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Effect of potassium on the physicochemical properties of molybdenum oxide catalyst supported on sol–gel alumina–zirconia

S.N. Koc[a,*], G. Gürdağ[a], E. Löffler[b], M. Orbay[a], M. Muhler[b]

[a] *Department of Chemical Engineering, Istanbul University, Avcilar, 34320 Istanbul, Turkey*
[b] *Laboratory of Industrial Chemistry, Ruhr University, D-44780 Bochum, Germany*

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Abstract

Potassium-promoted molybdenum oxide/alumina–zirconia catalysts were prepared by the sol–gel method. The catalysts were characterized by nitrogen physisorption, X-ray diffraction, scanning electron microscopy, Raman spectroscopy, and Fourier transform spectroscopy measurements. It was observed that potassium addition did not drastically disturb the textural properties and led to a redispersion of the molybdenum oxides composed both of octahedral and tetrahedral structures. Molybdenum oxide mainly led to the formation of Brönsted acid centers while alumina–zirconia support contained Lewis acid centers. Potassium led to a decrease in the number of Brönsted acid centers rather than that of Lewis centers.

Keywords: Molybdenum oxide; Potassium addition; Sol–gel method; Alumina–zirconia support

1. Introduction

Molybdenum oxide catalysts have been extensively investigated for industrially important selective oxidation, hydroprocessing and higher alcohol synthesis reactions [1–4]. Molybdenum oxide catalysts have a complex structure in nature. The type of molybdenum oxide and its dispersion on the catalyst surface, oxidation state and acidity of the catalyst strongly depend on its interactions with support material, promoters and preparation conditions [5,6]. In general, molybdenum oxide can occur in the following structures: crystalline MoO_3, amorphous three-dimensional MoO_3 aggregates, tetrahedral MoO_4^{2-}, octahedral $Mo_7O_{24}^{6-}$, and two-dimensional polymeric molybdates [7–9]. The type of molybdenum oxide on the catalyst surface, and acidity and textural properties of the catalyst have a great importance on catalytic activity and product selectivity in selective oxidation [10–13]. The surface acidity of the catalysts can be adjusted by alkali metal addition, but this metal addition may also change the surface area and pore structure, and may give rise to some undesired phases in the catalyst, leading to total oxidation.

The sol–gel method has popularity in ceramics and catalysts preparation due to its high purity, ability to control textural properties (surface area), well-developed pore structure, molecular mixing, and uniform distribution of active sites through support material [10,14,15]. Different types of support materials (Al_2O_3, TiO_2, SiO_2 and ZrO_2) and their mixtures can be easily prepared by the sol–gel method. By using this technique, textural properties and thermal stability can be provided in binary metal oxides [15]. In the sol–gel method, mixed oxides are prepared by the hydrolysis of alkoxide precursors by using water and an acid/base catalyst in the presence or absence of a complexing agent and by following condensation of hydrolysis products [16].

In the present work, the sol–gel method was preferred for the preparation of alumina–zirconia support material due to the advantages mentioned above. The effect of potassium on the structure (type) of molybdenum oxide, the surface acidity of the catalyst, and the textural properties of the support material were investigated.

2. Experimental details

2.1. Catalyst preparation

Aluminum-sec-butoxide (Fluka), zirconium (IV) propoxide (70% in propanol, Fluka), ethylacetoacetate (Merck),

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[*] Corresponding author. Tel.: +90-212-591-2479; fax: +90-212-591-1997.
E-mail address: nacik@istanbul.edu.tr (S.N. Koc).

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i-propanol (Merck), ammonium heptamolybdate (Merck), aqueous ammonia solution (25%) (Carlo Erba), KOH (Merck) were used as they were supplied without any treatment. All catalysts were prepared by the sol–gel method with a constant molar ratio of Al_2O_3 and ZrO_2 (1:1). In the preparation of catalysts, aluminum-sec-butoxide and zirconium (IV) propoxide have been added to the mixture of *i*-propanol and ethylacetoacetate stirred vigorously so that the molar ratios of alkoxide:*i*-propanol and alkoxide:ethylacetoacetate in the final mixture would be 1:3 and 2:1, respectively. Then, ammonia solution, 0.5 M KOH, 0.25 M ammonium heptamolybdate solution and water have been added dropwise in 30 min; the molar ratios of water and ammonia to total alkoxide were 7:1 and 5:1, respectively. The amount of ethylacetoacetate, which acts as a complexing agent providing the controlled gelation, has been kept constant at some certain values, determined by preliminary experiments, due to the fact that it affects the properties of the final oxide. The reaction mixture was heat-treated at 80 °C in an oven to obtain viscous gel. All gels were dried at 120 °C for 8 h and calcined in air at 540 °C for 3 h. After calcination, the molar ratio of $Mo/(Al_2O_3 + ZrO_2)$ was 1:9. K has been added according to K/Mo molar ratios of 0, 0.05, 0.15, 0.25, 0.50 and the amount of K in the samples is indicated as K0 (K-free), K005, K015, K025, K050 in all tables and figures.

2.2. Catalyst characterization

Nitrogen physisorption was carried out at 77 K with 150 mg samples by a Quantachrome Autosorb 1C apparatus preceded by high vacuum degassing of the catalysts at 300 °C. The X-ray diffraction (XRD) patterns were obtained from a Siemens D-type diffractometer by using Cu Kα radiation. The Raman spectra were recorded a using Nicolet Nexus FT-Raman spectrometer equipped with an InGaAs detector. Raman scattering was excited with an Nd-YAG laser operated between 150 and 1200 cm^{-1} with 4 cm^{-1} scans. Scanning electron microscopy (SEM–EDX) analysis was carried out by a JEOL JXA 840A instrument with an energy dispersive spectroscopy (EDS) analyzer which had a Si(Li) dedector (Mn Kα). Ammonia-diffuse reflectance infrared Fourier transform spectroscopy (NH_3-DRIFTS) experiments were carried out with a Nicolet Protégé FT-IR instrument containing a Spectratech high-temperature chamber. Prior to the measurements, 30 mg powder catalyst samples were degassed at 300 °C in high vacuum conditions. During the measurements, 0.5% NH_3 in 20 ml/min nitrogen flow passed in the system for 30 min.

3. Results and discussion

In the sol–gel preparation of oxides, there are many parameters, which can affect the properties of end-oxide, such as solvent and raw material type, acid–base ratio, amount of water, drying and calcination conditions [17]. Adsorption–desorption isotherms and pore size distribution curves of K-free, K015 and K050 catalysts are presented in Figs. 1 and 2, respectively. In the isotherms there is no radical change even at the highest potassium-loaded K05 sample. Both K0 and K-loaded samples have a type-IV isotherm and the shape of the hysteresis loop changed slightly with potassium addition. It is also seen from the pore size distribution curves that K0 has a great number of narrow pores and its maximum is 25 Å. It is gradually increased to 35 Å in the K05 sample. In all pore size distribution curves the highest limit of pores are approximately 50 Å. This indicates a well-organized mesoporous system with a narrow pore size distribution. Surface area (*S*), pore volume (*V*) and mean pore diameter (*d*) results are presented in Table 1. The surface area of K0 catalyst is 252 $m^2\,g^{-1}$,

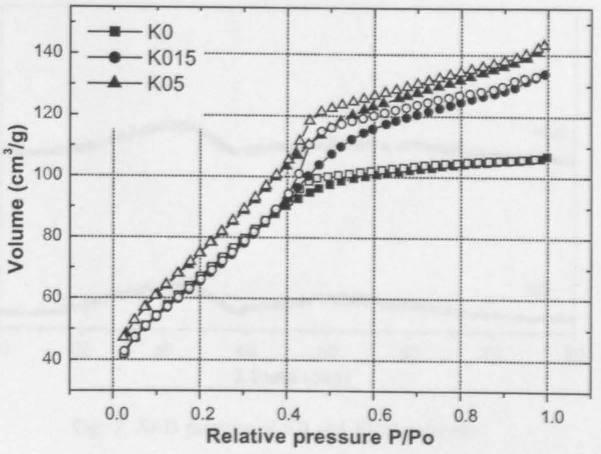

Fig. 1. Nitrogen adsorption–desorption isotherms of K0, K015 and K050 catalysts. The closed and open symbols represent adsorption and desorption data, respectively.

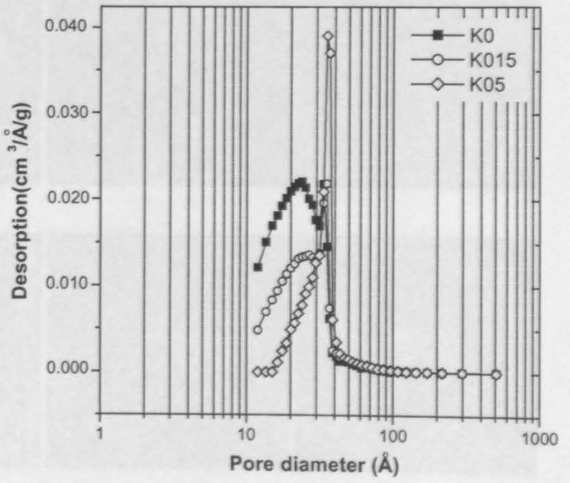

Fig. 2. Barrett–Joyner–Hallenda pore size distribution curves of K0, K015 and K050 catalysts.

Table 1
Nitrogen physisorption results of K–$MoO_x/Al_2O_3–ZrO_2$

Catalyst	S (m^2/g)	V (cm^3/g)	d (Å)
K0	252	0.105	22
K005	294	0.142	20
K015	283	0.135	19
K025	280	0.137	19
K050	246	0.132	17

it is increased to 294 $m^2 g^{-1}$ with lowest potassium loading and the highest K-loaded K050 catalyst had practically the same surface area value as K0 had.

The pore volume results also showed a similar trend. This behavior results from the gelation conditions during the catalyst preparation. The increase in pH value of the solution facilitates the condensation reactions of the hydroxyl groups, which are produced by hydrolysis of the alkoxide compounds in the sol–gel method. This means that the faster the condensation reactions are the more crosslinked gel network occurs. This may lead to the formation of thermally stable pores in higher amounts. Therefore, the surface area and pore volume values were preserved even though further K-loading and the plugging effect of potassium to pore mouth [11,18] of the catalysts were not considerable.

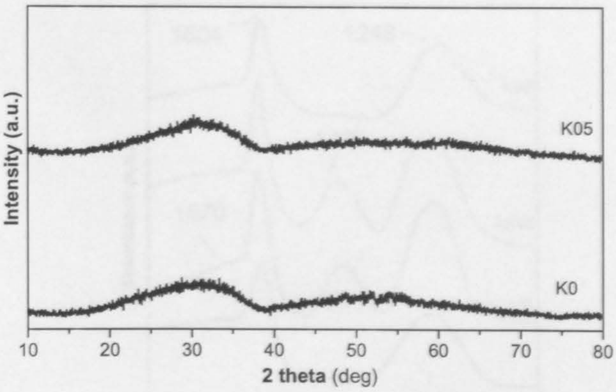

Fig. 3. XRD patterns of K0 and K050 catalysts.

X-ray diffractograms of K-free and K050 catalysts are shown in Fig. 3. It is obvious that both catalysts do not contain crystalline structures. Only a broader shoulder at a diffraction angle $2\theta \approx 31.1°$(JCPDS/24-1164) may indicate the presence of a small amount of tetragonal zirconia phase but it is not clear. Neither crystalline

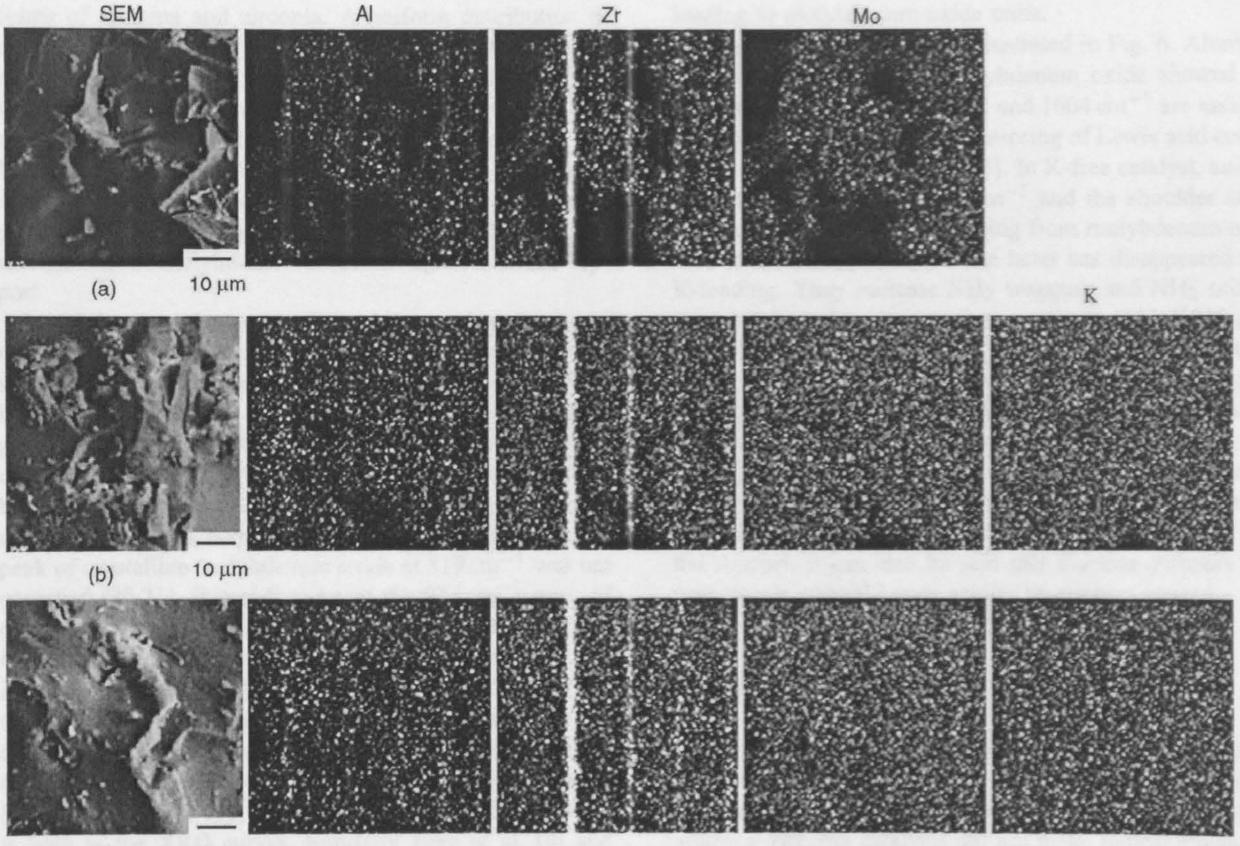

Fig. 4. SEM–EDX results: (a) K0, (b) K015 and (c) K050.

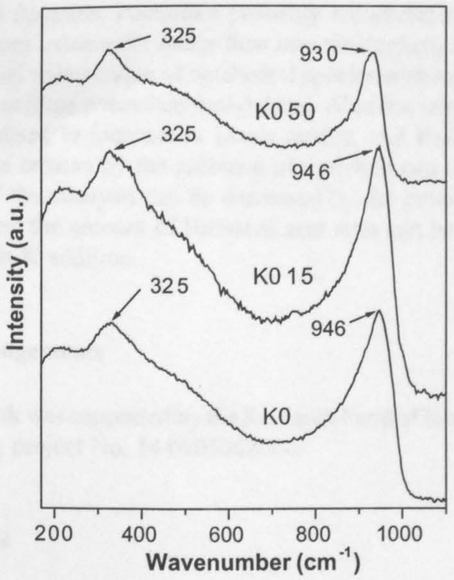

Fig. 5. Raman spectra of K–MoO_x/Al_2O_3–ZrO_2 catalysts.

molybdenum nor potassium compounds are observed (Fig. 3).

SEM–EDX results are shown Fig. 4. In all cases there are no clear grains, which can be attributed to the crystalline forms of alumina and zirconia. A uniform distribution of support material took place as indicated by XRD results. It qualitatively indicates that Mo dispersed in Al-rich environment but a small amount of localization was observed in the Zr-rich environment of K0 catalyst. It was reported earlier that molybdenum oxide could spread easily on alumina support in comparison to zirconia or other conventional supports [19,20]. In K015 and K05 catalysts K loading led to a redispersion of molybdenum oxide through the mixed support.

Molybdenum oxide can be formed in complex structures, depending on its surface density and the interaction with support when it is deposited on different materials. Raman spectra of the catalysts are given in Fig. 5. The 325 cm^{-1} peak is due to the Mo=O bonds of isolated tetrahedral molybdenum oxide species [21–23]. The 226 and 946 cm^{-1} peaks belong to Mo–O–Mo and Mo=O bonds of octahedral molybdenum oxide units, respectively [21,22]. The characteristic peak of crystalline molybdenum oxide at 819 cm^{-1} was not observed [20,21]. It was found that the 946 cm^{-1} peak of octahedral units shifted to 930 cm^{-1} at highest K loading in the K050 catalyst. It can be explained by the potassium incorporation into octahedral molybdenum oxide units. Interaction of K with MoO_x may shift the wavenumber of octahedral units to lower degrees and by bearing in mind that potassium molybdates peaks are observed at 924 cm^{-1} [13]. However, no crystalline potassium molybdate phase is seen in the XRD curves. Similarly Bian et al. [4] and Williams and Eckert [22] have reported this peak at 932 and 926 cm^{-1}, respectively. Furthermore, octahedral units can be produced by condensation of tetrahedral species during calcination and potassium addition can suppress this restructuring. Adamski et al. [23] reported a similar behavior for potassium-promoted V_2O_5–ZrO_2 catalysts. It can explain the decrease in the intensity of octahedral units in comparison to tetrahedral species and spreading effect of potassium loading to molybdenum oxide units.

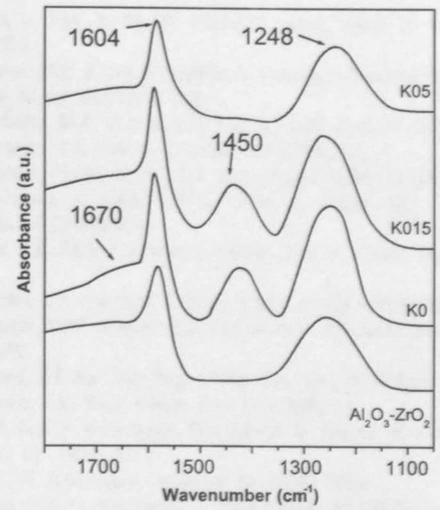

Fig. 6. NH_3-DRIFTS results of K–MoO_x/Al_2O_3–ZrO_2 catalysts.

NH_3-DRIFTS spectra are illustrated in Fig. 6. Alumina–zirconia support without molybdenum oxide showed two main peaks. The peaks at 1248 and 1604 cm^{-1} are assigned to N–N stretching and NH_2 scissoring of Lewis acid centers of the support, respectively [13]. In K-free catalyst, another peak at approximately 1450 cm^{-1} and the shoulder at approximately 1670 cm^{-1}, resulting from molybdenum oxide incorporation, appeared but the latter has disappeared with K-loading. They indicate NH_2 wagging and NH_2 scissoring of Brönsted acid centers, respectively [13]. K015 catalyst showed a similar behavior to the K-free counterpart, but peaks of Brönsted acid centers disappeared at the highest potassium loading, namely K050 catalyst. It is obvious that Brönsted acid sites were produced in the presence of molybdenum oxide. Furthermore, the disappearance of Brönsted acidity with increasing potassium loading may indicate that potassium interacts with molybdenum oxide units rather than the support. It can also be said that alumina–zirconia support mainly caused Lewis acidity by support cations.

4. Conclusions

Alkali addition to a mixed oxide is an important tool to adjust the textural properties of the oxide in catalytical activity respect. Potassium loading to molybdenum oxide/sol–gel alumina–zirconia catalysts did not make radical changes in the textural properties of the catalysts. Molybdenum oxide units are composed mainly both of isolated tetrahedral and octahedral domains. Potassium probably incorporated into molybdenum oxide units rather than into the support, and it led to partial redispersion of octahedral species without producing crystalline potassium molybdates. Alumina–zirconia support caused to increase in Lewis acidity, and Brönsted acidity was created by the presence of molybdenum oxide. Acidity of the catalysts can be decreased by the potassium addition and the amount of Brönsted acid sites can be controlled with K addition.

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