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GENESIS OF PHASE COMPOSITION IN Fe-Mn CATALYSTS FOR SYNTHESIS OF OLEFINS FROM CO AND H_2 UNDER CATALYTIC CONDITIONS IN SITU

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Genesis of the phase composition in oxide Fe-Mn catalysts for olefin synthesis under close to catalytic conditions has been studied in a high temperature X-ray chamber.

В условиях, приближенных к условиям каталитического синтеза, в высокотемпературной рентгеновской камере изучен генезис фазового состава оксидных Fe-Mn катализаторов синтеза олефинов.

Oxide Fe-Mn compositions are known as selective catalysts for olefin (primarily C_2-C_4) synthesis from CO and H_2 [1-2]. In our previous publication [2] we have studied the effect of preparation methods for precipitated Fe-Mn catalysts on their selectivity and activity in CO + H_2 reaction.

Unlike the previous studies [2-3], in the present study we have investigated the genesis of phase compositions in Fe-Mn catalysts obtained by the optimum method [2] at different steps of activation and catalytic reaction under conditions eliminating their contact with air.

Experiments were carried out in a high temperature X-ray chamber enabling to achieve real experimental conditions in it and to perform X-ray phase analysis with controlled medium and temperature. The composition of gas phases was 2 % H_2/He and $CO/H_2=1/1$; gas flow rates were 1.8-2.5 dm^3/h. Ratios of components in the catalysts (Fe/Mn) were ranging from 100/0 to 0/100 mol %.

The data obtained (Table 1) indicate that thermal treatment under all the conditions examined leads to the interaction of components to form mutually promoted phases. The oxidation degrees for Fe and Mn ions depend on the thermal treatment media. Reduced samples placed in air are partially oxidized.

Samples dried at 343-378 K are mixtures of manganese carbonate and an X-ray amorphous phase. With Fe/Mn > 70/30 their diffractograms exhibit diffuse diffraction maxima of goethite.

After 4 h thermal treatment at 673 K in flowing air, we have identified a hematite type phase (α-Fe_2O_3) for samples with component ratios above 50/50. If Fe/Mn=50/50, we observe α-Fe_2O_3 and a phase designated as A in Table 1, characterized by interplanar distances of 2.841_{26}, 2.401_{100}, 2.132_{35}, 1.645_{32} and 1.404_{10} Å. With further decreasing Fe/Mn, phase A becomes fundamental. For the sample with Fe/Mn=0/100 this phase is also present along with Mn_3O_4. The phase A has not been detected previously. Apparently, it is an intermediate oxide-carbonate compound, since according to IR spectroscopic data, samples with phase A contain CO_3^{2-} anions whose amount grows with increasing this phase content. Temperature increase above 773 K stimulates further evolution of CO_3^{2-} anion and formation crystalline oxide compounds. The latter are: in air cubic modifications of Mn_2O_3 and under reduction in hydrogen at 673 K gradually crystallizing Mn_3O_4. Phase A transforms into Mn_3O_4.

A comparison of the X-ray phase analysis data for α-Fe_2O_3 with the literature [4] reveals their discrepancy, testifying to the interaction of components and the formation of a mixed oxide whose structure is typical for a defective hematite [5].

Table 1

Phase composition of samples after thermal treatment corresponding to various steps of preparation, activation and catalytic reaction

Nos	Fe/Mn	Air 673 K, 4 h	2 % H_2/He 673 K, 4 h	$CO/H_2 = 1/1$ 573 K, 3 h
1	100/0	α-Fe_2O_3	Fe_3O_4	Fe_3O_4, Fe^0, carbide Fe
2	90/10	α-$Fe_2O_3^*$	Fe_3O_4-$MnFe_2O_4$	Fe_3O_4, Fe^0, carbide Fe
3	70/30	α-$Fe_2O_3^*$	$MnFe_2O_4$	$MnFe_2O_4 \cdot Fe_3O_4$ $Mn_AFe_{1-A}O$
4	50/50	α-$Fe_2O_3^*$ phase A	$MnFe_2O_4$ $Fe_XMn_{1-X}O$	$MnFe_2O_4 \cdot Fe_3O_4$ $Fe_XMn_{1-X}O$, $Mn_AFe_{1-A}O$
5	30/70	α-$Fe_2O_3^*$ phase A	$MnFe_2O_4$, $Fe_XMn_{1-X}O$, $Mn_3O_4^*$	$MnFe_2O_4$, $Mn_AFe_{1-A}O$, $Fe_XMn_{1-X}O$
6	20/80	traces of α-$Fe_2O_3^*$ phase A	$MnFe_2O_4$, $Fe_XMn_{1-X}O$, $Mn_3O_4^*$	$Fe_XMn_{1-X}O$, $MnFe_2O_4$, traces of $Mn_3O_4^*$
7	10/90	phase A	$Fe_XMn_{1-X}O$, $Mn_3O_4^*$	$Fe_XMn_{1-X}O$, traces of $Mn_3O_4^*$
8	0/100	Mn_3O_4, phase A	Mn_3O_4, traces of MnO	Mn_3O_4, MnO

* Promoted phases.

Hydrogen reduction of the samples having high concentrations of iron provides the formation of only spinel phases: from Fe_3O_4 (100/0) to $MnFe_2O_4$ - Fe_3O_4 (70/30). With higher concentrations of Mn, besides a spinel phase the samples contain a phase of lower manganese oxide. The parameters for its crystal lattice (Fig. 1) indicate the formation of a mixed oxide. Under reduction, the phase Mn_3O_4 is crystallized and then its content drops and simultaneously there appears and grows the quantity of the phase of a lower manganese oxide.

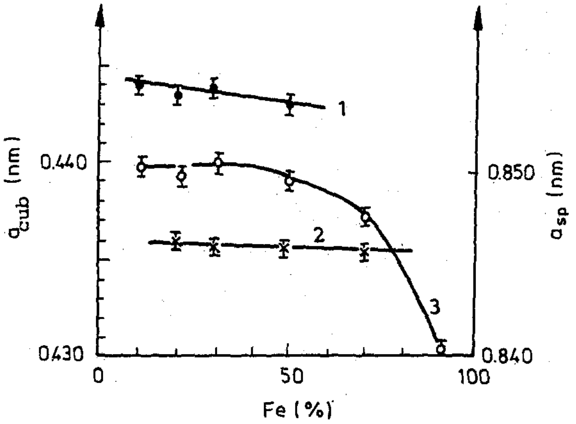

Fig. 1. Changes in the parameters of crystal lattices:
1 - $Fe_XMn_{1-X}O$ (a^o_{MnO} = 0.4445 nm),
2 - $Mn_AFe_{1-A}O$ (a^o_{FeO} = 0.4307 nm),
3 - spinel phases after activation in hydrogen and $CO + H_2$

In the course of a catalytic reaction in a $CO + H_2$ mixture, deeper reduction of catalysts take place. Table 1 represents phase compositions of the samples after 3 h treatment by the reaction mixture. With increasing treatment time in $CO + H_2$ mixture, intermediate spinel phases are completely reduced and solid solutions based on lower oxides $Mn_AFe_{1-A}O$ and $Fe_XMn_{1-X}O$

are formed. According to data on the lattice parameters (Fig.1, curves 1 and 3), solid solutions based on FeO for the samples with Fe/Mn=70/30 - 20/80 have practically constant compositions and contain 25-30 % Mn.

Kinetic changes in the intensities of diffraction lines of the observed phases for the samples with different ratios of their components are illustrated in Fig. 2. Studies of these changes indicate that first a solid solution $Mn_{1-X}Fe_XO$ of variable composition is formed under the reduction of a Mn_3O_4-based mixed phase and then the reduction of a mixed oxide type α-Fe_2O_3 produces a lower oxide $Fe_{1-A}Mn_AO$ through an intermediate spinel phase. The composition of the latter in samples with Fe/Mn=70/30 - 20/80 is constant and corresponds to $MnFe_2O_4$.

Thus the results indicate that the formation of mutually promoted phases of lower oxides follows two mechanisms. These mechanisms can be revealed only by high-temperature X-ray phase analysis in a controlled medium, since under contacting with air the high-activity lower oxides of Fe and Mn react with oxygen already at room temperature to form poorly crystallized higher oxides [6]. Therefore the real ratio for the contents of phases has been observed only under reaction conditions and the phase composition of catalysts was reversibly changed depending on these conditions.

A comparison of the phase compositions for Fe-Mn catalysts and of the sample with Fe/Mn = 100/0 under similar conditions indicates that the mutual promotion stabilizes the phases of lower oxides from reduction till metal states and the formation of iron carbides. And it is, apparently, this fact that accounts for the selective hydrogenation of CO on these catalysts.

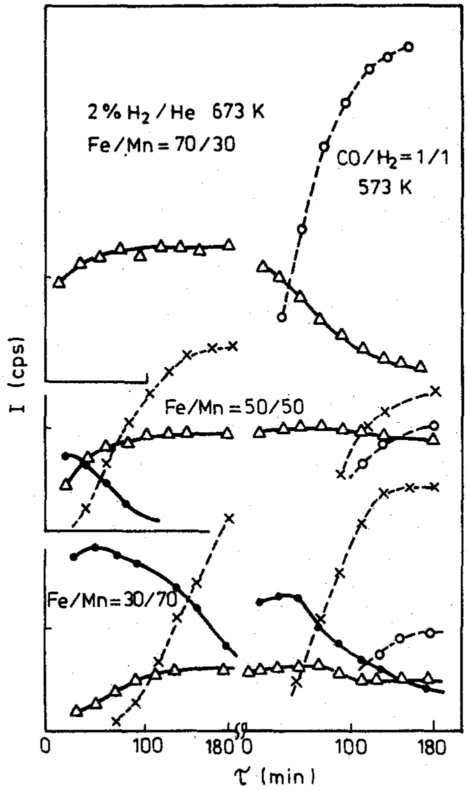

Fig. 2. Kinetic variations in the intensities of diffraction lines under activation in hydrogen and CO + H_2:
Δ - spinel phase (220);
• - Mn_3O_4 (121),
x - $Fe_XMn_{1-X}O$ o - $Mn_AFe_{1-A}O$ (200).

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