

EFFECT OF CALCINATION TEMPERATURE ON PHYSICO-CHEMICAL AND CATALYTIC CHARACTERS OF Sn-Mo-O CATALYST

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The effect of calcination temperature on physico-chemical characters of Sn-Mo-O catalyst (Sn:Mo = 1:3), calcined at different temperature (400-900°) were studied by X-ray and IR spectroscopic methods. It was proposed that the increase in activity and selectivity of catalyst calcined at 600° in acetone formation from propylene and methyl ethyl ketone formation from butene-1, were caused by molybdenum diffusion over the surface. Also, the increase in catalytic activity of Sn-Mo-O catalyst calcined at 600° in ketones formation can be explained by the enrichment of catalysts surface with molybdenum ions as a result of high temperature diffusion, leading to an increase of active centres concentration, which determines the catalytic acidity and leads to its high activity and selectivity in ketone formation reaction.

Key words: Calcination, Silica, Sn-Mo-O catalyst.

Introduction

The calcination of the silica at 500° for different time intervals causes a decrease in the intensities of all the IR bands of both the pre-treated and non-treated samples [1]. The intensity of the 999 cm⁻¹ band considerably decreases after the calcination due to the destruction of the silicomolybdic acid entities at 733 K [1] and this decomposition also has an impact on the Mo dispersion, co-ordination and effects the oxomolybdic species with a terminal Mo=O bond [1]. Furthermore, the 860 cm⁻¹ band of bridged Mo-O-Mo vibrations is shifted to higher wavenumber due to an increase in the condensation degree after calcination, reflecting a shortening in the Mo-O band [1]. Moreover, the shift becomes more important for the modified silica, due to a significant change in the bond strength of Mo-Fe [1].

Also, it has been observed that the intermediary bands (940- 965 cm⁻¹) disappeared completely in the non-calcined samples for both modified and non-modified samples [2-6]. The effect of H₂ reduction and O₂ re-oxidation on the calcined bimetallic catalysts were studied [7-12], and illustrated that, when the monometallic MoO₃/SiO₂ catalyst is reduced with H₂ at 723 K for 2 hr. the intensity of the bands in the region of 975-940 cm⁻¹ decreases and a broad shoulder appears at 937 cm⁻¹. Moreover, a shift in the Mo- O-Mo bands is also observed [7-12]. On the other hand, when the monometallic Cu/SiO₂ catalyst is exposed to H₂ under the same conditions, a shift to higher wavenumber for both bands from 903 and 680 cm⁻¹ to 910 and 684 cm⁻¹ respectively is detected. This means that H₂ chemisorption on the Cu surfaces is quite possible, however, conflicting results about the difficulty in the H₂

adsorption is usually proposed [7]. In this work we studied the relation between calcination temperature and physico-chemical, catalytic characters of Sn-Mo-O catalyst (Sn: Mo = 1:3).

Experimental

Sn-Mo-O catalyst were prepared by precipitation from an aqueous solution of ammonium paramolybdate solution of metallic tin in concentrated nitric acid. Obtained solution with precipitate was heated until evaporation and then was dried. The catalyst was calcined at 400°, 500°, 600°, 700°, 900° for 5 hr. The suspension formed was evaporated at 100°-110°. The residue was dried at 130°- 140° and then calcined at 250°-300° for 3 hr. and 500° for 10 hr.

Molybdenum trioxide was prepared by decomposition of ammonium paramolybdate at 500°. Tin dioxide was prepared by solution of metallic tin in nitric acid and then precipitation of tin hydroxide by ammonia.

X-Ray investigation was done on diffractometer DRON-0.5 (Cu- radiation, Ni-filter). IR spectra of catalysts were photographed on LIR-20 device. Surface area of samples were measured with chromatographic method. The activity of samples were measured in flow-type apparatus in both propylene and butene oxidation reactions. The ratio, olefin: air: water steam (N₂) = 10:90:100 (ml/min) and volume speed equal 2400 hr⁻¹.

Results and Discussion

Comparing X-ray of Sn-Mo-O catalyst samples calcined at different temperature (400°, 500°, 600°, 700° and 900°) with those of individual molybdate (MoO₃) as in Fig.1. The observed coincidence of values of d/n characterized maximum, but relative intensity of diffraction pattern of Sn-Mo-O cata-

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lyst relatively to MoO_3 is markedly differ; this can be explained by the molybdenum cations replacement by tin in solid solution formation [5].

High calcination temperature leads to rearrangement of the structure and growth of crystals. At $550^\circ\text{-}600^\circ$ molybdenum ions of crystal lattice acquire very high mobility for their diffusion on the surface. Molybdenum diffusion at 700° leads to accumulation of MoO_3 phase on catalysts surface. That is confirmed by coincidence of corresponding X-ray patterns of both Sn-Mo-O catalyst and individual MoO_3 calcined at 700° . Further raising of calcination temperature will accelerate process of MoO_3 sublimation, and the calcined catalyst at 900° is mainly tin dioxide.

IR spectra of Sn-Mo-O catalyst samples are characterised by bands of MoO_3 absorption ($990, 870, 820$ and 600 cm^{-1}). They also reflect changes in solid solution structure as a result of calcination. Increasing calcination temperature from $500\text{-}700^\circ$ leads to relative density in absorption band 870 and 600 cm^{-1} . That may be considered as a proof of MoO_3 structure formation with octahedral coordinated molybdenum ions. Spectrum of calcined catalyst at 900° shows a dislocation of absorption band 600 cm^{-1} , and the appearance of both 550 cm^{-1} band and shoulder 960 cm^{-1} due to the enrichment of catalyst with SnO_2 phase. The catalyst spectrum shows absorption bands 990 and 820 cm^{-1} and dislocation of absorption bands 870 cm^{-1} into 840 cm^{-1} , indicating weakness of molybdenum - oxygen bridges and reconfirms above mentioned proposal about molybdenum ions redistribution between the bulk and the surface of the catalyst.

After catalytic process, specific surface area of catalysts were decreased (Table 1) and independently on calcination temperature, that may be due to the accumulation of condensation products on catalyst surfaces. Condensation of products was proved by special experiments in Adjamov study [13]. In propylene oxidation by Sn-Mo-O catalyst, the acetone and CO_2 are formed and also acetic acid. The high rate of acetone and CO_2 formation was noticed in catalyst calcined at 600° (Fig. 2) in this case acetone selectivity is about 70%.

With Sn-Mo-O catalyst, butene-1 was converted into methyl ethyl ketone, acetic acid, CO_2 , *Cis* and *trans* butene-2.

TABLE 1. SPECIFIC SURFACE OF SN-MO-O CATALYSTS.

Calcination temperature ($^\circ\text{C}$)	Specific surface, m^2/g	
	Before catalytic process	After catalytic process
400	28	7
500	29	7
600	27	6
700	8	6

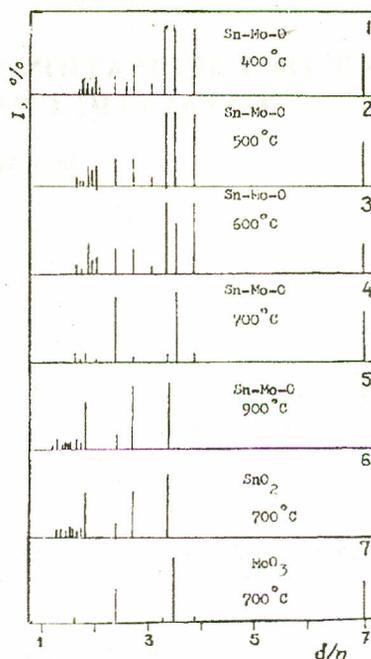


Fig. 1. Diagram of Sn-Mo-O catalysts, SnO_2 and MoO_3 at different calcination temperatures.

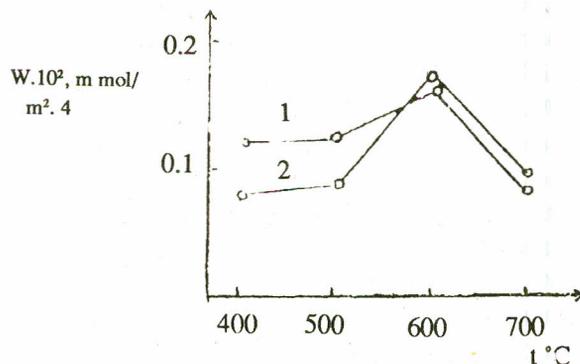


Fig. 2. Activity of Sn-Mo-O catalysts at different calcination temperature in oxidation reaction of propylene.

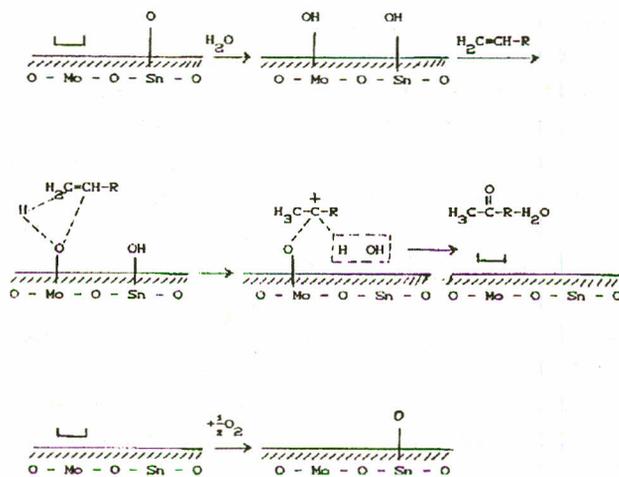


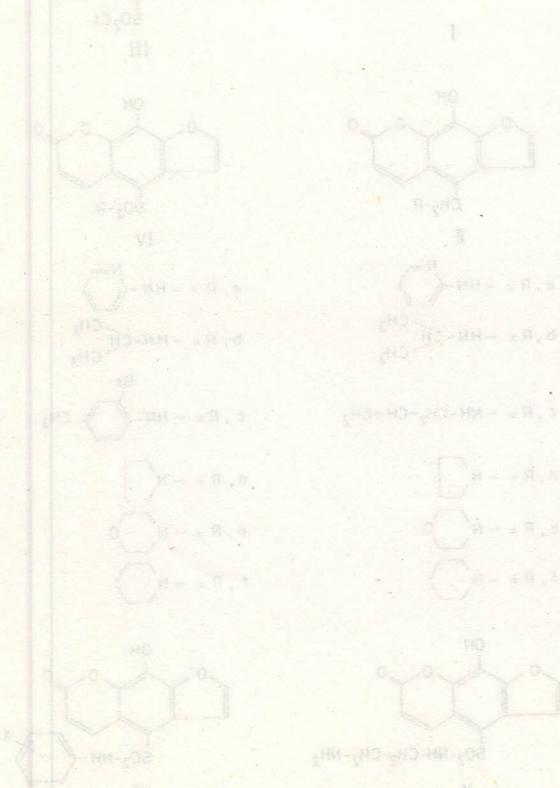
Fig. 3. Possible scheme of ketone formation of Sn-Mo-O catalyst calcined at 600°C .

The high rate of methyl ethyl ketone, CO₂ and butene-2 isomers formation was observed also in calcined catalyst at 600°. Since acidic characters of oxidic catalysts can be evaluated by rate of butene-1 and butene-2 isomerization [14,15].

Possible scheme of ketone formation on Sn-Mo-O catalyst calcined at 600° is presented in Fig. 3. Water vapour is adsorbed by dissociation on catalysts surface, based on above mentioned evaluation of acidity of the active centres, we expect more mobility of hydrogen of Mo-OH group than that of Sn-OH group and accordingly more participation of Mo-OH in the formation of carbonic form of adsorbed olefin. Separation of hydrogen from middle carbonic atom occurs with participation of nucleophilic oxygen, bound with Sn ion.

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Scheme 1

Results and Discussion

Mannich reaction of xanthoxal (I) using primary or secondary amines i.e. 2-aminopyridine, isopropylamine, allylamine, pyrididine, morpholine and piperidine gave the corresponding Mannich bases (II-V). The structures were confirmed by correct chemical analysis. All the compounds gave green colour reaction with aqueous ferric chloride solution. The infrared spectrum of compound (Ib) shows characteristic bands at 1730 cm⁻¹ (C=O, δ-lactone), at 3500 cm⁻¹ (OH), at 1590 cm⁻¹ (C-N) and at 3200 cm⁻¹ (NH). The ¹H NMR spectrum of compound (Ib) in CDCl₃ + D₂O, shows signals at δ = 7.1 and 7.9 ppm as doublet (J = 3 Hz) for the 2 protons of furanoid moiety, at δ = 6.2 and 8.2 ppm as doublet (J = 10 Hz) for the 2 protons of the pyridinoid moiety, at δ = 2.1 ppm as singlet 2H for the CH₂- and at δ = 1.65 and 3.2 ppm as multiplet 8H for the pyrididine moiety (Scheme 1).

The chlorosulphonation of compound (I) using chlorosulphonic acid at 0° led to the formation of 9-hydroxy-9-oxo-4-sulphonylchloride (III) [9], which allowed to react with primary and secondary amines i.e. 2-aminopyridine.

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