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Effect of MgF_2 and Al_2O_3 supports on the structure and catalytic activity of copper–manganese oxide catalysts

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Structure and catalytic activity of double copper–manganese oxide catalysts supported on MgF_2 and Al_2O_3 have been studied. All samples were calcined at 400 °C and those supported on Al_2O_3 also at 550 and 950 °C. The properties of surface species have been characterized by low temperature adsorption of nitrogen, XRD and TPR-H_2. The catalytic activities have been tested in low-temperature CO oxidation and in NO reduction by propene. The supported oxides react with each other during calcination to form $CuMn_2O_4$ spinel. The spinel seems to be responsible for the catalytic activity of the double copper–manganese catalysts. The temperature of calcination changes the strength of interaction between the active phase and the supports influencing the catalytic activity.

KEY WORDS: copper–manganese oxide catalysts; CO oxidation; NO reduction; TPR; XRD; MgF_2; Al_2O_3.

1. Introduction

Transition metal oxides have been widely used as catalysts of oxidation and dehydrogenation processes. They are usually deposited on supports whose role is to increase their effectiveness. The most often applied active phases include copper and manganese oxides, usually supported on Al_2O_3 [1–6], SiO_2 [7–9], TiO_2 [9, 10] or ZrO_2 [11, 12]. The support influences the surface structure of the active phase complexes taking part in the catalytic process, so the proper choice of the support is of great importance.

A very interesting although little known support is magnesium fluoride [13]. It has almost chemically inert surface, good thermal stability up to ~500°C [14] and high hardness. Its surface of mesoporous structure is relatively large (~45 $m^2\ g^{-1}$). Earlier studies on transition oxides and metallic active phases supported on MgF_2 have provided active and selective catalysts in thiophene hydrodesulfurisation [15, 16], hydrodechlorination of chloro-fluoro-hydrocarbons [17, 18], reduction of NO [19] and oxidation of CO.

The present study has been undertaken to examine the performance of mixed copper–manganese oxide systems supported on MgF_2. According to the preliminary results [20], the Cu–Mn–O/MgF_2 catalysts show high activity in the reaction of NO reduction with propene. However, the lack of detail characterisation of the system studied has prompted us to make an attempt at determination of the structure of such catalyst surface as a function of the concentration of the active phases, and at identification of the type of complexes responsible for the reactions of CO oxidation and NO reduction with propene. For comparison, analogous systems supported on Al_2O_3 – a commonly used support – have also been tested.

2. Experimental

2.1. Preparation of catalysts

Magnesium fluoride was obtained in the reaction of aqueous solutions of magnesium carbonate and 20% hydrofluoric acid. After drying at 105 °C the support was calcined for 4 h at 400 °C [21]. Aluminium oxide was prepared by hydrolysis of aluminium isopropoxide according to an earlier described procedure [22]. The obtained aluminium hydroxide washed out of isopropyl alcohol, was dried at 110 °C for 24 h, then calcined at 400, 550 or at 950 °C for 4 h.

The obtained magnesium fluoride of the mesh size 0.2–0.5 mm was impregnated with $Cu(NO_3)_2{\cdot}3H_2O$ dissolved in H_2O. The appropriate amount of copper nitrate was added to obtain 2 wt% Cu content. The water was evaporated on continuous stirring and then the solid was dried at 105 °C for 24 h. Finally, it was calcined at 400 °C for 4 h. The sample was labelled as Cu_2/F-4, where "2" is the wt% copper content in and 4 means the calcination temperature 400 °C.

MnO_x/MgF_2 were obtained in a similar way as the copper catalyst, with manganese introduced from the

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aqueous solution of $Mn(CH_3COO)_2{\cdot}4H_2O$ to get 2, 4 and 8 wt% content of manganese. The samples were labelled as Mn_x/F-4, where "*x*" stands for the content of Mn in wt%, while 4-indicates the calcination temperature (400 °C).

Copper and manganese oxides were supported on Al_2O_3 in the same way as on MgF_2. The samples were calcined at 400 or 550 or 950°C for 4 h and were labelled as Cu_2/A-T or Mn_x/A-T, where "2" is wt% the content of copper, "*x*" is wt% the content of manganese, while *T* is the temperature of calcination (400, 550, 950 °C).

The co-impregnated catalysts CuO–MnO/MgF_2 and CuO–MnO/Al_2O_3 were obtained by introduction of calcined magnesium fluoride or aluminium oxide of the mesh size 0.2–0.5 mm to aqueous solutions of a mixture of $Cu(NO_3)_2{\cdot}3H_2O$ and $Mn(CH_3COO)_2{\cdot}4H_2O$. The water was evaporated, and the solids were dried and calcined in the same way as monoxide catalysts. The amounts of copper (II) nitrate and manganese (II) acetate were chosen to obtain the desired weight proportions of Cu/Mn of 1/1, 1/2, 1/4. The samples were labelled as Cu_2Mn_x/F-4 and Cu_2Mn_x/A-T, where "2" is the wt% content of Cu, and "*x*" is the wt% content of Mn, while "*T*" is the temperature of calcination (400, 550 or 950 °C).

2.2. UV–VIS spectra

The contents of metals in the catalysts were determined by the UV–VIS spectrometry. The content of copper was determined using the reaction of Cu(II) with sodium dietyldithiocarbamate at pH ranging from 4 to 11. Absorbency was measured at 436 nm. The content of manganese was determined using the reaction of manganese ions with 1-(2-pyridylazo)-2-naphtholo (PAN) at pH ranging from 8 to 10. Absorbency was measured at 564 nm.

2.3. Surface area

Low temperature (−196 °C) adsorption of nitrogen was performed by a ASAP 2010 Micromeritics sorptometer. Specific surface area was determined using the BET method and the pore size distribution was evaluated on the basis of the BJH method, using a desorption isotherm.

2.4. XRD spectra

X-ray examination was carried out with an M-62 diffractometer working with a HZG-3 powder goniometer employing Cu Kα radiation with a Ni filter. The 2Θ range of measurement was 20–70° and step size 0.01°.

2.5. TPR-H_2

The temperature programmed reduction experiments were carried out with an ASAP ChemiSorb 2705 (Micromeritics). Portions of 100 mg of the catalyst or 15–20 mg of unsupported oxides were reduced in a mixture of 10 vol. % H_2 in Ar (99.999%) at a flow rate of 30 $cm^3\ min^{-1}$, and at 10°C min^{-1} heating rate up to a final temperature of 800 °C.

2.6. CO oxidation

The catalyst activity in the oxidation of CO was tested in a flow reactor placed in a thermostat bath after 15 min on stream. The conditions of the catalytic tests were as follows: 30 °C, catalyst weight −0.1 g, reaction mixture: 15 ml min^{-1} of 1% vol. CO in helium and 55 ml min^{-1} of air. 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.

2.7. NO reduction

Reduction of NO was carried out by propene in the presence of oxygen in a flow reactor at 370 °C. The flow rate of the reaction gases (NO of purity ≥99.999%), C_3H_6 (≥99%) and O_2 (≥99.999%) diluted in helium (≥99.999%)) was 35 ml min^{-1} (GHSV = 21000 h^{-1}), and the content of individual components was selected to provide a desired proportion of NO and O_2. The proportion of NO/O_2 has changed from 0,4 for $R < 1$ to 0,05 for $R > 1$. The paper presents the activities of the catalysts after 2 h on stream determined at different values of the *R* coefficient corresponding to the reducing $R < 1$, stoichiometric $R = 1$, and oxidising $R > 1$ conditions. This coefficient was calculated from the formula given by Tanaka et al. [23]:

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

The reaction products were subjected to chromatographic analysis using liquid nitrogen cold trap to separated N_2 from nitric oxides. The products were analysed using Carlo Erba 6000 GC equipped with 2 m long column filled with 13 X molecular sieves (2/3) and chromosorb 104 (1/3).

3. Results

3.1. Low-temperature N_2 adsorption

The characterization of catalysts supported on MgF_2 is given in Table 1. The concentration of copper oxide in the catalysts was constant of 2 wt% of Cu, while the concentration of manganese oxides was ~2, 4 or 8 wt% Mn. Introduction of copper–manganese active phases on MgF_2 resulted in a decrease of its surface area and pore volume, while the mean pore diameter increased. The loading of 2 wt% of Mn reduced the surface area by ~9%, while the loading of 4 and 8 wt% reduced the surface area by almost 1/3. The behaviour of the catalysts supported on Al_2O_3 was different. The CuMn

Table 1
Characterisation of copper–manganese catalysts supported on MgF_2 or Al_2O_3

Catalysts	Calcination temperature (°C)	Content of active phase (wt%)		Average pore diameter (Å)	Pore volume ($cm^3\ g^{-1}$)	Surface area ($m^2\ g^{-1}$)
		Cu	Mn			
F-4	400	0.00	0.00	154	0.21	42
Cu_2Mn_2/F-4	400	1.92	1.84	213	0.20	38
Cu_2Mn_4/F-4	400	1.88	3.83	206	0.19	29
Cu_2Mn_8/F-4	400	1.95	7.75	199	0.15	29
A-4	400	0.00	0.00	45	0.41	270
Cu_2Mn_2/A-4	400	1.78	1.83	34	0.40	253
Cu_2Mn_4/A-4	400	1.99	4.03	35	0.39	249
Cu_2Mn_8/A-4	400	1.79	7.99	36	0.37	252
A-5	550	0.00	0.00	40	0.42	205
Cu_2Mn_2/A-5	550	1.88	1.83	30	0.40	243
Cu_2Mn_4/A-5	550	1.92	3.72	29	0.40	240
Cu_2Mn_8/A-5	550	1.01	8.10	29	0.39	239
A-9	950	0.00	0.00	35	0.28	179
Cu_2Mn_2/A-9	950	2.21	2.02	32	0.20	164
Cu_2Mn_4/A-9	950	2.12	4.21	26	0.19	63
Cu_2Mn_8/A-9	950	2.23	7.88	22	0.12	12

catalysts calcined at 400 and 550 °C revealed a small decrease in the surface area, irrespective of the amounts of manganese introduced, whereas, the surface area of the catalysts calcined at 950 °C rapidly decreased with increasing content of Mn.

3.2. X-ray study

Figure 1 presents X-ray diffractograms of MgF_2, monoxide catalysts, unsupported mixture of the oxides and the catalyst Cu_2Mn_4/F-4. The unsupported mixture (Cu_2Mn_2-4) composed of copper and manganese oxides was prepared in order to identify the type of crystalline phases forming in the copper–manganese double oxide catalysts. It was obtained by mixing of copper nitrate with manganese acetate and calcination of the mixture at 400 °C. The spinel phase $CuMn_2O_4$ gives a peak at $2\Theta = 36°$ [19]. The signal was observed in the diffractograms of the unsupported mixture and the catalyst Cu_2Mn_4/F-4. The same spinel structure was reported for the mixed copper manganese oxides in the form of hopcalite after calcination at 400 °C and at higher temperatures [24]. Apart from the spinel, the diffraction patterns revealed the lines characteristic of CuO and Mn_2O_3, also present in the diffractograms of the respective monoxide catalysts.

The diffraction patterns of the Cu–Mn catalysts supported on Al_2O_3 and calcined at 400 and 550 °C show exclusively the diffraction lines characteristic of the support, which indicates that after calcination at these temperatures the active phase has amorphous structure. The diffractograms taken of the samples calcined at 950 °C (Fig. 2) show the peaks assigned to CuO and the spinel $CuAl_2O_4$.

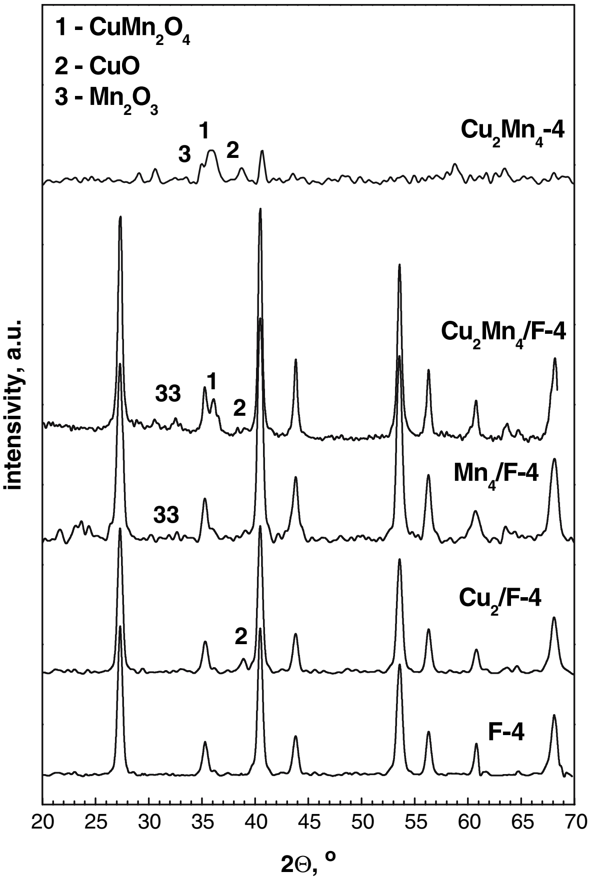

Figure 1. Diffraction patterns of the copper, manganese and copper–manganese catalysts supported on MgF_2 and of the unsupported mixture, all calcined at 400 °C.

A comparison of the diffraction patterns of the catalysts supported on MgF_2 and Al_2O_3 has shown that magnesium fluoride permits development of the crystalline phases at lower temperatures than on Al_2O_3. Moreover, on MgF_2 the copper and manganese oxides interact forming the crystallites of $CuMn_2O_4$ spinel whose formation has not been evidenced for the samples supported on Al_2O_3 on which the spinel $CuAl_2O_4$ appears.

3.3. Temperature programmed reduction H_2

Additional information on the state of the supported oxide phases has been provided by the temperature-programmed reduction with hydrogen. Fig. 3a presents the reduction profiles of the unsupported oxides mixture (Cu_2Mn_2-4) and of individual oxides supported on MgF_2. The profile of Cu_2/F-4 shows a complex reduction signal with three low-intensity maxima. Because of the changes in copper valency upon reduction, the appearance of only 2 peaks was expected, the third one can be related to the highly dispersed oxide. According to the literature data on copper oxide supported on SiO_2 [25] or ZrO_2 [26] well-dispersed CuO is much easier reducible than bulk CuO. Therefore, the first stage of

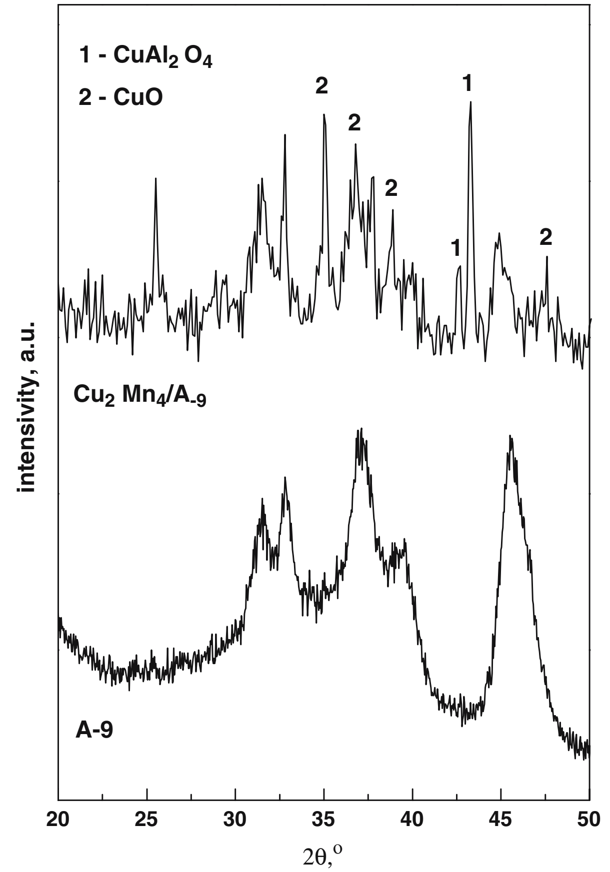

Figure 2. Diffraction patterns of Al_2O_3 and copper–manganese catalysts supported on Al_2O_3 calcined at 950 °C.

the reduction (285 °C) could be related to well-dispersed copper oxide [27]. The profile of manganese oxide shows two very broad peaks at ~295 and ~432 °C, assigned to the reduction of MnO_2 or Mn_2O_3 to Mn_3O_4, and then to MnO [28]. The profile of the unsupported mixture reveals two maxima at 333 and 390 °C. Fig. 3b shows the reduction profiles of double oxide catalysts supported on MgF_2. The peaks in these profiles are shifted towards lower temperatures relative to those of individual phases, except for the profile of the sample with the highest content of manganese. The authors of [29] assigned this course of reduction to the spinel $CuMn_2O_4$. The profile of the catalyst of the lowest content of manganese (Cu_2Mn_2/F-4) shows a single peak with weak shoulders. With increasing manganese content, the peak splits into two maxima. Reduction of the excessive copper and manganese oxides, not bound in the spinel, cannot be excluded as the temperatures of their reduction are partly overlapped by the range of temperatures corresponding to the reduction of the double oxide catalyst.

Reduction profiles of the samples supported on Al_2O_3 are presented in Fig. 4. The profiles of individual copper and manganese phases after calcination at 400 °C are weak and broad with single maxima at 305 and 384 °C, respectively, Fig. 4a. The profile of the corresponding double oxide catalyst is asymmetric with maximum at 306 °C. The peaks in the profiles of the monoxide catalysts supported on the high-temperature alumina (A-9) are highly intense. The profiles of monoxide preparations calcined at 550 °C are similar and intensities of the profile signals are intermediate between those of the samples supported on Al_2O_3 and calcined at 400 or 950 °C. These differences are most probably related to the strength of the interactions between the oxides supported and the support, they are significant for the low-temperature support and small for the high-temperature one. In the binary systems the mode of interactions of the oxides supported with the support changes, which is manifested by the appearance of intense signals of reduction assigned to the

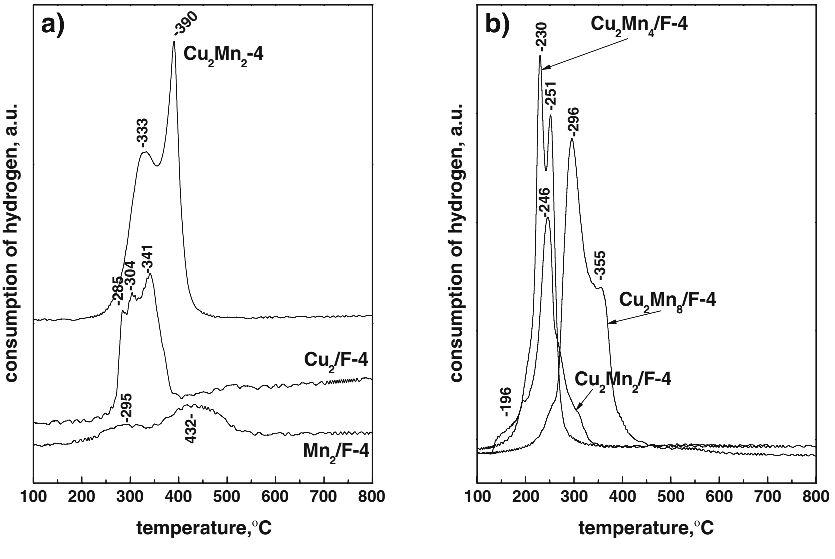

Figure 3. TPR-H_2 profiles of the unsupported mixture, monoxide catalysts (a) and double oxide catalyst (b) supported on MgF_2 and calcined at 400 °C.

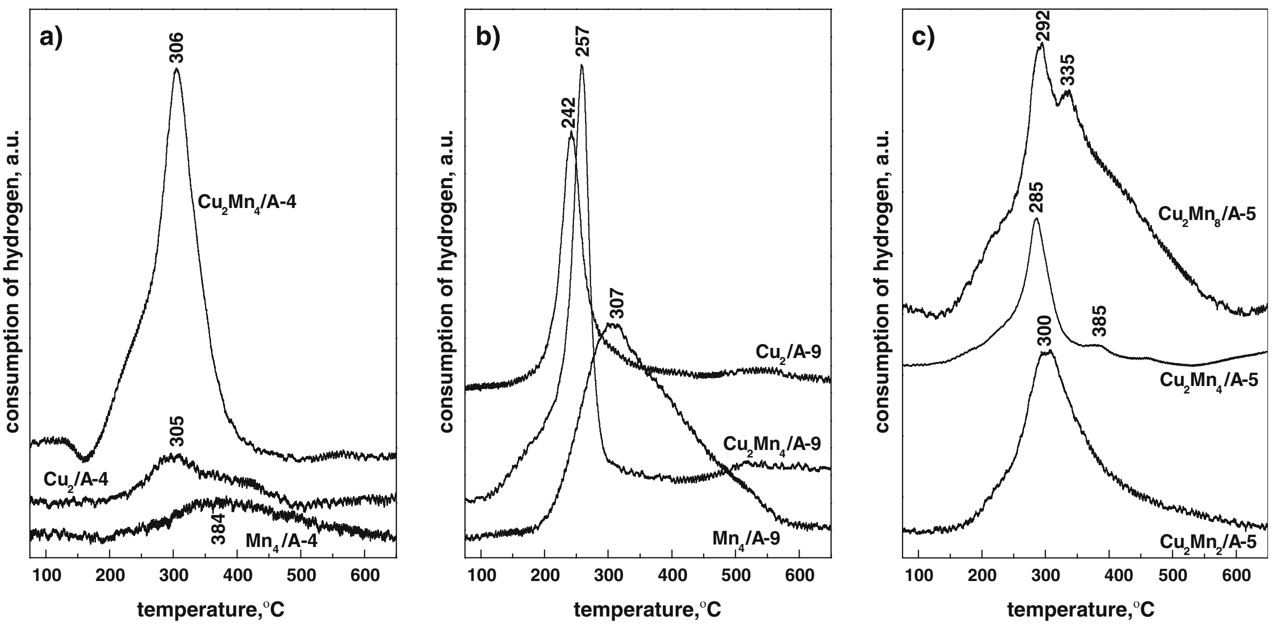

Figure 4. TPR-H_2 profiles of the monoxide catalysts and double oxide catalyst supported on Al_2O_3 and calcined at 400 °C (a) and at higher temperatures (b), (c).

phase not strongly interacting with the support. Not only copper but also manganese are in this phase as evidenced by the reduction profiles shown in Fig. 4 (the manganese phase disappears to the advantage of the joint phase in the Cu_2Mn_4/alumina catalysts) and the changes in the reduction profiles with increasing content of manganese in the catalysts calcined at 550 °C, Fig. 4c. In these catalysts only an excess of manganese leads to the appearance of the second reduction signal at 335 °C accompanied by the broadening of the profile towards higher temperatures. Most probably, the copper and manganese compound obtained as a result of a reduction to a new phase is the $CuMn_2O_4$ spinel, not detected by XRD because it is amorphous. A characteristic feature is that the maxima of reduction of this new phase are shifted towards lower temperatures (over ~50 °C) with increasing temperature of the support calcination reaching the same value as those of the catalysts supported on MgF_2 (~250 °C). This observation can be related to the strength of the interaction of the new phase formed on Al_2O_3-higher in the low-temperature catalysts and lower in the high-temperature ones.

3.4. Catalytic activity

The catalysts were tested in the reactions of CO oxidation and NO reduction with propene. The catalytic activity of the copper–manganese catalysts differed significantly depending on the type of the support.

In the reaction of CO oxidation particularly active among all transition metals are copper oxides. Their activity is higher than that of manganese oxides [24, 30]. In our study the most active among monoxide catalysts was the copper catalyst supported on MgF_2; the CO conversion at room temperature reached 40%. The activity of CuO supported on Al_2O_3 was much lower and the conversion of CO over the most active sample Cu_2/A-9 did not reach 15%. Introduction of manganese oxide as the second component caused an increase in the catalytic activity. Fig. 5 presents the activity of double oxide catalysts. The degree of conversion depends on the type of support used and calcination temperature. The use of magnesium fluoride ensures high activity varying insignificantly with the Cu/Mn ratio. The activity of the double oxide catalysts supported on Al_3O_3 and calcined at 400 °C was much lower than that of those supported on MgF_2. The catalysts supported on Al_2O_3 calcined at higher temperatures (550 and 950 °C) showed activities comparable with that of the catalysts supported on MgF_2.

The effect of manganese as the second component of the copper–manganese catalysts was well pronounced in the reaction of NO reduction with propene. Similarly as in CO oxidation, the mixed catalysts were more active than the monoxide ones. The most active monoxide catalyst Cu_2/F-4 gave the NO conversion reaching 60% in the reducing, almost 50% in stoichiometric and 42% in the oxidising conditions. Much less active were the monoxide catalysts supported on Al_2O_3, which provided the degree of conversion not exceeding 26%. The most active double oxide catalysts gave the NO conversion to N_2 reaching over 90%, depending on the composition of the reaction mixture (Fig. 6). In the reducing and stoichiometric conditions the most active was the double oxide catalyst supported on MgF_2. In the oxidising

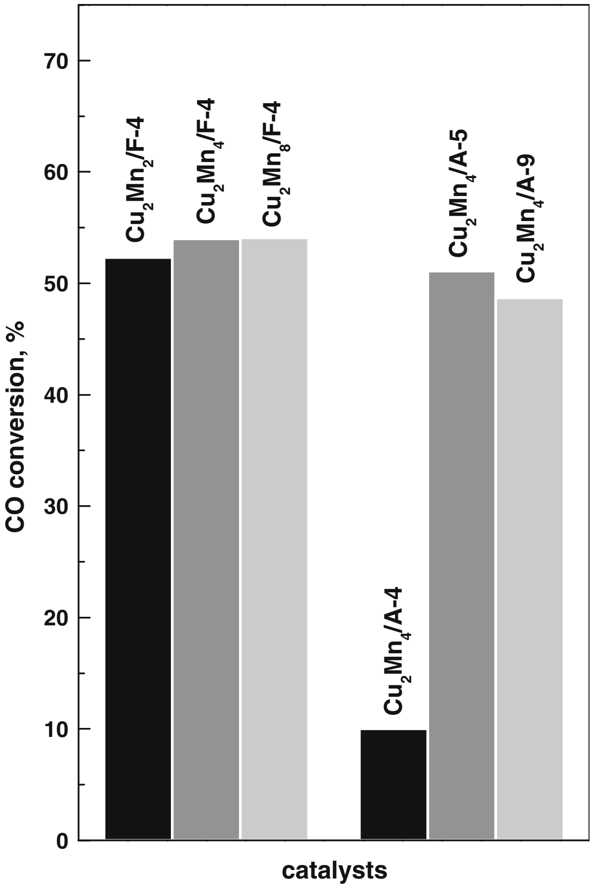

Figure 5. Activity of copper–manganese catalysts in low-temperature CO oxidation.

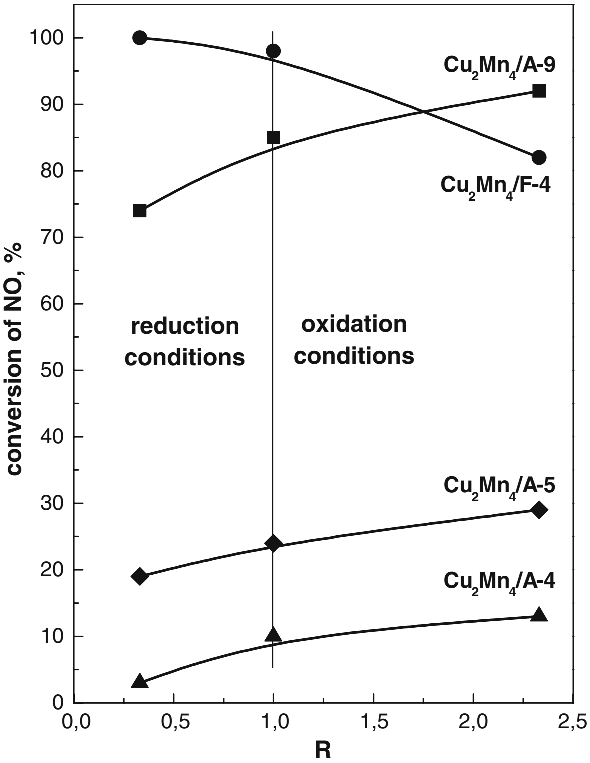

Figure 6. Activity of copper–manganese catalysts in the reaction $NO + C_3H_6$ at 370 °C for different compositions of the reaction mixture.

conditions the performance of the high-temperature Cu_2Mn_4/A-9 catalyst was even better. The activities of the double oxide catalysts supported on Al_2O_3 and calcined at lower temperatures were significantly smaller. Depending on the composition of the reaction mixture their activities changed analogously as that of Cu_2Mn_4/A-9, so they were more active in oxidising conditions. All the systems studied, irrespective of the support, were characterised by high selectivity in NO reduction to N_2, reaching almost 100%.

The weight ratio of Cu to Mn has some effect on the activity of the systems studied. The optimum activity in the NO reduction with propene was observed at the Cu/Mn = 2/4 ratio, like it was for CO oxidation Fig. 7. For the catalysts supported on Al_2O_3 the effect of the Cu/Mn ratio was limited the degree of conversion significantly depending on the calcination temperature: the higher was this temperature the higher was the conversion.

A comparison of the double oxide copper–manganese catalysts supported on MgF_2 and Al_2O_3 in the reactions of CO oxidation and NO reduction has shown that the catalysts supported on MgF_2 were very active and their activities were even higher than that of high temperature Al_2O_3 based catalysts.

4. Discussion

The physicochemical properties of the copper–manganese catalysts depended on the type of the support used. MgF_2 was calcined only at 400 °C, as above this point it undergoes sintering-after calcination at 500 °C its surface area drastically decreases [31]. MgF_2 has a rutile type structure [32] with the outward layer made of fluoride anions. On the MgF_2 surface there is some number of hydroxyl groups (3–4 per nm^2) [31] but twice lower than on Al_2O_3 [33]. The surface of MgF_2 is almost inert with very weak acid–base centres. The acidic centres are the coordinatively unsaturated magnesium ions, while the basic centres are OH^- groups and F^- ions.

The other support used was Al_2O_3. In the temperature range studied (400–950 °C), this support undergoes structural changes from a mixture of γ and χ oxides in A-4 to a mixture of γ and χ with an admixture of δ and traces of α oxides in A-9 [33]. The supports have low crystallinity. The surface of Al_2O_3 has strong acid–base properties therefore, it is used as a catalyst of reactions involving acidic and basic centres. It is also used as a support of different active phases.

Four series of catalysts with the same weight proportions of Cu to Mn were prepared. Because of significant differences in the surface area of the supports used varying from 42 $m^2\ g^{-1}$ for F-4 and 270 $m^2\ g^{-1}$ for A-4, the surface concentration of the active phases also varied over a wide range. The loading of MgF_2 with copper oxide was ~0.4 monolayer (calculated on the basis of CuO density), while the loading of Al_2O_3 varied from ~0.06 for A-4 to ~0.1 for A-9. The loading with manganese oxides (calculated on the basis of Mn_2O_3 density) varied from 0.4 to 1.8 monolayer for F-4, 0.07–0.3 for A-4, 0.07–0.3 for A-5 and 0.1–0.4 for A-9.

The systems obtained by supporting the active copper–manganese phase on MgF_2 and Al_2O_3 revealed different catalytic properties. Particularly active were the catalysts supported on MgF_2. Among the catalyst supported on Al_2O_3 only those calcined at high temperatures ensured comparable conversions. The XRD and TPR-H_2 results have shown that the copper and manganese oxides supported on MgF_2 interact with each other and not with the support, leading to formation of the spinel $CuMn_2O_4$. A similar situation occurs for Al_2O_3 but the difference is that the supported monoxides strongly interact with the support as indicated by the appearance of a new crystalline phase, i.e. the $CuAl_2O_4$ spinel, after calcination at 950 °C. The XRD data indicate that this reaction is not completed and irrespective of the calcination temperature there is still some amount of CuO. As far as manganese oxides are concerned, there is no direct evidence for the presence of crystalline manganese phases. However, a strong decrease in the surface area of the catalysts calcined at 950 °C with increasing content of manganese suggests that manganese oxides also partially react with Al_2O_3. This would be in agreement with literature data indicating the formation of the spinel $MnAl_2O_4$ in the reaction of manganese oxides and Al_2O_3 at ~1000 °C [34]. The compounds formed are well-dispersed and of amorphous structure, so undetectable by the XRD method. Another explanation of the rapid decrease in the surface area of the samples calcined in high temperature is the known phenomenon of transformation of aluminium oxides into the phase α-Al_2O_3 under the effect of manganese that can take place at about 1000 °C [35]. The phase α-Al_2O_3 is characterised by a low surface area.

Analysis of the performance of the Cu/Mn catalysts supported on MgF_2 and Al_2O_3 (Fig. 7) has shown that addition of the manganese oxide affects the catalyst activity. Thus, the catalysts activity should be first of all related to the copper–manganese oxide phase [16, 36, 37]. Such a phase in the double oxide catalyst seems to be the $CuMn_2O_4$ spinel. As follows from the TPR-H_2 data, this spinel is present in all mixed catalysts, but the temperatures of the reduction maxima of the spinel are different for the catalysts on different supports. However, their values are close for the most active catalysts, that is the one of copper–manganese oxide supported on MgF_2 and on the high-temperature Al_2O_3. The samples supported on Al_2O_3 calcined at lower temperatures are the less active and their spinel phase is the most difficult to reduce, probably because of a stronger interaction with the support.

In our earlier study we have tested the effect of copper catalysts doped with cobalt oxides [38]. Therefore, we are now able to conclude that the introduction of manganese oxides instead of cobalt oxides has resulted in obtaining more active catalysts, especially in the NO reduction with propene.

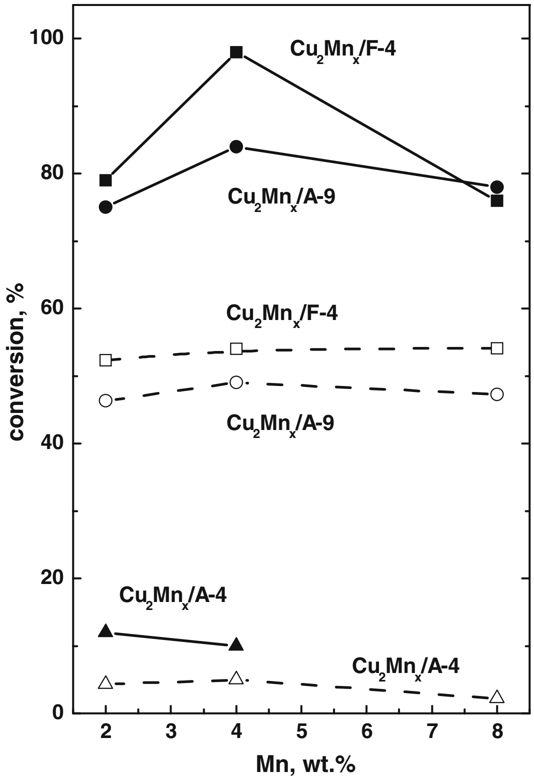

Figure 7. Conversion in the CO oxidation at 30 °C (broken line) and in the NO reduction with propene at stoichiometric conditions (solid line) versus the content of manganese.

5. Conclusions

1. Magnesium fluoride proved to be an interesting support for copper and manganese oxide catalysts very active in CO oxidation and NO reduction with propene.
2. Copper and manganese oxides supported on MgF_2 or Al_2O_3 react during calcination giving very active $CuMn_2O_4$ spinel phase.
3. Interaction between the spinel phase and the support surface influences the catalytic activity; the weaker the interactions the higher the activity.

Acknowledgments

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