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## CATALYSIS: FROM SCIENCE TO INDUSTRY

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## The influence of the order of active component introduction on catalytic properties of Mo–Fe–O/SiO<sub>2</sub> catalysts in selective oxidation of 1, 2-propanediol

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The priority challenge of modern science is the opportunity to use the products of processing of renewable natural sources. For instance, propylene glycol can be produced via the processing of biomass, biodiesel and by-products of these processes [1]. In its turn, propylene glycol is an in-demand raw material that produces valuable organic compounds, such as methylglyoxal, hydroxyacetone, lactic acid, etc., during its catalytic oxidation.

Fe–Mo–O catalysts, due to industrial application in methanol oxidation to formaldehyde, are widely studied [2]. However, an interest in such systems grows steadily. In the literature, the studies of bulk Fe–Mo–O catalysts are mainly presented. In some cases supported catalysts possess the activity, which was close to the one of industrial catalysts [3]. Therefore, the aim of the present work is to synthesize the supported Mo–Fe–O/SiO<sub>2</sub> catalysts with different Mo/Fe ratio and to study the influence of the preparation method on the phase composition and catalytic properties of the obtained catalysts in propylene glycol oxidation to methylglyoxal.

The Mo–Fe–O/SiO<sub>2</sub> catalysts were synthesized by methods of sequential and joint incipient wetness impregnation. Silica (KSKG, LLC "Salavat Catalyst Plant", with surface area of 300 m<sup>2</sup>/g) was used as a carrier. A series of Mo–Fe–O/SiO<sub>2</sub> catalysts was synthesized by the co-impregnation method with citrate solution containing both ammonium paramolybdate and ferric nitrate in corresponding concentrations. The Mo/Fe molar ratio varied from 0.5 to 3. The resulting samples were dried at 120 °C and calcined in air flow at 550 °C. For the series of MoO<sub>3</sub>/Fe<sub>2</sub>O<sub>3</sub>/SiO<sub>2</sub> and Fe<sub>2</sub>O<sub>3</sub>/MoO<sub>3</sub>/SiO<sub>2</sub> catalysts prepared by sequential impregnation by varying the order of introduction of the components, the Mo/Fe molar ratio was 3. The resulting samples were dried at 120 °C and calcined in air flow at 550 °C after each impregnation step.

The catalysts were characterized by XRD, UV-vis, Raman spectroscopy, low-temperature N<sub>2</sub> adsorption and TPR methods. The catalytic properties of the Mo–Fe–O/SiO<sub>2</sub> catalysts were studied in the gas-phase propylene glycol oxidation to methylglyoxal at the temperature 350°C (mixture composition: 3% C<sub>3</sub>H<sub>6</sub>(OH)<sub>2</sub>, 3.7% O<sub>2</sub>, 62% N<sub>2</sub>, 30% H<sub>2</sub>O). The major reaction products were methylglyoxal, formaldehyde, and hydroxyacetone.

According to catalytic test data, propylene glycol conversion of 18% and selectivity towards methylglyoxal of 41% were observed over the Mo–Fe–O/SiO<sub>2</sub> catalyst with the lowest content of iron oxide (Mo/Fe=3) prepared by co-impregnation method. For catalysts prepared by the sequential impregnation method (Mo/Fe=3), the order of introduction of the components on the support surface is shown to play an important role. Thus, for the MoO<sub>3</sub>/Fe<sub>2</sub>O<sub>3</sub>/SiO<sub>2</sub> catalyst (the support is firstly impregnated with an iron nitrate solution and then with ammonium heptamolybdate solution), methylglyoxal selectivity of about 63% with a propylene glycol conversion of 15% are obtained. In the reverse order of the introduction of components, a decrease in total activity of Fe<sub>2</sub>O<sub>3</sub>/MoO<sub>3</sub>/SiO<sub>2</sub> catalyst was observed along with the predominance of selectivity for hydroxyacetone, which indicates a change in the mechanism of the propylene glycol oxidation reaction. The report will present and discuss the scheme of transformations taking place on the surface of Fe–Mo–O/SiO<sub>2</sub> catalysts.

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### References

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