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CO oxidation catalysts based on copper and manganese or cobalt oxides supported on MgF_2 and Al_2O_3

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Abstract

The catalytic activity of a mixed phase of copper–cobalt and copper–manganese oxides supported on magnesium fluorine or alumina has been studied in low temperature CO oxidation at 30 °C. During calcination, the oxides studied partially react to form different type spinels depending on the calcination temperature. These spinels have different effect on the catalytic activity. In low temperature CO oxidation the copper–manganese catalysts are more active than the copper–cobalt ones.

Keywords: CO oxidation; Copper-manganese or cobalt oxides; MgF_2; Al_2O_3

1. Introduction

The best catalysts for low temperature CO oxidation are noble metals [1–3], however, their high price prompts the search for cheaper systems. The promising cheaper catalysts are oxides of transition metals, copper among them. The catalysts containing copper oxide are well known to be active in catalytic oxidation of carbon monoxide, hydrocarbons and ammonia [4,5]. The activity of copper oxide based catalysts can be tailored either by the support or by introduction of different modifiers. The modifiers often used together with copper oxide are manganese oxides [6] or cobalt oxides [7,8]. The most often applied supports for such catalysts are the oxides: Al_2O_3 [9,10], SiO_2 [11], TiO_2 [12] and ZrO_2 [13].

In this study we decided to test a support without oxygen in its structure, that is magnesium fluoride. Magnesium fluoride has been already tested as a support of metallic phases in the processes of hydrogenation of chlorofluorocarbons [14,15] and sulphur containing compounds [16,17]. Its surface shows very weak acid–base properties, it has a mesoporous structure and thermal resistance up to ~500 °C [18]. In this study we were interested in catalytic properties of double oxide phases: copper–manganese and copper–cobalt, supported on this unconventional support. Such systems have not been tested in low temperature CO oxidation. For comparison, analogous measurements were performed over similar active phases supported on an alumina calcined at different temperatures.

2. Experimental

Magnesium fluoride was obtained in the reaction of magnesium carbonate with 20% aqueous solution of hydrofluoric acid. After drying at 105 °C the support was calcined for 4 h at 400 °C [19]. Aluminium oxide was prepared by hydrolysis of aluminium isopropoxide according to an earlier described procedure [20]. The aluminium hydroxide obtained after washing out of isopropyl alcohol was dried at 110 °C for 24 h, then calcined at 400, 550 or 950 °C for 4 h.

The co-impregnated copper–manganese oxides/MgF_2 and copper–manganese oxides/Al_2O_3 catalysts were obtained by introduction of calcined magnesium fluoride or aluminium oxide of the mesh size 0.2–0.5 mm to an aqueous solution of a mixture of $Cu(NO_3)_2{\cdot}3H_2O$ and $Mn(CH_3COO)_2{\cdot}4H_2O$. The samples were evaporated, dried and calcined again. Copper(II) nitrate and manganese(II) acetate were introduced to the solutions in the amounts needed to obtain a desired weight proportions of Cu/Mn of 1/1, 1/2, 1/4. The samples are labelled as Cu_2Mn_x/F-4 and Cu_2Mn_x/A-T, where “2” is the content of Cu in wt.%, and “x” is the content of Mn in wt.%, F-MgF_2, A-Al_2O_3 and “T” refers to the calcination temperature: 4–400, 5–550, 9–950 °C. The co-impregnated copper–cobalt oxides/MgF_2 and copper–cobalt oxides/Al_2O_3 catalysts were obtained

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Table 1
Characterization of the supports

Catalyst	Temperature of calcination (°C)	Surface area (m^2/g)	Structure
F-4	400	42	Well crystallized, rutile-type structure
A-4	400	270	Very poor crystallized, mixture of γ and χ phases
A-5	550	205	Very poor crystallized, mixture of γ and χ phases
A-9	950	179	Poor crystallized, mixture of γ and χ with an admixture of δ oxide

in the same way as the above Cu_2Mn_x samples. Aqueous solutions of the mixtures of $Cu(NO_3)_2{\cdot}3H_2O$ and $Co(NO_3)_3{\cdot}9H_2O$ were used for the impregnation. The amounts of copper(II) and cobalt(III) nitrates 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" is the concentration of Cu, "*x*" the concentration of Co in wt.%, and "*T*" refers to the calcination temperature: 4–400, 5–550, 9–950 °C.

The catalyst activity in the oxidation of carbon monoxide was tested in a continuous-flow reactor, placed in a thermostat bath, after 15 min on time on stream. The conditions of the catalytic tests were as follows: reaction temperature 30 °C, 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.

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.

3. Results and discussion

A short characterisation of the supports is given in Table 1. MgF_2 after calcination at 400 °C revealed a well-developed crystalline phase, while the aluminium oxides were poorly crystalline and their crystallinity increased with increasing the temperature of calcination. The surface area of MgF_2 was the smallest, about seven times smaller than that of Al_2O_3 calcined at 400 °C. The surface area of the supports loaded with the oxide phases decreased after the final calcination. For catalysts supported on MgF_2 the decrease reached even 1/4 of the initial value, while for aluminium oxide the changes were insignificant. The exception were the catalysts $2Cu_xMn$/A-9 calcined at 950 °C, whose surface area at 4 wt.% and 8 wt.%% Mn content decreased to 63 m^2/g, and 12 m^2/g, respectively.

As follows from our earlier study, the optimum amount of copper oxide supported on MgF_2 corresponds to 2 wt.% Cu [21]. This amount of Cu oxide was also used in this study and the concentration of the other component was changed. According to literature data, the copper oxide catalysts deactivate to some extent during CO oxidation [22]. For this reason in this study the initial activity of the catalysts was measured after 15 min of time on stream. Fig. 1 presents the activities of copper–manganese catalysts supported on MgF_2 and Al_2O_3 in CO oxidation. The best performance was obtained over catalysts supported on MgF_2 (Fig. 1a). Within the experimental error all Mn containing catalysts had similar activity (see Fig. 1a). The most important factor determining the activity of the catalysts supported on Al_2O_3 proved to be the calcination temperature. The activity of the samples calcined at 400 °C was very weak (Fig. 1a), whereas that of the samples calcined at high temperatures (550 and 950 °C) were active (Fig. 1b). The highest activities were obtained for the catalysts calcined at 550 °C.

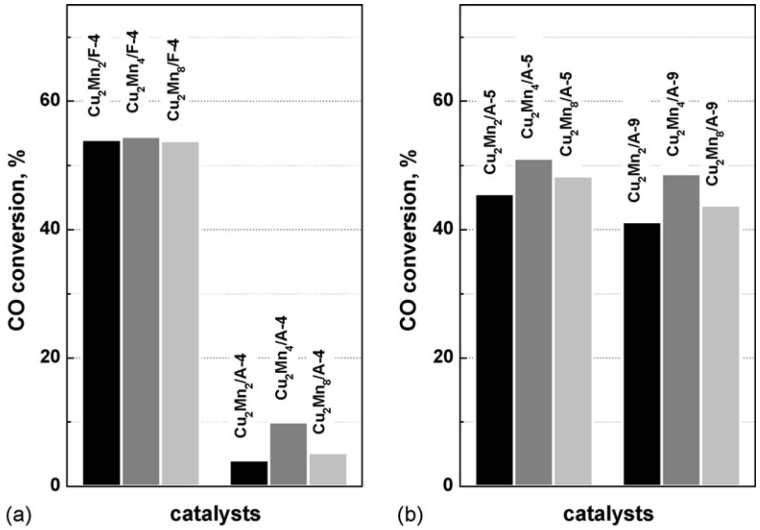

Fig. 1. Catalytic activity in CO oxidation at 300 °C after 15 min on stream of copper and manganese oxides supported on MgF_2 (a) and alumina calcined at 400 °C (a), 550 and 950 °C (b) in CO oxidation.

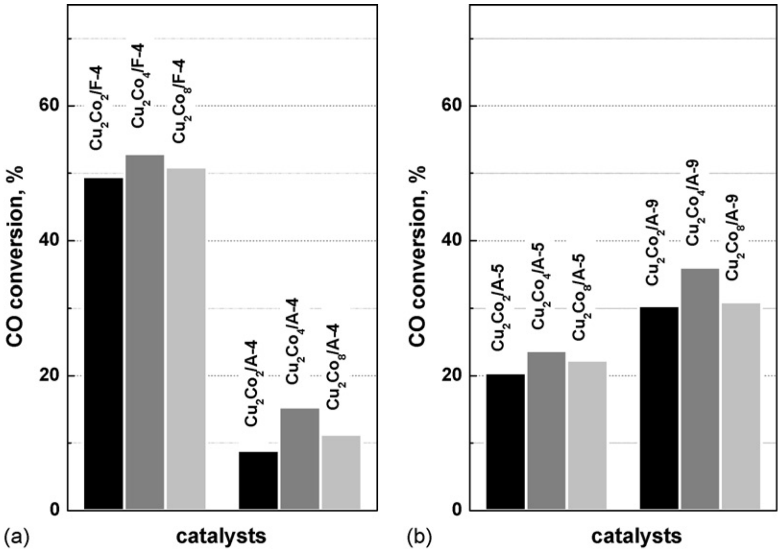

Fig. 2. Catalytic activity in CO oxidation at 300 °C after 15 min on stream of copper and cobalt oxides supported on MgF_2 (a) and alumina calcined at 400 °C (a), 550 and 950 °C (b) in CO oxidation.

Fig. 2 presents the activities of the copper catalysts modified with cobalt oxide, supported on MgF_2 and Al_2O_3. The catalysts on MgF_2 were much more active than those on Al_2O_3. The best performance was observed over the catalyst containing 2 wt.% Cu and 4 wt.% Co (Cu_2Co_4/F-4). These ratios were also the best for alumina based samples. The activity of the catalysts supported on Al_2O_3 strongly depended on the calcination temperature, similarly as over copper–manganese catalysts. Contrary to the copper–manganese catalysts, the activity of copper–cobalt/Al_2O_3 catalysts increased gradually with the temperature of calcination. The highest activity was obtained after calcination at 950 °C (Fig. 2a and b).

Analysis of results obtained in CO oxidation over Cu/MgF_2 catalysts modified with manganese or cobalt oxides has shown that the activities are slightly higher over Cu–Mn oxide mixtures. The same observation holds for the alumina supported catalysts, except the sample calcined at 400 °C.

It has already been shown that single oxide catalysts are less active than mixed oxides ones [23]. Indeed, in our study the conversion of CO over the Cu_2/F-4 single oxide catalyst was only 17%. The catalyst activity is determined by the phases formed on their surface as a result of the surface reactions taking place during the calcination. It is supposed that in the Cu–Mn catalysts the most active phase for low temperature CO oxidation is an amorphous $CuMn_2O_4$ spinel [23,24]. In the most active Cu–Mn catalysts supported on MgF_2 studied such a phase exists, as indicated by the XRD spectra shown in Fig. 3. The intensity of the signals assigned to the spinels $CuMn_2O_4$ ($2\Theta = 36.1$) and Mn_2O_3 ($2\Theta = 30.5$ and 32.5) increases with raising the manganese content, which suggests increasing crystallinity of the phases. In the most active catalyst the Cu/Mn ratio was 1:2, exactly like in the $CuMn_2O_4$ spinel. Further crystallisation of the spinel or an excess of manganese oxides does not promote catalytic activity. Therefore, the phase most likely to control the catalyst activity seems the amorphous or poorly crystallised $CuMn_2O_4$ spinel.

In the copper–cobalt catalysts supported on MgF_2, besides copper and cobalt oxides, a new phase formed after calcination is probably the $CuCo_2O_4$ spinel. For the catalysts supported on Al_2O_3, the situation is more complicated as besides the reaction between the supported phases each of them reacts with the support. As a result, the following spinels: $CuAl_2O_4$ [25,26], $CoAl_2O_4$ [27] are formed. Only a small amount of manganese oxide reacts with the support to form the spinel $MnAl_2O_4$, as this process takes place above 900 °C [28,29]. For the Cu–Co system, the analysis of XRD data is difficult because three different compounds, such as Co_3O_4, $CuCo_2O_4$, $CoAl_2O_4$, have comparable XRD patterns: Therefore, it is impossible to distinguish which phase is present in our copper–cobalt

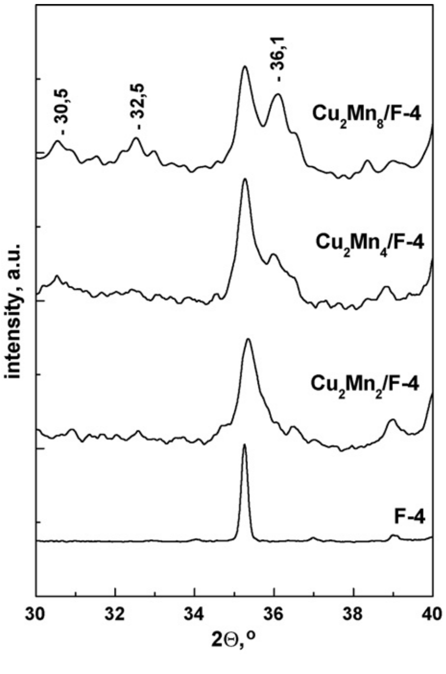

Fig. 3. X-ray diffraction patterns of Cu–Mn catalysts supported on MgF_2.

samples. The catalysts studied have a rather low content of the oxides, which is responsible for the poor quality XRD patterns. It is known from literature that the $CuCo_2O_4$ spinel is formed at 200–300 °C [30]. However, taking into account a distinct dependence between the catalytic activity of catalysts calcined at high temperature and the best proportion of Cu/Mn or Cu/Co equal to 1:2, we suppose that the most active phases are copper–manganese and copper–cobalt spinels. The unreacted Cu, Co and Mn oxides seem to play a smaller role in the CO oxidation reaction. Similarly, the low-temperature (calcined at 400 °C) alumina based double oxide catalysts with a high content of these unreacted oxides show low activities.

Analysis of the effect of the supports MgF_2 and Al_2O_3 on the performance of the copper–manganese and copper–cobalt catalyst clearly indicates a better performance of magnesium fluoride.

4. Conclusions

1. MgF_2 performance as a support for copper–manganese and copper–cobalt phases is better than that of Al_2O_3.
2. The copper–manganese catalysts are more active in CO oxidation than the copper–cobalt ones.
3. The active phases in CO oxidation are the spinels formed during calcination of copper–manganese and copper–cobalt catalysts.

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References

[1] K. Ruth, M. Hayes, R. Burch, S. Tsubota, M. Haruta, Appl. Catal. B 24 (2000) L133.
[2] C.K. Costello, M.C. Kung, H.-S. Oh, Y. Wang, H.H. Kung, Appl. Catal. 232 (2002) 159.
[3] G.B. Hoflund, S.D. Gardner, D.R. Schryer, B.T. Upchurch, E.J. Kielin, Appl. Catal. B 6 (1995) 117.
[4] A. Severino, J.L. Brito, J. Lain, J.L.G. Fierro, A. López Agudo, J. Catal. 177 (1998) 82.
[5] H. Hamada, Catal. Today 22 (1994) 21.
[6] N.B. Stankova, M.S. Khristova, D.R. Mehandjiev, J. Colloid Interf. Sci. 241 (2001) 439.
[7] D. Panatayov, Appl. Catal. 34 (1987) 65.
[8] D. Panatayov, J. Catal. 156 (1995) 219.
[9] P. Artizzu, E. Garbowski, M. Primet, Y. Brulle, J. Saint-Just, Catal. Today 47 (1999) 83.
[10] K. Sun, J. Liu, N.D. Browning, Appl. Catal. B 38 (2002) 271.
[11] P. Carniti, A. Gervasini, V.H. Modica, N. Ravasio, Appl. Catal. B 28 (2000) 175.
[12] T. Miyadera, Appl. Catal. B 16 (1998) 155.
[13] D. Pietrogiacomi, D. Sannino, S. Tuti, P. Ciambelli, V. Indovina, M. Occhiuzzi, F. Pepe, Appl. Catal. B 21 (1999) 141.
[14] A. Malinowski, W. Juszczyk, J. Pielaszek, M. Bonarowska, M. Wojciechowska, Z. Karpiński, Stud. Surf. Sci. Catal. 130 (2000) 1991.
[15] A. Malinowski, W. Juszczyk, J. Pielaszek, M. Bonarowska, M. Wojciechowska, Z. Karpiński, J. Chem. Soc., Chem. Commun. (1999) 685.
[16] M. Wojciechowska, M. Pietrowski, S. Lomnicki, J. Chem. Soc., Chem. Commun. (1999) 463.
[17] M. Wojciechowska, M. Pietrowski, B. Czajka, Catal. Today 65 (2001) 349.
[18] M. Wojciechowska, M. Zieliński, M. Pietrowski, J. Fluorine Chem. 120 (2003) 1.
[19] M. Wojciechowska, R. Fiedorow, J. Fluorine Chem. 15 (1980) 443.
[20] F.S. Stone, L. Whalley, J. Catal. 8 (1967) 173.
[21] M. Wojciechowska, J. Haber, S. Lomnicki, J. Stoch, J. Mol. Catal. 141 (1999) 155.
[22] T.-J. Huang, D.-H. Tsai, Catal. Lett. 87 (2003) 173.
[23] S.B. Kanungo, J. Catal. 58 (1979) 419.
[24] G.J. Hutchings, A.A. Mirzaei, R.W. Joyner, M.R.H. Siddiqui, S.H. Taylor, Appl. Catal. A 166 (1998) 143.
[25] J.A. Anderson, C. Marquez-Alvarez, M.J. Lopez-Munoz, I. Rodriguez-Ramos, A. Guerrero-Ruiz, Appl. Catal. B 14 (1997) 189.
[26] W.M. Shaheen, Thermochim. Acta 385 (2002) 105.
[27] D. Stoyanova, M. Christova, P. Dimitrova, J. Marinova, N. Kasabova, D. Panayotov, Appl. Catal. B 17 (1998) 233.
[28] L.M. Gandia, M.A. Vicente, A. Gil, Appl. Catal. 196 (2000) 281.
[29] P.-O. Larsson, A. Andersson, Appl. Catal. B 24 (2000) 175.
[30] W.M. Shaheen, A.A. Ali, Mater. Res. Bull. 36 (2001) 1703.