Cr concentration increases, this maximum shifts towards lower temperatures. This peak occurs in the range of temperatures typical of Cr_2O_3 reduction [23]. The profiles of mono- and double oxide systems also differ in the shifts of the maximum of Cr^{3+} reduction with increasing concentration of Cr_2O_3, that is for the chromium systems this shift is ~10 °C, while for magnesium–chromium it is greater than 90 °C. This shift of the reduction temperature is probably related to formation of new amorphous structures in the MgO–Cr_2O_3/MgF_2 system.

For the mono- and double- oxide catalysts supported on Al_2O_3 one-step reduction profiles in similar temperature have been obtained, figure 3. These single peaks are connected with the presence of Cr_2O_3 have different intensity, lower for the preparations calcined at 950 °C. This lower intensity is probably connected

Table 1
Characterisation of 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_2Cr_2/F-4	2	2	26.9	–	–
Mg_2Cr_4/F-4	2	4	36.2	–	–
Mg_2Cr_8/F-4	2	8	32.8	0.136	155
A-4	–	–	226.7	0.369	65.1
Mg_2/A-4	2	–	229.9	0.350	60.9
Cr_2/A-4	–	2	255.4	0.360	56.7
Cr_4/A-4	–	4	257.7	0.343	53.3
Cr_8/A-4	–	8	259.8	0.326	50.3
Mg_2Cr_2/A-4	2	2	230.8	0.347	60.2
Mg_2Cr_4/A-4	2	4	231.9	0.335	57.8
Mg_2Cr_8/A-4	2	8	199.8	0.288	57.7
A-9	–	–	100.7	0.348	135.9
Mg_2/A-9	2	–	102.3	0.350	136.9
Cr_2/A-9	–	2	90.9	0.346	152.4
Cr_4/A-9	–	4	86.4	0.330	152.8
Cr_8/A-9	–	8	81.5	0.310	152.5
Mg_2Cr_2/A-9	2	2	86.6	0.326	150.9
Mg_2Cr_4/A-9	2	4	86.4	0.325	150.5
Mg_2Cr_8/A-9	2	8	94.3	0.329	139.7

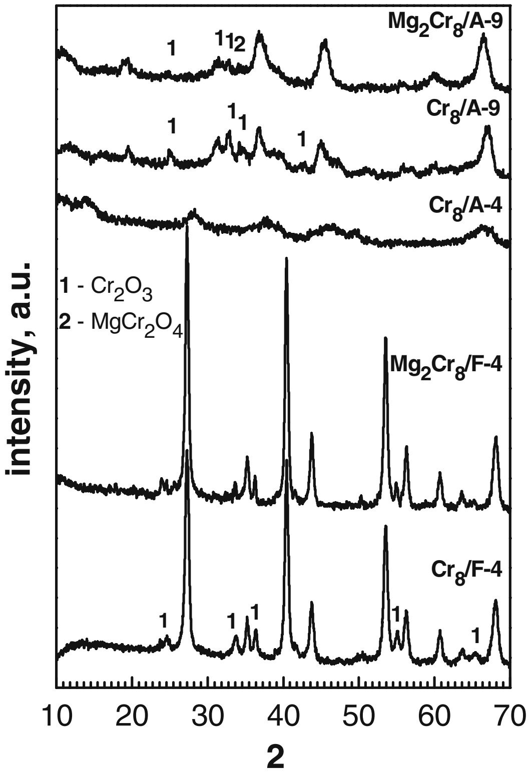

Figure 1. Diffraction patterns of chromium and magnesium–chromium catalysts supported on MgF_2 and Al_2O_3.

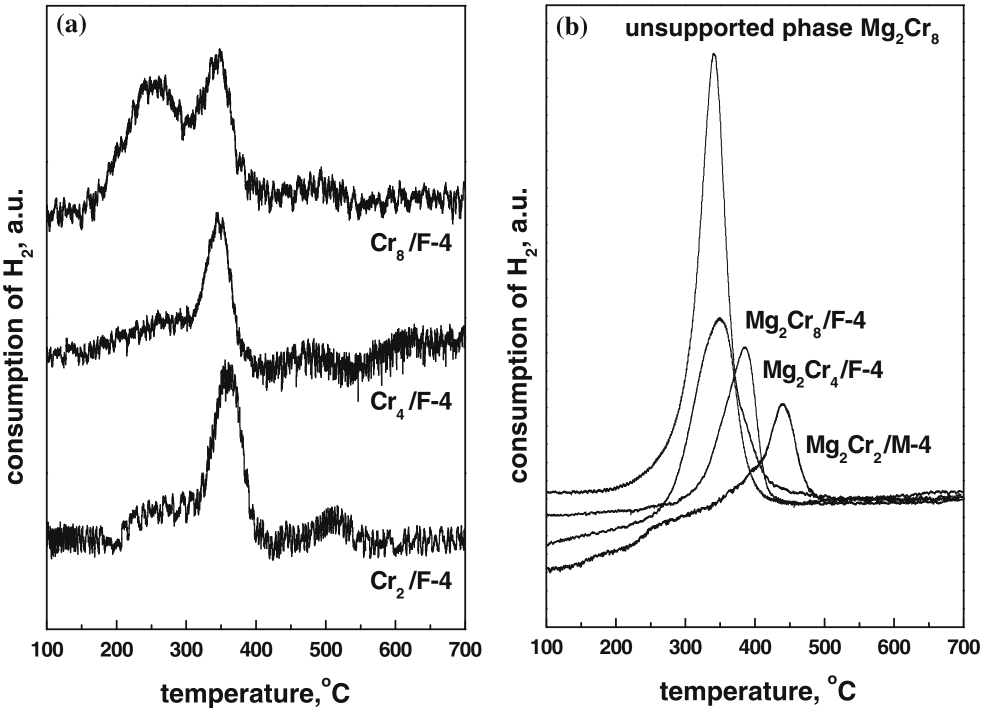

Figure 2. TPR profiles of Cr_x/F-4 (a) and Mg_2Cr_x/F-4 (b) catalysts calcined at 400 °C.

with formation of the phases that are reduced beyond the range of the reduction measurements. The lack of distinct reduction effect of the MgO–Cr_2O_3 unsupported mixture, calcined at 950 °C confirmed this supposition (figure 4b). For the identical unsupported sample calcined at 400 °C, only one strong reduction maximum is recorded at 343 °C, in the range typical of Cr_2O_3 reduction. A characteristic reduction feature of

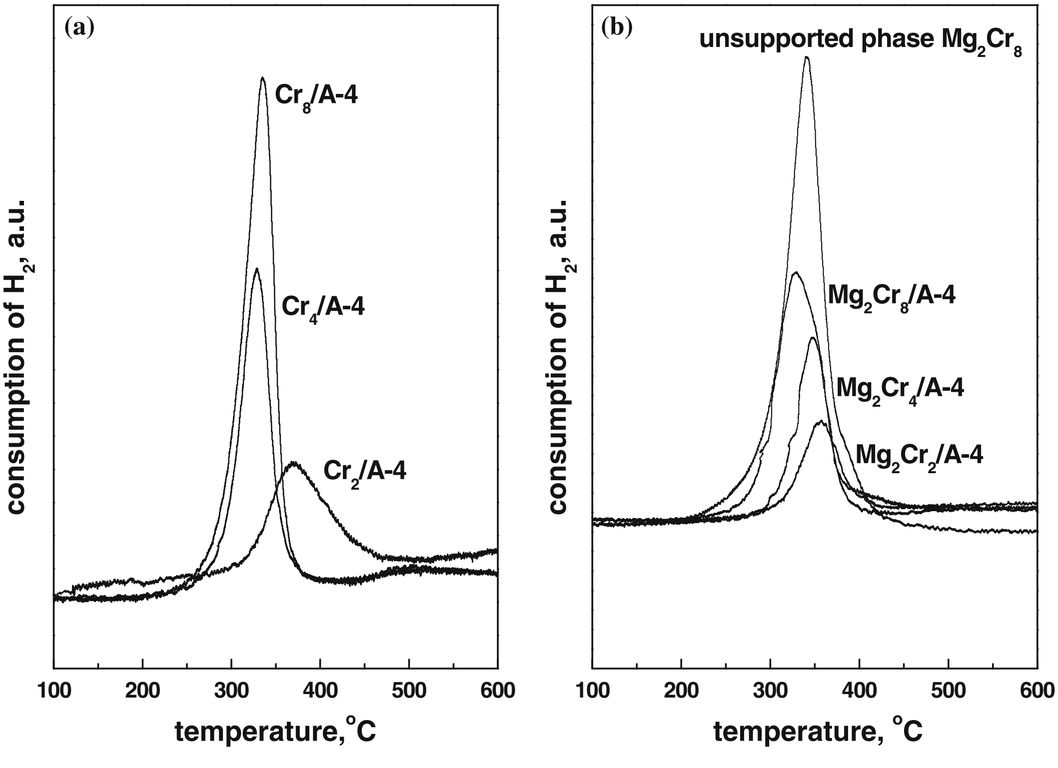

Figure 3. TPR profiles of Cr_x/A-4 (a) and Mg_2Cr_x/A-4 (b) catalysts calcined at 400 °C.

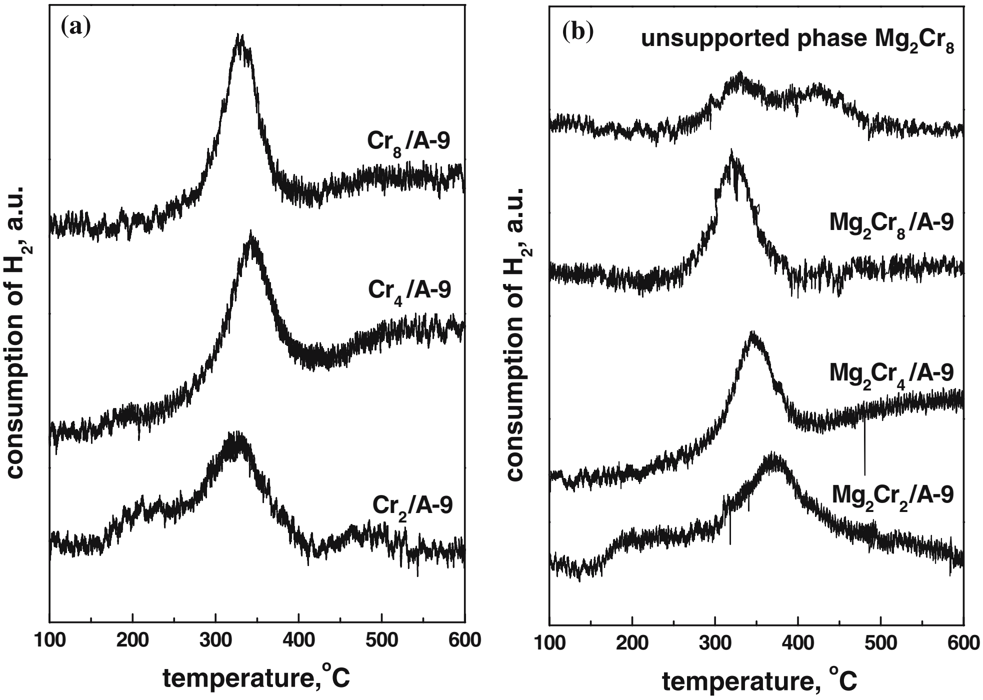

Figure 4. TPR profiles of Cr_x/A-9 (a) and Mg_2Cr_x/A-9 (b) catalysts calcined at 950 °C.

chromium and magnesium–chromium catalysts on Al_2O_3, irrespective of the presence of MgO and calcination temperature, is the peaks shift (20–30 °C) towards lower temperatures with increasing chromium concentration. We suppose that the interactions of magnesium or chromium oxides and the surface of Al_2O_3 are so strong that they restrict the direct reaction between MgO and Cr_2O_3 at low temperatures. At high temperatures the harder reducible compounds are formed whose reduction takes place beyond the temperature range of our experiments. The unreacted Cr_2O_3 is stabilized on the support surface, which causes a small increase in the reduction temperature at low chromia contents [23].

3.4. Catalytic activity

The catalytic activity of all samples was examined in the 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 accompanied the secondary hydrogenation reaction. The main difference between the samples supported on MgF_2 and Al_2O_3 was that these based on MgF_2 catalysed selectively dehydrogenation of cyclohexene to benzene and these based on Al_2O_3 activated also hydrogenation of cyclohexene to cyclohexane. The activities of the preparations calcined at 400 °C in the dehydrogenation reaction are shown in figure 5. Both supports doped with magnesium only were inactive. The catalytic activity appeared after introduction of chromium oxide. The activity of the mixed catalyst supported on MgF_2 increased with increasing amount of chromium and was the highest for Mg_2Cr_8/F-4 from among all samples studied. The activities of the remaining preparations were similar and they did not change much with increasing chromium concentration. The double oxide catalysts on Al_2O_3 showed a maximum activity at 4 wt.% Cr content. As mentioned above, the catalysts supported on Al_2O_3 activated hydrogenation of cyclohexene to cyclohexane (figure 6). The activity appeared when chromium oxide

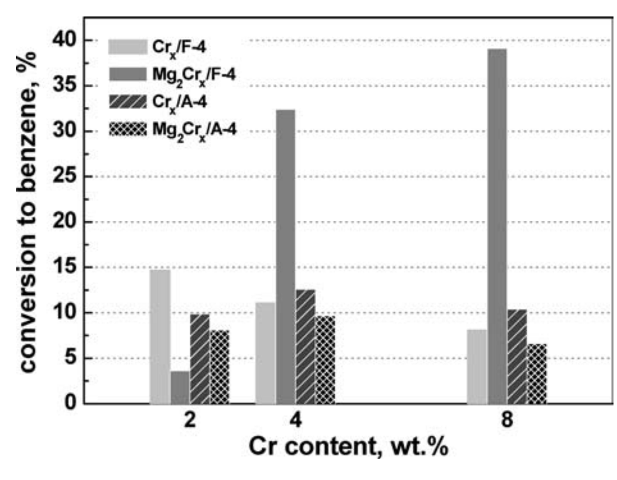

Figure 5. Activity of Cr_x/F-4, Mg_2Cr_x/F-4 and Cr_x/A-4, Mg_2Cr_x/A-4 catalysts calcined at 400 °C in the reaction of cyclohexene dehydrogenation.

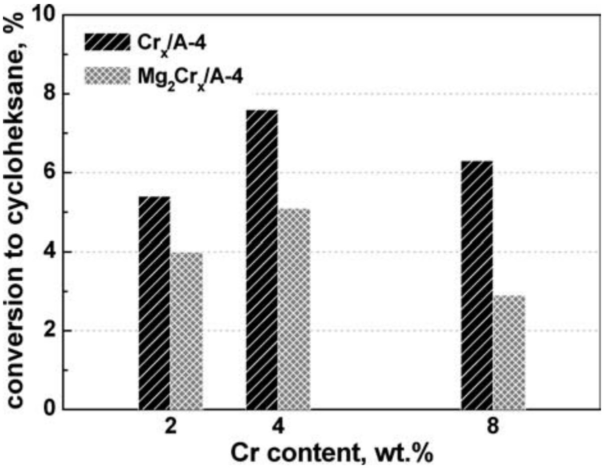

Figure 6. Activity of Cr_x/A-4 and Mg_2Cr_x/A-4 catalysts calcined at 400 °C in the reaction of cyclohexene dehydrogenation.

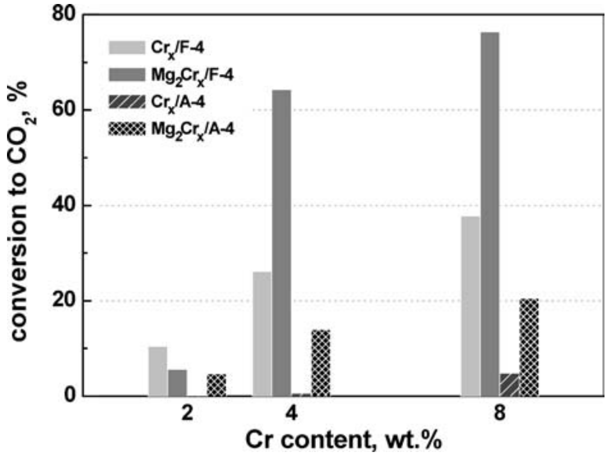

Figure 8. Activity of Cr_x/A-4, Mg_2Cr_x/A-4, Cr_x/F-4 and Mg_2Cr_x/F-4 catalysts calcined at 400 °C in the reaction of CO oxidation.

was introduced. In this case, the addition of magnesium decreased the conversion of the samples calcined at 400 °C. The catalysts supported on alumina and calcined at 950 °C were less active and their activity only slightly changed with the amount of chromium introduced (figure 7).

All catalysts prepared were also tested in CO oxidation reaction. None of the supports itself catalysed this reaction. The activity appeared only after the introduction of oxide phases. From among the samples calcined at 400 °C, the most active were those supported on MgF_2 (figure 8). Especially active were the mixed catalysts Mg_2Cr_x/F-4 containing 4 wt.% chromium or more.

Mono-oxide chromium catalysts supported on alumina calcined at low (figure 8) as well as at high temperature (figure 9) revealed slight activity. The presence of magnesium oxide caused an increase in their activity, particularly in the samples with higher Cr_2O_3 concentrations calcined at 950 °C.

4. Discussion

Two types of chromium and magnesium–chromium oxide catalysts have been studied in this work, one supported on MgF_2 and calcined at 400 °C and the other supported on Al_2O_3 treated at 400 °C and 950 °C. Results of the XRD and TPR-H_2 measurements have confirmed that in chromium and magnesium–chromium catalysts the predominant phase was Cr_2O_3. In the monooxide chromium sample supported on MgF_2, Cr^{6+} appeares as a result of partial oxidation of chromium from Cr^{3+} to Cr^{6+} [24]. Such a change in the oxidation stage was not observed in the presence of magnesium ions. Also, the presence of Cr^{6+} was not detected in the samples supported on alumina.

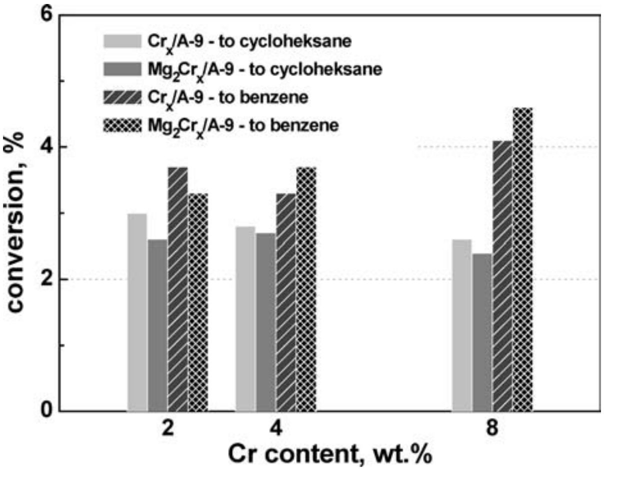

Figure 7. Activity of Cr_x/A-9 and Mg_2Cr_x/A-9 catalysts calcined at 950 °C in the reaction of cykloheksene dehydrogenation and cykloheksene hydrogenation.

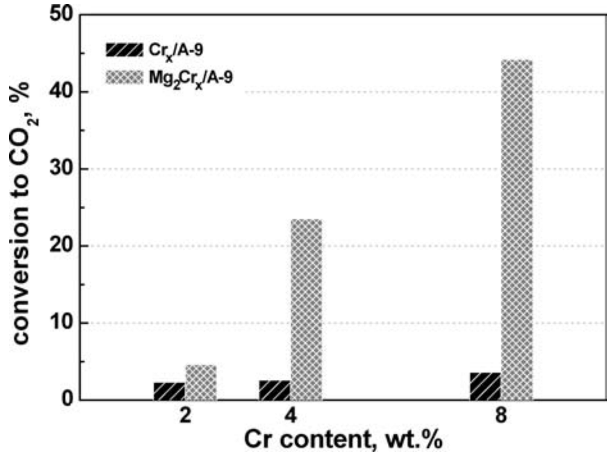

Figure 9. Activity of Cr_x/A-9 and Mg_2Cr_x/A-9 catalysts calcined at 950 °C in the reaction of CO oxidation.

The types of surface chromium complexes depended also on the calcination temperature. The peaks corresponding to the reduction of the chromium phase were observed to decrease in the chromium and magnesium–chromium catalysts supported on Al_2O_3 and calcined at 950 °C. In the mixed preparations, it was probably connected with formation of $MgCr_2O_4$ spinel. The evidence for formation of such a spinel phase already at 400 °C was given earlier [10], although, in our XRD investigation the presence of $MgCr_2O_4$ spinel after calcination at 400 °C was not revealed. The TPR-H_2 results of preparations supported on MgF_2 clearly indicated that the supported oxides interact with each other. In the catalysts calcined at 950 °C the supported oxides of magnesium and chromium partially reacted to the $MgCr_2O_4$ spinel. At this temperature the unsupported mixture of Mg and Cr oxides reacted to spinel with the efficiency ~80%. The magnesium oxide might react with Al_2O_3 support leaving free chromia. We could expect the formation of another kind of spinel: a magnesium–aluminium one [7], though the diffraction patterns obtained did not reveal the presence of such a phase. Moreover, the decrease in the Cr concentration in the monooxide catalysts calcined at 950 °C could have been a result of formation of substituted solid solutions in Cr_2O_3–Al_2O_3 systems [7].

There is another difference between state of magnesium–chromium oxides supported on MgF_2 or Al_2O_3. The data obtained for double oxides catalysts supported on MgF_2 calcined at 400 °C showed a shift reaching ~100 °C between the maxima of chromium reduction in the samples of the lowest and the highest content of Cr and the same content of MgO. For the analogous chromium preparations supported on alumina, the maximum shift is quite small (~25 °C). The recorded difference in the behaviour of the active phases supported on MgF_2 and Al_2O_3 could be a result of the different interactions of these phases with the support surface. MgO or Cr_2O_3 oxides supported separately on MgF_2 react with the support in different ways. If MgO is supported on MgF_2, significant changes in the support texture are observed, which indicates the occurrence of a reaction between MgO and MgF_2 support at 400 °C. Literature data suggest a possibility of formation of the MgOHF phase in the near surface layer [25]. However, the presence of chromium oxide significantly hinders this reaction and promotes a reaction between the deposited magnesium and chromium oxides. If Cr_2O_3 is supported on MgF_2, smaller changes are observed in the surface area of samples investigated. Extend of the changes depended on Cr_2O_3 content. A possible explanation of this effect is mechanical blocking of some pores of the support.

The catalytic activity of catalysts was related to the type of chromium surface complexes. In both reactions tested, the dehydrogenation of cyclohexene and CO oxidation, a significant influence of MgO on the activity of the chromium phase was noted. It is particularly apparent for the oxides supported on MgF_2 and also for high-temperature double oxide catalysts supported on Al_2O_3 in CO oxidation. It seems that in the low-temperature treated samples, the amorphous spinel-like MgO–Cr_2O_3 structures are responsible for their catalytic activity. The behaviour of the high–temperature Mg_2Cr_8/A-9 catalyst suggests that in this sample the active phase is the $MgCr_2O_4$ spinel.

5. Conclusions

1. Interaction between magnesium and chromium oxides is easier when they are supported on MgF_2 than on Al_2O_3.
2. After calcination at low temperature (400 °C) the interactions between MgO and Cr_2O_3 lead to creation of a spinel-like phase and after calcination at higher temperature the $MgCr_2O_3$ spinel forms.
3. The presence of magnesium oxide influences significantly the catalytic activity and selectivity of chromium catalysts, especially those supported on MgF_2.
4. Special advantages of MgO–Cr_2O_3/MgF_2 systems are the high catalytic activity in the reaction of CO oxidation at room temperature and selectivity in the reaction of dehydrogenation of cyclohexene.

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