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ABSTRACTS

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Effect of the Nature of Manganese Species in Mn-Ce-Zr Mixed Oxide Systems on Catalytic Properties in CO Oxidation

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Ceria-zirconia mixed systems are promising catalysts for CO oxidation [1]. Additional modification with transition metal oxides allows extending the temperature range of their operation [2]. Manganese oxides can be successfully used as modifiers [3]. The method of Mn introducing can affect the bulk and surface structure of the triple oxide systems. Therefore, this work is aimed to reveal the influence of the preparation method on the structural and catalytic properties of MnO_x-$CeZrO_x$ (Mn-CZ, Ce:Zr = 4) in CO oxidation.

Two types of mixed oxide systems were prepared: (method 1) Mn-CZ (S_{BET} = 40 m^2/g) — by the CTAB-templated (where CTAB is cetyltrimethylammonium bromide) EISA method [2, 4] and (method 2) Mn-CZ IM (S_{BET} = 48 m^2/g) by impregnation of pre-prepared double oxide CZ with manganese acetate. CZ (S_{BET} = 83 m^2/g) and MnO_x (S_{BET} = 20 m^2/g) systems were also synthesized by method 1. Then the obtained samples were dried and calcined at 500°C for 3.5 h (method 1) or at 400 °C for 2 h (method 2). The target Mn content in both systems was 8 wt.%. Catalytic tests were carried out in the fixed-bed microcatalytic setup at pulse feeding of the reaction mixture (2 vol.% CO, 1 vol.% O_2 in He) in the temperature range from 100 to 400°C. Analysis of the reaction products was performed by GC.

Bulk and surface composition of prepared systems was investigated by XRD, Raman spectroscopy and XPS. The reflections of Mn_2O_3 and the spinel hausmannite phase of Mn_3O_4 are observed in the diffraction pattern of MnO_x. The XRD patterns of CZ, Mn-CZ and Mn-CZ IM comprise main reflections characterized the cubic fluorite phase. No diffraction peaks of manganese oxides are observed in the patterns of both Mn-modified samples despite the presence of Mn-enriched areas in Mn-CZ IM detected by SEM-EDS. Raman spectroscopy confirmed that both Mn-modified systems contain the CZ mixed oxide phase, but the spectrum of Mn-CZ IM has a separate Mn_3O_4 band. This fact, along with the intensity and position of the F_{2g} line, indicates a weak interaction of manganese with the CZ in Mn-CZ IM. According to XPS results, Mn^{3+} prevails on the surface for all Mn-containing samples, while the relative content of Mn^{2+} species is at least two times higher of Mn-CZ IM compared to Mn-CZ.

The broad EPR spectra of CZ, Mn-CZ IM, and MnO_x with different g-factors (Fig. 1, a) can indicate the presence of paramagnetic particles adsorbed on the surface, and clustered Mn ions. In contrast, the EPR spectrum of Mn-CZ contains hyperfine structure with six intense lines which are related to the presence of isolated Mn^{2+} ions located in defect sites with a noncubic symmetry or in the substitutional sites of the CZ lattice. The TPR method also confirms that both modified systems contain Mn^{2+} and Mn^{3+}.

Catalytic results (Fig. 1, b) show that modification of CZ with manganese oxides contributes to a noticeable increase in CO conversion, especially at the low-temperature range (150 - 350 °C). Mn-CZ IM is somewhat more active in the range from 100 °C to 250 °C. The reducing of the contact times of catalysts with the reaction mixture by decreasing catalyst loadings into the reactors allowed revealing more significant differences between Mn-CZ and Mn-CZ IM. In this case Mn-CZ IM provides higher CO conversion than Mn-CZ, especially at 250–350°C. Moreover, the absence of the hysteresis loop for Mn-CZ IM (Fig. 1, c) indicates the higher stability of this catalyst.

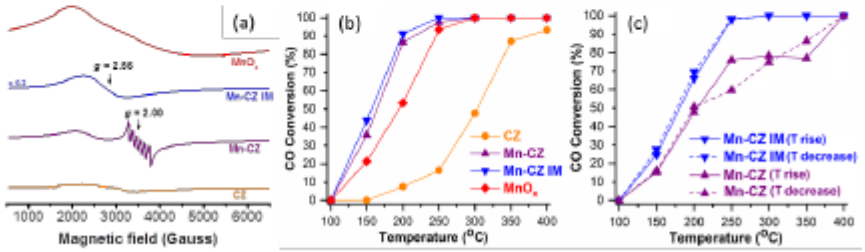

Figure 1. EPR spectra (a) and CO conversion plots at 100 mg (b) or 50 mg (c) catalyst loading

Thus, despite decreasing of S_{BET} values, modification of CZ by MnO_x during both synthesis procedures leads to significantly improvement of catalytic properties in CO oxidation. It is probably caused by the presence of separate phases of manganese oxides in various oxidation states, which provide active adsorption centers on the surface. Mn-CZ IM is more active than Mn-CZ in spite of similar properties detected by several physicochemical methods (both contain mixed CZ oxide phase and highly dispersed Mn^{2+}, Mn^{3+} oxide particles; their specific surface areas are nearly equal). However, the distribution and speciation of manganese in the synthesized catalysts depends on the Mn incorporation technique. In Mn-CZ a minor part of the Mn-modifier is not available for reagents adsorption because of the incorporation of manganese ions into the CZ crystal lattice. In contrast, the presence of surface locations enriched with MnO_x and other locations comprising mainly CZ and depleted with MnO_x in Mn-CZ IM can provide the additional adsorption sites and the supply of active oxygen species by spillover mechanism during CO oxidation, respectively.

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