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## Influence of the preparation method of supported Fe-Mo-O/SiO<sub>2</sub> catalysts on their catalytic properties in selective oxidation of propylene glycol

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The processes of catalytic oxidation of organic substances are the sources of the most important compounds that are widely used in various industries. The selective vapor-phase oxidation of propylene glycol is a method for production of a number of available compounds such as hydroxyacetone (used in food and medical industries) [1], pyruvic acid (used in cosmetology) [2], methylglyoxal (used in medicine and food industry) [3, 4], etc. The catalysts based on oxides of transition metals, including iron and molybdenum (Fe-Mo-O), are widely used for the processes of selective oxidation of monoatomic alcohols. In industry, the Fe-Mo-O catalysts are used in the process of selective oxidation of methanol to formaldehyde [5]. The catalytic properties of supported Fe-Mo-O/SiO<sub>2</sub> catalysts in the process of selective oxidation of propylene glycol were not investigated.

The aim of the present work is to determine the influence of the order of introducing of the components (precursors of iron and molybdenum oxides) to the SiO<sub>2</sub> surface on the active surface state, the adsorption and catalytic properties of the supported Fe-Mo-O/SiO<sub>2</sub> catalysts in the selective oxidation of propylene glycol. The supported catalysts were prepared by the impregnation method without excess at Mo/Fe molar ratio of 1.5 and 3. The MoO<sub>3</sub> content was 10%wt. Spherical mesoporous silica gel grains were used as a support (Salavatsky catalyst plant, a specific surface was 300 m<sup>2</sup>/g). For the 1.5Fe<sub>2</sub>O<sub>3</sub>/MoO<sub>3</sub>/SiO<sub>2</sub> and 3Fe<sub>2</sub>O<sub>3</sub>/MoO<sub>3</sub>/SiO<sub>2</sub> samples, the first stage included the impregnation of the support with a citric acid solution of ammonium heptamolybdate followed by drying at 100 °C and calcination at 600 °C. Then the catalyst sample was impregnated with a solution of iron (III) nitrate with the appropriate concentration. After each stage of sequential impregnation, the samples were dried and calcined in a stream of air at 600 °C for 4 h. The MoO<sub>3</sub>/Fe<sub>2</sub>O<sub>3</sub>/SiO<sub>2</sub> samples with different Mo/Fe ratios were prepared using the reverse order of component introducing. The catalysts were investigated by electronic spectroscopy of diffuse reflection (DRS), Raman spectroscopy, TPR-H<sub>2</sub>, XRD, low-temperature nitrogen adsorption, TPR<sub>x</sub> methods. According to the DRS data, the absorption bands at 300-450 and 450-600 nm characterized the samples prepared. According to the literature data, these bands corresponded to the absorption regions of MoO<sub>3</sub> and Fe<sub>2</sub>O<sub>3</sub>. The reaction ability of the catalyst surface was investigated by the TPR-H<sub>2</sub>. The hydrogen consumption in the high-temperature region (550-620 °C) was typical for all samples. According to the literature data, the reduction of Fe<sub>2</sub>O<sub>3</sub> proceeds at 350 °C. Molybdenum oxide inhibits the reduction of iron oxide, thus, a shift of the TPR peak towards the high temperature region was observed, which indicated the interaction between the two active phases.

The investigation of the catalytic properties showed that the highest selectivity towards methylglyoxal was observed for the 3MoO<sub>3</sub>/Fe<sub>2</sub>O<sub>3</sub>/SiO<sub>2</sub> sample (67 % at 360 °C). While the order of introduction of the active components onto the silica surface was varied, the significant redistribution of the reaction products occurred (the selectivity towards methylglyoxal decreased to up to 0%). The variation of the order of deposition of oxides for the samples with the Mo/Fe ratio of 1.5 showed negligible changes in the selectivity towards basic products. The catalytic properties of the materials prepared were compared with those for the supported MoO<sub>3</sub>/SiO<sub>2</sub> and bulk Fe-Mo-O catalysts. The role of iron oxide in the formation of Mo-containing species on the catalyst surface is discussed.

### References

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