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Copper–cobalt oxide catalysts supported on MgF_2 or Al_2O_3—their structure and catalytic performance

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Abstract

The surface structure and catalytic properties of a mixed phase of copper and cobalt oxides supported on magnesium fluoride and alumina have been studied. The surface properties have been characterised by low temperature adsorption of nitrogen, XRD and TPR-H_2. Catalytic activity of the catalysts have been examined in CO oxidation and NO reduction by propene. The oxides studied react with each other to spinels: $CuCo_2O_4$ after calcination at 400 or 550 °C and $CoAl_2O_4$ after treatment at 950 °C. The spinels have different effect on catalytic activity. In CO oxidation, the spinels are more effective than monoxide phases, however, in NO reduction by propene the copper oxide supported on MgF_2 is the most active.

Keywords: Copper–cobalt oxide catalysts; CO oxidation; NO reduction; TPR; XRD; MgF_2; Al_2O_3

1. Introduction

Transition metal oxides, in particular copper oxides, are known to catalyse many reactions including such important ones as CO oxidation and NO reduction by hydrocarbons [1,2]. The activity of such catalysts can be increased by introduction of another oxide, for example cobalt oxide, also catalysing the above reactions.

Mixed oxides of transition metals are capable of mutual interactions, leading to the formation of complex structure of spinel or perovskite type [3]. The catalytic activity of mixed oxides is usually higher than that of their individual components. When using a mixture of copper oxide and cobalt oxide, the phase $CuCo_3O_4$ starts forming already at ~300 °C [4] and remains stable up to ~800 °C. In the presence of an excess of copper or cobalt in the mixture, separate phases of CuO or Co_3O_4, respectively, appear. The presence of such an excessive phase is responsible for thermal stability of the metal ions of the other component at a higher degree of oxidation. When a mixture of these two oxides is supported on Al_2O_3, cobalt oxide reacts during calcination not only with CuO but also with Al_2O_3, which leads to formation of the spinel $CoAl_2O_4$ [5]. When the same oxides are supported on silica, they interact to form the spinel $CuCo_2O_4$ [6].

The aim of the study was to establish the surface structure and properties of the systems of copper and cobalt oxides on different supports as a function of concentration of the active phases and their catalytic activity in CO oxidation and NO reduction by propene. The supports studied were Al_2O_3 and MgF_2, the former is well known while the latter is a relatively new one. It is characterised by almost inert surface, good thermal stability almost up to 500 °C and high hardness. Its surface area reaches ~45m^2/g and it shows a well-developed mesoporous structure [7]. Magnesium fluoride has already been used as a support of oxide and metallic active phases [8] to obtain active and selective catalysts of such processes as hydrodesulfurization of organic compounds [9,10], hydrodechlorination of chlorofluorocarbons [11,12] and NO reduction [13], important from the point of view of the environment protection. MgF_2 has not been used hitherto as a support of mixed phase of copper and cobalt oxides, so the system studied in this work is completely new.

2. Experimental

2.1. Preparation of catalysts

Magnesium fluoride was obtained in the reaction of magnesium carbonate with 20% aqueous solution of hydro-

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fluoric acid. After drying at 110 °C the support was calcined for 4 h at 400 °C.

Aluminium oxide was prepared by hydrolysis of aluminium isopropoxide according to an earlier described procedure [14]. The aluminium hydroxide obtained after washing out isopropyl alcohol was dried at 110 °C for 24 h, then calcined at 400, 550 or 950 °C for 4 h.

The impregnated CuO_x/MgF_2 solid sample was obtained by introducing an aqueous solution of $Cu(NO_3)_2{\cdot}3H_2O$ to the earlier prepared and calcined at 400 °C magnesium fluoride of grain size 0.2–0.5 mm. The obtained solid was dried at 110 °C for 24 h and calcined in the air at 400 °C for 4 h. The concentration of the $Cu(NO_3)_2$ solution was chosen to obtain the desired concentration of copper oxide (2 wt.% of Cu). The prepared solid was labelled as Cu_2/F-4, where “2” stands for the concentration of copper in wt.%, and “4” means that it was calcined at 400 °C.

The impregnated, CoO_x/MgF_2 solid samples were obtained in a similar way as the CuO_x/MgF_2 one with the only difference that an aqueous solution of $Co(NO_3)_3{\cdot}9H_2O$ was applied. The amounts of the solution were chosen to obtain the desired concentration of cobalt oxide. The prepared solids were labelled as Co_x/F-4, where “x” is the concentration of Co in wt.%, and “4” means that it was calcined at 400 °C.

The impregnated CuO_x/Al_2O_3 and CoO_x/Al_2O_3 solid samples were obtained by introducing onto aqueous solutions of appropriate nitrates aluminium oxide of the grain size 0.2–0.5 mm. Further preparation method was the same as for the catalysts supported on MgF_2, however, the active phases supported on Al_2O_3 were calcined not only at 400 °C but also at 550 and 950 °C, for 4 h. The preparations were labelled as Cu_2/A-T or Co_x/A-T, where “2” stands for copper concentration in wt.%, x for the cobalt concentration in wt.%, and T for the temperature of calcination (400, 550, 950 °C).

The co-impregnated preparations CuO_x–CoO_x/MgF_2 and CuO_x–CoO_x/Al_2O_3 were obtained by introducing into aqueous solutions of the mixtures of $Cu(NO_3)_2{\cdot}3H_2O$ and $Co(NO_3)_3{\cdot}9H_2O$ the earlier calcined magnesium fluoride or aluminium oxide of the grain size 0.2–0.5 mm. The amount of the copper(II) nitrate(V) and cobalt(III) nitrate(V) solution was chosen to ensure wetting of the whole surface of the support. The samples were dried and calcined at 400 °C in air for 4 h. The catalysts samples supported on Al_2O_3 were also calcined at 550 and 950 °C. The amounts of copper(II) and cobalt(III) nitrates(V) introduced into the solutions were chosen to ensure the desired Cu/Co weight ratio of 1/1, 1/2, 1/4. The samples were labelled as Cu_2Co_x/F-4 and Cu_2Co_x/A-T, where “2” stands for the concentration of Cu, “x” for the concentration of Co in wt.%, and “T” for the temperature of calcination of 400, 550 or 950 °C.

2.2. UV–vis spectra

The content of metal in the catalysts was determined by the UV–vis spectrometry. The content of copper was determined using the reaction of Cu(II) with sodium dietyldithiocarbamian at pH ranging from 4 to 11. Absorbency was measured at 436 nm. The content of cobalt was determined using the reaction of cobalt ions with potassium rhodanate. Absorbency was measured at 620 nm.

2.3. Surface area

Low temperature (−196 °C) adsorption of nitrogen was performed by a sorptometer ASAP 2010 made by Micrometrics. The surface area was established by the BET method.

2.4. XRD spectra

The X-ray diffraction patterns were obtained with an M-62 diffractometer, using a powder goniometer HZG-3 and Cu Kα radiation with a Ni filter in 2Θ range 20–70 ° with step size 0.01 °.

2.5. TPR-H_2

The measurements were performed on Chemi Sorb 2705 instrument made by Micrometrics. The gases used in the measurements were of high purity: a mixture of 10% H_2/90% Ar—99.999%. The susceptibility to reduction was measured in a stream of 10% H_2/90% Ar. The volume rate flow of the gas mixture was 30 ml/min and the temperature changed at the rate of 10 °C/min, in the range 25–800 °C.

2.6. Catalytic activity—CO oxidation

CO oxidation (15 ml/min of a mixture of 1 vol.% CO in helium) by air oxygen (55 ml/min) was carried out in a flow reactor. The reaction products were analysed chromatographically. The reaction was conducted at the room temperature.

2.7. Catalytic activity—NO reduction

Reduction of nitrogen oxide (2800 ppm) was carried out by propene (4300 ppm) in the presence of different amounts of oxygen in a flow reactor at 370 °C.

The flow rate of the reaction gases (NO, C_3H_6 and O_2 diluted in helium) was 35 ml/min (GHSV = 31 500 h^{-1}), the content of NO and C_3H_6 was constant and concentrations of oxygen were selected to provide a desired value of R.

The coefficient R was calculated from the formula given by Tanaka et al. [15]:

$$R = \frac{[NO] + 2[O_2]}{9[C_3H_6]}$$

The paper presents the activities of the catalysts determined at different values of the coefficient R corresponding to the reducing $R < 1$, stoichiometric $R = 1$, and oxidising $R > 1$ conditions. The reaction products were subjected to chromatographic analysis.