Complete Oxidation of Harmful Organic Compounds Over Alumina Supported Cu-Mn Mixed Oxide Catalysts

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The catalytic activity of mixed alumina-supported copper-manganese oxides during complete oxidation of CO, ethylacetate, toluene and benzene is investigated. The samples were prepared by impregnation of γ-Al_2O_3 with aqueous solutions of copper and manganese formates at room temperature and subsequent calcination at 670 K .All samples have been obtained using a fixed ratio between the two components in the impregnating solutions. The use of formates as precursors permits formation of mixed formates and their decomposition without preliminary melting thus resulting in the formations of oxide phases of high dispersity. The content of supported active metals was determined by chemical analysis. The specific surface area of the samples was measured using BET method and the magnetic susceptibility depending on temperature was investigated by the Faraday method at temperatures up to 620 K. The catalytic activity of the catalysts was measured in flow reactor.

Keywords: mixed oxide catalysts; Cu-Mn oxide system; complete oxidation

The purification of harmful organic substances from waste gazes is an important task in respect to environmental protection [1-4]. The main problem of this is the creation of catalysts, active even at low temperatures and low concentration of the harmful component. Irrespective to the large number of publications on this topic the investigations continue in respect to optimization of the processes of complete oxidation of harmful organic substances [5-10].

It is known, that the reactions of complete oxidation on oxide catalysts proceed by oxidation-reduction mechanism. An important condition for this mechanism is the presence of metal couples in a different oxidation state that could be oxidized or reduced so that to be realized the reaction. These metal ions in various oxidation states form catalytic active sites mentioned earlier as catalytc active complex. In this case the oxidation-reduction mechanism in the complete oxidation of organic substances is facilitated by this complex and the catalysts show high activity at low temperatures.

In some of our papers [11,12] it has been shown that cooper-manganese oxides with a spinel-like structure are highly active in the neutalization of various toxic gases such as CO and NO. Mixed cooper and manganese oxides differing in their crystal structure are also known. In recent studies the acetate precursors are often applied for preparation of catalysts by pore volume impregnation of γ-Al_2O_3 instead of traditional metal nitrate solutions [13]. In [14] it has been shown that when copper and manganese formates are used as initial compounds, $Cu_{0.4}Mn_{4.5}O_8$ or $Cu_{1.5}Mn_{1.5}O_4$ can be formed at low temperatures (below 710 K) of formates as precursors permits formation of mixed formates an their decomposition without preliminary melting thus resulting in the formation of oxide phase of high dispersity [15]. This is especially important for the synthesis of supported oxide catalysts. The formation of the catalytically acive oxide phase in this case is a complex process because it is affected both the presence of a chromatographic effect [16] and the crystallization in the pores of the support [17]. The chemical nature of the support on which the spinel phase is formed also influences the catalytic activity [18].

For that reason the present paper is aimed at studying the effect of the coper manganese ratio and the structure of mixed alumina-supported cooper-manganese oxides prepared by using metal formate solution for pore volume impregnation of γ-Al_2O_3 on the catalysts activity during complete oxidation of CO, ethylacetate, toluene and benzene.

Experimental part

The samples were prepared by impregnation of γ-Al_2O_3 (Rhone Poulenc, BET specific surface area of 335 m^2/g, pore volume of 0.46 cm^3/g, grain size of 0.3-0.6 mm) with aqueous solutions of copper and manganese formates at room temperature and subsequent calcination at 670 K as described in [16].

The content of supported active metals was determined by chemical analysis [14]. The specific surface area of the samples investigated was measured by the low temperature adsorption of nitrogen using the BET method. The magnetic susceptibility depending on temperature was investigated by the Faraday method at temperatures up to 620 K.

The catalytic activity of the samples was measured in flow reactor having a mixing system, thermostat regulator for hydrocarbon vapour control and flow controls for air. The analysis was carried out with an on-line Hewlett Packard Gas Chromatograph Model 5840A and using a Chromosorb 102 and Porapak Q packed column [19]. The complete oxidation of benzene and toluene was studied at 100 ppm concentration of hydrocarbon in air and the following space velocities : 10000, 15000 and 20000 h^{-1}.

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Table 1

CATALYST CHARACTERISTICS

Sample	Content of active metals				Specific
	Cu (wt.%)	Mn (wt.%)	ΣCu+Mn (wt.%)	atomic ratio Cu:Mn	surface area (m^2/g)
1	3.80	-	3.80	-	295
2	3.40	0.25	3.65	11.80	312
3	5.30	1.10	6.40	4.20	283
4	1.60	1.10	2.70	1.20	379
5	0.70	1.80	2.50	1.30	378
6	-	2.70	2.70	-	242

When the efficiency of conversion was estimated, a catalyst volume of 0.6-1.0 cm^3, space velocity of 20000 h^{-1}, a CO content of 0.5 vol.%, an ethylacetate content of 0.05 vol.% were used [20]. The inlet and outlet gas mixtures were analyzed on a Unicam Cromatograph with a FID detector. The CO_2 content was determined by an Infralyt analyzer.

Results and discussion

Table 1 summarizes the experimental data obtained by the chemical analysis for the content of the active metals (copper and manganese in the alumina supported phases, the ratio copper manganese in the samples investigated) as well as the results for the BET specific surface. All samples have been obtained using a fixed ratio between the two components in the impregnating solutions. However, the chromatographic effect consisting in predominant adsorption of copper ions significantly changes the present ratio.

The specific surface exhibits an interesting alteration which is evidenced by the table 1. An increase of the values is observed when the mixed oxides are deposited on the support. This is associated with the application of copper and manganese formates as precursors in the presence of which, as already mentioned, decomposition takes place without preliminary melting and this leads to a high active phase dispersion. In this case the crystallization of the formates and the subsequent decomposition to oxides occur in the mesopores and the solid phase formed does not block the pores. On the contrary, it forms oxide agglomerates on the support surface, which enlarges the specific surface area.

In order to elucidate the role of the structure and the ratio between the two metals, it was necessary to identify the phase composition of the oxides on the support surface. The X-ray analysis gave not information in this respect, because the oxide phase was present in a relatively small amount and was amorphous. That is why magnetic measurements were used for identification of the supported metal oxides. As was already pointed out, according to a preliminary paper [14], under these preparation conditions and in the absence of copper, a Mn_5O_8 phase appears, while in the absence of manganese, CuO is obtained. With a low copper content, $Cu_{0.4}Mn_{4.6}O_8$ is obtained whereas the spinel $Cu_{1.5}Mn_{1.5}O_4$ is formed when a Cu: Mn atomic ratio is close to 1.

The probable phase composition of the samples, the magnetic moments calculated on their basis and the values found experimentally by magnetic measurements, were seen in table 2. The formula:

$$\mu_{eff} = 2.828 (\chi_m T \pm \theta)^{½}$$

where:

μ_{eff} - the effective magnetic moment (BM);

χ_m – the molar susceptibility;

θ – Weiss constant (K), was used for calculating the magnetic moments obtained experimentally, and corresponding corrections for diamagnetism of the ions and the support were made.

The value of 100, which is close to that experimentally found in [14] for the spinel, was used for the Weiss constant. The table shows a rather good agreement between theoretical and experimental magnetic moments. This permits assuming that the phases in question are really present on the support surface.

In order to compare the catalytic activities of the samples, the temperatures of 50% conversion (“light-off” temperature) were determined (table 3). The data concerns CO and ethylacetate oxidation.

Obviously, the activities have close values. However, it should be pointed out that the active component contents in them as well as the phase compositions are different.

It was of interest to study the change of the activity depending on the type of the toxic compound. Figure 1

Table 2

POSSIBLE COMPOSITION OF THE SUPPORTED ACTIVE PHASE AND MAGNETIC PROPERTIES OF THE SAMPLES

Sample	Possible composition of the supported active phase	μ_{eff} (BM)	
		theoretical	experimental
1	CuO	molecular antiferromagnetism	
2	$CuO+0.063Cu_{1.5}Mn_{1.5}O_4$	2.52	2.78(θ=150 K)
3	$CuO+0.189Cu_{1.5}Mn_{1.5}O_4$	2.90	2.99(θ=50 K)
4	$0.259CuO+Cu_{1.5}Mn_{1.5}O_4$	4.23	4.33(θ=100 K)
5	$Cu_{1.5}Mn_{1.5}O_4+0.726Cu_{0.4}Mn_{4.6}O_8$	9.11	9.06(θ=150 K)
6	Mn_5O_8	10.20	10.50

Table 3
CATALYTIC PROPERTIES OF THE SAMPLES

Sample	"Light-off" temperatures (K)		Average oxidation rate of CO	
	CO	ethylacetate	(g/g_{cat}.h)	(g/g_{am}.h)
1	508	543	13.00	3.40
2	568	603	5.40	1.50
3	473	508	15.60	2.40
4	538	545	6.30	2.30
5	528	565	6.60	2.70
6	543	543	4.00	1.50

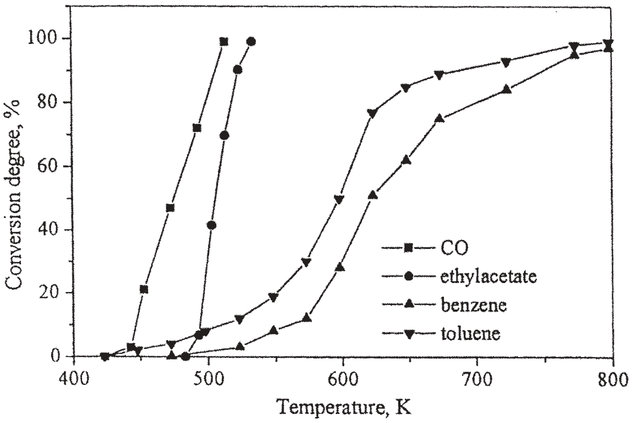

Fig. 1. Temperature dependencies of conversion degree of CO, ethylacetate, toluene and benzene for sample 3 at 20000 h^{-1} space velocity

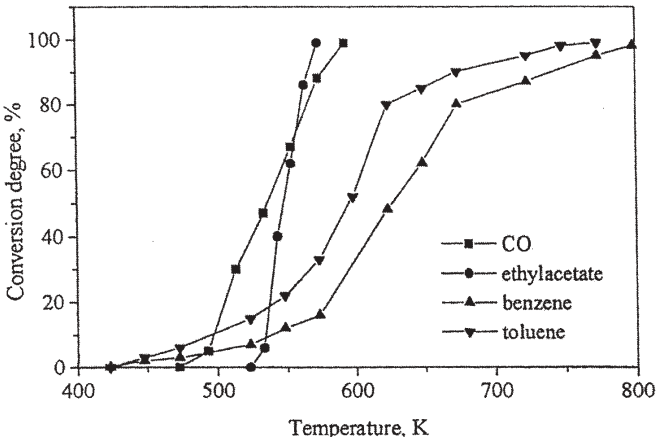

Fig.2. Temperature dependencies of conversion degree of CO, ethylacetate, toluene and benzene for sample 4 at 20000 h^{-1} space velocity

presents the conversion degree temperature dependencies for sample 3 with the highest CuO content.

The results obtained for complete oxidation of CO, ethylacetate, toluene and benzene over sample 4 which is mainly a spinel are shown in figure 2. With both samples almost the same picture is observed.

Carbon monoxide and ethylacetate are easiest to oxidize (at the lowest temperature). Oxidation is more difficult to achieve with toluene and most difficult with benzene. This is not unexpected in view of the bonds which have to be broken during the complete oxidation.

The comparison of the catalytic properties of the two samples shows that sample 3 with the highest CuO content is more active towards CO and ethylacetate oxidation than sample 4 which is mainly a spinel (its " light-off " temperatures are nearly 50 K lower, respectively, table 3).

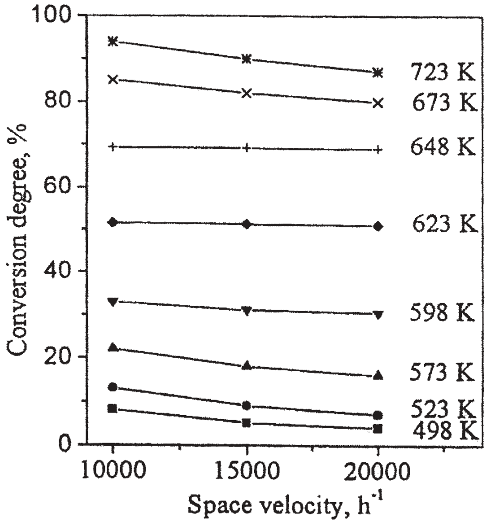

Fig. 3. Variation of the benzene conversion with space velocity on the sample 4

In figure 3 the variation of benzene conversion with space velocity of gas mixture on sample 4 is shown. It is seen that the space velocity only weakly affect the catalytic activity of the samples. This effect confirm that the access of reactant is not limited by external diffusion.

The dependencies for the other samples investigated are analogous. The same is observed with the reaction of the complete oxidation of toluene over the above catalysts. Within the 573-623 K temperature range is observed an ignition point (the reaction exotermicity increases abruptly). Near 40-50 K above this ignition temperature, the reaction is more difficult to control. This accounts for the apparent non-variation of conversion with space velocity.

In order to compare the activities of the separate phases, the average oxidation rates, i.e. the amounts of oxidized toxic elements (g) per hour (h) per 1 g catalyst (g_{cat}) or 1 g deposited on alumina active metals (g_{am}) were calculated. The results obtained for CO oxidation at 510 K are given in table 3. The most active is the copper oxide catalyst but the spinel phase has also a relatively high activity. The samples 4 and 5 are most interesting. They have a high activity at relatively low temperatures despite of the low content of the alumina supported active phase (table 1). This once more confirms the conclusion concerning the catalytic activity of the spinels. With this type of spinels the ion distribution is Cu^+ [$Cu^{2+}_{0.5}$ $Mn^{4+}_{1.5}$] O_4. According to our investigation [21] the presence of two different ions in an octahedral position in the spinel lattice is indispensable for a high activity and even enhanced insensitivity towards catalytic poisons.

Conclusions

It is found that mixed copper and manganese formates solutions are suitable for preparation of supported catalysts by impregnation of alumina. Copper and manganese containing samples are promising for complete oxidation of toxic organic compounds. The $Cu_{1.5}Mn_{1.5}O_4$ spinel phase is responsible for the effectiveness of the supported mixed oxide catalysts. In the complete oxidation of benzene the space velocity only weakly affect the catalytic activity of the samples. This effect confirms that the access of reactant is not limited by external diffusion.

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