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PHASE COMPOSITION OF MANGANESE-ALUMINA CATALYSTS FOR THE REACTIONS OF DEEP OXIDATION

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Abstract

X-ray powder diffraction, transmission electron microscopy and differential dissolution were used for investigation of the phase transformation peculiarities of biphasic manganese-alumina catalysts during their thermal treatment. An effect of interaction between aluminium and manganese oxides depending on the sample preparation procedure was found.

Keywords: Manganese-alumina catalysts, structure, phase composition

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INTRODUCTION

Manganese-alumina catalysts for the reactions of deep oxidation are well known as active, thermally stable systems. Publications [1-3] are devoted to the study of their catalytic activity. Thus, an effect of the thermal activation of a MnO_x/Al_2O_3 catalyst in the temperature range between 800 and 1100°C has been reported [4]. It was found that an increase of the catalytic activity in oxidation reactions was caused by the dispersion of the supported manganese oxide component as a result of chemical and phase transitions in this system during the thermal treatment. The active component was characterized by an imperfect structure closely related to that of the tetragonal Mn_3O_4 spinel. It was also found that Mn ions might partially exchange for Al ions in the structure of the active component [5]. This might be a key factor responsible for the structural formation of the active phase and such characteristics as catalytic activity, thermal stability and poison resistivity of the catalysts. Therefore, a detailed

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study of structure formation of manganese-alumina catalysts is of great interest to elucidate the possible interaction between manganese and aluminium oxides. This problem is the subject of the present paper.

Undoubtedly, the sample preparation procedure should affect strongly the character of the interaction between the two oxides. Therefore, we studied samples prepared by impregnation of γ-Al_2O_3 with manganese nitrate solution (I) and by mixing of plastified $Al(OH)_3$ with MnO_2 (II) and MnO_2+$Mn(NO_3)_2$ (III). In the latter case, the samples differed from each other by the particle sizes of the initial manganese oxide.

EXPERIMENTAL

After impregnation (or mixing) and drying, the samples (I - 6% MnO_2/Al_2O_3; II - 10% MnO_2/Al_2O_3 ; III - 10% MnO_2/Al_2O_3) were calcined in air in the range of 400 - 1100°C (with a 100°C step) for 6 h at each temperature. X-ray powder diffraction analysis (XRD) was performed on a URD-6 diffractometer using CuKα radiation. Transmission electron microscopy data (TEM) were obtained with a JEM-100C electron microscope at a 100 kV accelerating potential. The phase composition of the samples was determined using differential dissolution (DD) method [6] with a Baird atomic-emission spectrometer.

RESULTS AND DISCUSSION

Table 1 shows data on the sample phase compositions which were obtained on the basis of a combined analysis of XRD and TEM results (oxide phases which may be modified by Mn or Al ions are designated with asterisks). These data indicate that there are only γ-Al_2O_3 and β-Mn_2O_3 phases in all the samples calcined below 800°C. The temperature increase up to 900°C initiates the formation of α-Al_2O_3 in all the catalysts. At the same time, processes of the active phase formation differ from each other in samples prepared in different ways. Thus, β-Mn_2O_3 phase is still preserved in sample (II) prepared by mixing. In the samples of series (III), an imperfect tetragonal spinel phase of the Mn_3O_4 type, which is characterized by a certain redistribution in the intensities of the X-ray diffraction peaks in comparison with the ideal Mn_3O_4 structure, appears together with Mn_2O_3 (particle sizes, D_{XRD} and D_{TEM}, are equal to 0.04 and 0.3 μm, respectively). In the samples obtained by impregnation, the isolated phase of manganese oxide is not observed. This fact may indicate the possible dissolution of manganese atoms in the structure of alumina. The Mn_2O_3 phase disappears, but a well-crystallized phase of Mn_3O_4 is formed (D_{XRD} and D_{TEM} are equal to

0.08 and 1.3 μm, respectively) in the samples of series (II) and (III) after their calcination at 950°C.

Table 1

XRD and TEM data on the phase compositions of the samples

Calcination temperature (°C)	Impregnation (I)	Mixing (II)	Mixing (III)
500	γ-Al_2O_3, MnO_2, Mn_2O_3	γ-Al_2O_3, Mn_2O_3	-
600	γ-Al_2O_3, Mn_2O_3	”	γ-Al_2O_3, Mn_2O_3
700	”	”	”
800	”	”	”
900	δ*-+ α-Al_2O_3	δ-+ α-Al_2O_3, Mn_2O_3	δ -+α-Al_2O_3, Mn_2O_3, Mn_3O_4*
950	δ*-+α-Al_2O_3	δ-+α-Al_2O_3, Mn_3O_4	δ-+α-Al_2O_3, Mn_3O_4*
1000	α-Al_2O_3, imperfect spinel	δ-+α-Al_2O_3, Mn_3O_4	δ-+α-Al_2O_3, imperfect spinel
1100	α-Al_2O_3, $MnAl_2O_4$	α-Al_2O_3, Mn_3O_4, $MnAl_2O_4$	α-Al_2O_3, $MnAl_2O_4$

TEM study revealed that particles of α-Al_2O_3 and small needle-like microcrystals of γ-Al_2O_3 were present in the sample (I) calcined at 950°C. A disperse supported phase of manganese oxide was not observed. At the same temperature, samples (II) consisted of large (over 1 μm) well-crystallized particles of Mn_3O_4 as well as particles of δ- and α-Al_2O_3. Samples of (III) series were characterized by the presence of δ- and α-Al_2O_3 microcrystals and particles ($D_{TEM} > 0.3$ μm) consisting of small (0.008-0.01 μm) blocks coherently stacking between each other. The phase composition of the latter was approximately identified as Mn_3O_4 by using selected area electron diffraction patterns.

Based on the data of Table 1, one can suppose that an interaction of manganese oxide with alumina leading to the formation of a mixed aluminium-manganese compound takes place in all the samples, but the character of this interaction depends strongly on the sample preparation procedure. In the case of the catalysts prepared by impregnation, complete dissolution of the manganese ions in the structure of alumina results in the formation of a cored solid solution on the basis of δ-Al_2O_3 with aluminium excess. For catalysts of series (III), a mixed manganese-alumina phase is likely to be formed on the basis of a tetragonal Mn_3O_4 spinel slightly modified by Al ions, though a small concentration of δ^*-Al_2O_3 may also exist in these samples. For catalysts (II) prepared by mixing, the interaction between two oxides is the weakest, as a well-crystallized Mn_3O_4 phase is clearly observed in their XRD spectra. At the same time, microcrystals of δ^*-Al_2O_3 with a disordered structure, which seems to be modified by Mn ions, are also present in these catalysts, as evident from TEM analysis.

At elevated temperatures (1000-1100°C), a strong interaction between δ-Al_2O_3 and Mn_3O_4 with the formation of a cubic spinel of the $MnAl_2O_4$ type is registered in all the samples.

Table 2

DD data on the phase compositions of the samples calcined at 950°C for 6 h

Preparation procedure	Cation ratios in soluble phases	Content of soluble phase (%)	Phase detected by XRD
Impregnation (I)	Mn : Al = 1 : 1	>90	δ^*-Al_2O_3
	Mn : Al = 1 : 5	<10	
Mixing (II)	Mn = 1	>90	Mn_3O_4
	Mn : Al = 1 : 2	<10	possibly, δ^*-Al_2O_3
Mixing (III)	Mn : Al = 1 : 0.12	about 100	Mn_3O_4*

XRD analysis of the insoluble residue revealed a mixture of δ- and α-Al_2O_3

To evaluate quantitatively the degree of the interaction between manganese and alumina, the DD method was used. Table 2 presents the ratios between Mn and Al ions in manganese-aluminium mixed oxides and the corresponding crystalline phases observed in the XRD spectra and TEM micrographs. DD data provide additional justification for the conclusion on the different character of interaction between manganese and aluminium oxides in the catalysts under study. During impregnation, two oxides interact strongly with the appearance of a mixed compound on the basis of δ-Al_2O_3 (samples I). Mixing (II) leads to the formation of only a small amount (10%) of the manganese-alumina phase: pure Mn_3O_4 phase predominates in the probe. But in samples (III) obtained also by mixing, a Mn_3O_4 phase partially doped with Al ions (10-15% mol) is formed. The difference between samples (II) and (III) seems to be associated with the particle sizes of the Mn_2O_3 parent phase: they were equal to 0.2 and 0.03 - 0.05 μm in series (II) and (III), respectively.

The real structure of mixed manganese-alumina phases formed at calcination temperatures from 900 to 950°C is of great interest. It has been mentioned earlier that the solid solution of Mn ions in δ-Al_2O_3 is a cored solid solution. Most of δ-alumina has practically no Mn ions in its structure. The XRD analysis of the insoluble residue after the DD procedure revealed a mixture of α- and δ-aluminas as its phase composition.

Dissolution of Al ions in the structure of Mn_3O_4 (samples III) results in the development of a micrograined structure of the latter. It should be noted that this microstructure has a high thermal stability. Calcination of sample (III) at 950°C for tens hours results in a complete transformation of δ-Al_2O_3 to α-alumina. At the same time, micrograin boundaries in the structure of Mn_3O_4* are still well developed. Moreover, this phase preserves at elevated (1100°C) temperature (naturally, if all the δ-Al_2O_3 phase transforms to α-Al_2O_3 and additional interaction between Mn_3O_4* and Al_2O_3 does not take place). It seems reasonable that Al ions are located predominantly in the vicinities of the micrograin boundaries, thus, preventing their annealing.

Thus, an effect of the interaction between manganese and aluminium oxides in MnO_x/γ-Al_2O_3 catalyst calcined at 900-950°C has been found. The sample preparation procedure affects strongly the character of interaction between the two oxides. Compounds formed on the basis of δ-Al_2O_3 are cored solid solutions, which appears to lead to their partial disintegration followed by the appearance of α-Al_2O_3 . In its turn, the solid solution of Al ions in Mn_3O_4 is in the metastable equilibrium state due to the specific micrograined structure characterized by well developed coherent boundaries in the vicinity of those Al ions.

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REFERENCES

1. L.P. Kiknadze, G.V. Cherenkov: *Heterogeneous Catalytic Processes*, p. 52. Leningrad State University, Leningrad 1979 (in Russian).
2. V.M. Vlasenko, I.A. Malchevski: *Theor. Exper. Chem.*, 20, 49 (1984).
3. M.A. Baltanas, A.B. Stilles, J.R. Katzer: *Appl. Catal.*, 20, 15 (1986).

4. P.G. Tsyrulnikov, V.S. Salnikov, V.A. Drozdov, S.A. Stuken, A.V. Bubnov, E.I. Grigorov, A.V. Kalinkin, V.I. Zaikovskii: *Kinet. Katal.*, **32**, 439 (1991).
5. G.N. Kryukova: *Electron diffraction and imaging at surfaces*, Arizona, Intern. School, January 2-6, p.16 (1996).
6. V.V. Malahov, A.A. Vlasov: *Kinet. Katal.*, **36**, 503 (1995).