Catalytic properties of Cr$_2$O$_3$ doped with MgO supported on MgF$_2$ and Al$_2$O$_3$

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Catalytic properties of Cr$_2$O$_3$ supported on MgF$_2$ or Al$_2$O$_3$ 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 fluoride interact with each other already at 400 °C, leading to formation of an amorphous spinel-like phase. On the Al$_2$O$_3$ support such an MgCr$_2$O$_4$ 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$_2$O$_3$.

KEY WORDS: magnesium–chromium oxide catalysts; MgF$_2$; Al$_2$O$_3$; MgCr$_2$O$_4$ 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, dehydrogenation of alcohols to produce aldehydes, ketones and alkenes, dehydrocyclization and 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$_2$O$_5$ [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$_2$O$_3$ 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$_2$O$_3$. Earlier works have shown that in an unsupported mixture of MgO and Cr$_2$O$_3$ 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$_2$O$_3$. The former support has not been hitherto applied for this phase. Al$_2$O$_3$ 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$_2$O$_3$, 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$_3$× 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-
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$_2$O$_3$ as a support, aluminium isopropoxide (Al[OCH(CH$_3$)$_3$]) 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$_2$O and Cr(NO$_3$)$_3$ $\times$ 9H$_2$O, respectively, onto MgF$_2$ powder of 0.25–0.50 mm grain size (preheated at 400 °C for 4 h). The Mg$_2$Cr$_x$/F-4 catalysts were prepared by the conventional co-impregnation method from the aqueous solutions of Mg(NO$_3$)$_2$ $\times$ H$_2$O and Cr(NO$_3$)$_3$ $\times$ 9H$_2$O. 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$_2$O$_3$, Cr$_x$/Al$_2$O$_3$ and Mg$_2$Cr$_x$/Al$_2$O$_3$ were obtained in the same way as these supported on MgF$_2$. The catalysts supported on Al$_2$O$_3$ 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$_2$O$_3$ 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$_2$Cr$_8$/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$_2$O$_3$) 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$_2$O$_3$ 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$_2$O$_3$. After calcination