Selective oxidation of propylene glycol over silica-supported iron–molybdenum oxide catalysts

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Abstract: Selective oxidation of propylene glycol is studied over silica-supported Mo-Fe-O catalysts with different Mo/Fe molar ratio. The catalysts are synthesized by wetness impregnation method and characterized by XRD, UV-vis, Raman spectroscopy, TPR and DFT methods. The catalytic properties are tested under gas phase conditions at 350 °C. The selectivity towards methylglyoxal formation is shown to be determined by the Mo/Fe molar ratio. The 67.8% selectivity towards methylglyoxal is achieved at Mo/Fe molar ratio of 3:1 through O–H activation and C–H bond scission route. C–C bond cleavage route results in predominant formaldehyde formation at the Mo/Fe molar ratio of 1:2.

Keywords: propylene glycol oxidation; iron molybdate; methylglyoxal.

1. Introduction

Currently, iron-molybdenum catalysts are widely studied due to their industrial application in formaldehyde manufacturing by methanol oxidation. Despite the fact that iron–molybdenum catalysts have long been known, the study of such systems is still of importance [1, 2]. At present, in the literature various methods to improve the features of Mo-Fe-O catalysts have been represented, such as effect of the nature of precursor and pH of the solution during the precipitation, thermal treatment, effect of Mo/Fe molar ratio in the catalyst composition, etc. The main attention in the literature is mainly paid to bulk catalysts. However, in Ref. [3] it is reported that the role of precursors of active components determines the extent of interaction and activity of the supported catalysts in alcohol oxidation. In some cases, the activity is close to the one of industrial catalysts.

The aim of the present work is to synthesize the supported Mo-Fe-O/SiO_2 catalysts with different Mo/Fe ratio and study the influence of the phase composition on the catalytic properties of the systems in the propylene glycol oxidation to methylglyoxal.

2. Experimental

The Mo-Fe-O/SiO_2 catalysts were synthesized by varying the Mo/Fe molar ratio from 0.5 to 3.0 (the Mo content in all samples was 10 wt. %). $Fe_2(MoO_4)_3$ was prepared as a reference sample according to the procedure described in [2]. The supported samples were prepared by incipient wetness impregnation of silica (KSKG, LLC "Salavat Catalyst Plant", with surface area of 345 m^2/g) with citrate solution containing ammonium paramolybdate and ferric nitrate as precursors. The resulting samples were dried at 120 °C and calcined in air flow at 550 °C.

The catalysts were characterized by XRD, UV-vis, Raman spectroscopy, TPR and DFT methods. The catalytic properties of the Mo-Fe-O/SiO_2 catalysts were studied in the gas-phase propylene glycol oxidation to methylglyoxal at 350°C (mixture composition: 3% $C_3H_6(OH)_2$, 3.7% O_2, 62% N_2, 30% H_2O). The major reaction products were methylglyoxal, formaldehyde, hydroxyacetone, and acetic acid.

3. Results and discussion

No crystalline phases have not been found by XRD on the surface of Mo-Fe-O/SiO_2 catalysts. In the composition of the reference sample, $Fe_2(MoO_4)_3$, the presence of $Fe_2(MoO_4)$ and MoO_3 phases was shown.

In fig. 1a the Raman spectra for the studied catalysts and supports are presented. On the surface of the support in silica-supported Mo-Fe-O catalysts the crystal structure of the iron molybdate is formed (band at 785 cm^{-1}). For the samples with the Mo/Fe ratio below 1.5, the presence of absorption bands corresponding to the individual iron oxide (bands at 285 and 218 cm^{-1}) is characteristic. An increase in the Mo/Fe ratio to up to 3 results in appearance of characteristic bands of individual molybdenum oxide (band at 823 cm^{-1}). Also using UV-vis and Raman methods, the Mo surface species both tetrahedrally and octahedrally coordinated with oxygen have been found. The composition of the bulk iron molybdate corresponds to $Fe_2(MoO_4)_3$ with the addmixture of MoO_3, which was also confirmed by the data of XRD, UV-vis and Raman spectroscopy.

Hydrogen consumption at 400-500°C for the catalysts with Mo/Fe ratio of 0.5 and 1 (fig. 1c) is connected with the reduction of Fe^{3+} and Mo^{6+} oxide species weakly bonded with the support surface. A shifting of T_{max} of hydrogen consumption to up to 560-590 ^{o}C as compared to the profile of individual Fe_2O_3/SiO_2 catalyst (fig. 1b) unambiguously indicates the formation of mixed phase between the supporting components over the $Fe_2(MoO_4)_3$ support surface. For the samples with low iron content the T_{max} in the TPR profile is shifted by 15-25 ^{o}C towards higher temperature region as compared to the TPR profile of individual MoO_3/SiO_2 (fig. 1b), which confirms the existence of the interactions of the supporting components between themselves and with the SiO_2 surface.

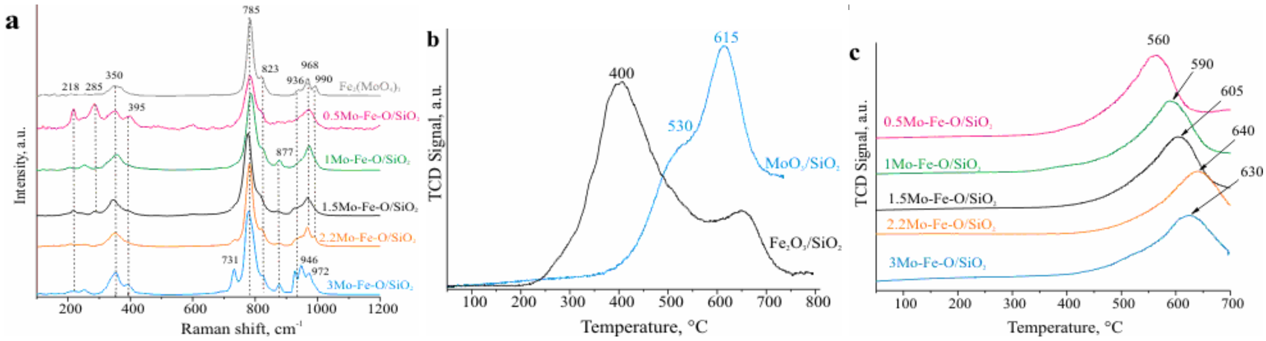

Figure 1. a - Raman spectra of silica-supported Mo-Fe-O catalysts with different Mo/Fe molar ratio and bulk $Fe_2(MoO_4)_3$; H_2-TPR: b - of individual Fe_2O_3/SiO_2 and MoO_3/SiO_2 catalysts, c - of Mo-Fe-O/SiO_2 catalysts with different Mo/Fe molar ratio.

Investigation of the catalytic properties of Mo-Fe-O/SiO_2 catalysts was carried out in vapor-phase oxidation of propylene glycol. Propylene glycol conversion of 7.5% and selectivities towards methylglyoxal of 67.8% were observed over the catalyst with the lowest content of iron oxide (Mo/Fe=3). The reduction of Mo/Fe molar ratio to up to 0.5 led to an increase of the propylene glycol conversion, which is accompanied by formation of larger amounts of by-products (formaldehyde and acetic acid). This evidences on the preferable realization of C–C bond cleavage route.

4. Conclusions

The influence of the Mo/Fe ratio in Mo-Fe-O/SiO_2 catalysts on the selectivity of formation of the main product, methylglyoxal, was revealed. The surface sites, containing tetrahedral and octahedral MoO_x stabilized by silanol groups of the support surface, can be active sites for selective formation of methylglyoxal. The report will present and discuss the results of Raman spectroscopy of the studied catalysts after catalysis.

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