Influence of ZrO$_2$ modifier and Mo precursor on the state of active component in MoO$_3$/Al$_2$O$_3$ catalysts

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Abstract. The effects of precursor and the method of support modification on the properties of supported metathesis catalysts for reaction of ethylene and trans-butene-2 into propylene are considered. The objects of the research are the catalyst comprising γ-Al$_2$O$_3$-supported molybdenum oxide as well as the modified alumina-based supports. The Mo precursors used is shown to significantly affect the state of the supported component. The distribution and morphology of the particles of active component inside the pores of the support differ for the ZrO$_2$-modified samples prepared by impregnation and wet mixing methods.

1. Introduction
The demand in olefins, especially ethylene and propylene, constantly increases and is connected with the rise of the consumption of the polymers on the basis thereof [1 - 2]. Currently, cracking and catalytic dehydrogenation are the main sources of olefins. Although these processes are widely used, the intensive studies on the development of alternative processes for production of light olefins are being carried out [1 - 3].

The metathesis reaction is considered a promising method for propylene production and comprises the redistribution of the alkylidene substitutes of the double bond [1, 4]. In case of propylene production, one molecule of trans-2-butene and one molecule of ethylene participate in the process yielding two propylene molecules. Besides propylene, pentenes and hexenes of various structure can be formed as a result of oligomerization and isomerization of propylene [5].

The catalysts for propylene production by ethylene and trans-butylene metathesis include the oxides WO$_3$, MoO$_3$, Re$_2$O$_7$ supported on γ-Al$_2$O$_3$, SiO$_2$, zeolites and some other supports [6 - 8]. Due to high cost of Re$_2$O$_7$ and its low stability towards catalytic poisons, the industry implements the WO$_3$-based catalysts. Such catalysts possess a relatively low activity, but are stable for long time. The MoO$_3$-based catalysts are promising systems, since they demonstrate the catalytic activity at lower temperatures than the WO$_3$-containing samples [9 – 10]. The activity of these samples depends on the degree of polymerization of the surface MoO$_x$ particles, and the isolated dimeric and dispersed polymeric particles are active in the given reaction [11 – 14], while the crystalline MoO$_3$ is not catalytically active [14 – 20]. Moreover, the support properties affect the activity of the MoO$_3$ particles in the metathesis process, e.g., the catalysts show higher catalytic activity, when supported on more acidic supports [21].

The acidity of the catalyst surface should be quite high facilitating the olefin sorption, however, too high acidity induces oligomerization of the adsorbed olefin molecules [5]. The modification of alumina by zirconia allows regulating the acidity of the support surface that should result in a decrease of the impact of this process. In the present work the effect of modification of alumina support by zirconia and
the nature of the precursor of Mo oxide on the state of active component in MoO₃-based catalysts for metathesis of ethylene and butene into propylene is considered.

2. Experimental

2.1. Methods of catalyst preparation
To prepare the catalysts, the unmodified and ZrO₂-modified alumina supports were used. The unmodified support represented the industrial granulated sample Al₂O₃ (CJSC “Industrial catalysts”, Ryazan, Russia). The modified supports were obtained by two methods. The support designated as ZrO₂/Al₂O₃ was obtained by wetness impregnation of alumina with the citric acid solution of zirconium nitrate followed by drying at 120°C and calcination at 500°C. The support designated as ZrO₂-Al₂O₃ was obtained by the wet mixing using the reprecipitated aluminum hydroxide of type C (γ-Al₂O₃) (CJSC “Industrial catalysts”, Ryazan, Russia) as a powder with a fraction of no more than 0.25 mm and citric acid solution of ZrO(NO₃)₂ (Aldrich). The mixed wet composite was dried at 120°C and then calcined at 500°C in nitrogen flow.

The active component was supported by the wetness impregnation method from water solution of molybdenum oxide precursor. (NH₄)₆MoO₃·4H₂O (CJSC “Vecton”) and H₃PMO₁₂O₄₀·17.26H₂O (CJSC “Vecton”) were used as a Mo precursor. To improve the solubility of the ammonium heptamolybdate (AHM), citric acid was used with the n(Mo) : n(CA) = 1:1. The samples after the impregnation were dried at 110°C during 48 h. The dried samples were calcined in air at 500°C during 2 h in the flow of argon.

2.2. Methods of sample characterization
Textural characteristics of the samples were determined by the method of low-temperature N₂ adsorption on the TriStar 3020 (Micromeritics, US). For all samples, a preliminary degassing was carried out at 200°C for 2 h. The specific surface of the samples was determined from the adsorption data according to the BET method, total pore volume and pore size distribution were determined according to the BJH method.

Phase composition of the samples was studied using X-ray diffraction (XRD) analysis on the XRD-6000 diffractometer (“Shimadzu”, Japan) with a monochromatized Cu Kα radiation (λ=1.5418 Å) in the range of angles of 10-70 (2θ) and a scanning rate of 2°/min. Analysis of phase composition was carried out using the PDF2 database.

To study the X-ray amorphous state of the supported modifier and/or active component using the temperature-programmed reduction (TPR) method, Raman spectroscopy and UV-vis DR spectroscopy were used. The TPR of the samples was carried out using the Micromeritics ChemiSorb 2750 (USA) with the gas mixture 10% H₂/Ar, 20 ml/min. The experiment was carried out in the temperature range of 25-900°C with a heating rate of 10°C/min. The UV-vis DR spectra were taken using the Evolution 600 Thermo Scientific (USA) spectrometer in the scanning range of 200-900 nm, with MgO used as a standard. Raman spectra were taken at ambient conditions on the inVia confocal Raman microscope (Renishaw, UK) using the 785 nm line.

3. Results and discussion
Table 1 shows the results of elemental analysis and textural characteristics of the prepared support samples and the catalysts on the basis thereof.

Chemical analysis shows that the amount of modifier in ZrO₂/Al₂O₃ and ZrO₂-Al₂O₃ supports is 4.5 and 6.1 % mass., respectively. Textural characteristics of ZrO₂/Al₂O₃ and ZrO₂-Al₂O₃ supports differ due to addition of ZrO₂ modifier using different methods. Despite close values of specific surface area, the maxima of bimodal pore size distribution are 7 and 14 nm for ZrO₂/Al₂O₃ support, while the one for ZrO₂-Al₂O₃ is 4 nm. Thus, the total pore volume for ZrO₂-Al₂O₃ support is practically two times lower as compared to ZrO₂/Al₂O₃ samples (Table 1).
Introduction of active component also results in reduction of specific surface and pore volume of the samples that is caused by the increase of their mass, and in case of $\text{H}_3\text{PMo}_{12}\text{O}_{40}$ is also connected with a slight sintering caused by a two-fold thermal treatment at 500 °C. The latter can also be connected with the effect of phosphorus oxide as a mineralizing agent. According to chemical analysis, the Mo content in the samples was 13.4–21.9 % mass.

| Samples                     | Content, % mass. | SSA, m²/g | $V_{pore}$, cm³/g |
|-----------------------------|------------------|-----------|-------------------|
| $\text{Al}_2\text{O}_3$    | -                | 230       | 0.57              |
| $\text{ZrO}_2/\text{Al}_2\text{O}_3$ | 4.5              | 224       | 0.52              |
| $\text{ZrO}_2\text{-Al}_2\text{O}_3$ | 6.1              | 246       | 0.28              |
| $\text{MoO}_3/\text{Al}_2\text{O}_3$ | -                | 191       | 0.45              |
| $\text{MoPO}_x/\text{Al}_2\text{O}_3$ | -              | 173       | 0.47              |
| $\text{MoO}_3/\text{ZrO}_2\text{-Al}_2\text{O}_3$ | 3.6              | 184       | 0.42              |
| $\text{MoPO}_x/\text{ZrO}_2\text{-Al}_2\text{O}_3$ | 3.6              | 157       | 0.41              |
| $\text{MoO}_3/\text{ZrO}_2\text{-Al}_2\text{O}_3$ | 5.9              | 167       | 0.20              |
| $\text{MoPO}_x/\text{ZrO}_2\text{-Al}_2\text{O}_3$ | 5.2              | 163       | 0.20              |

Figure 1 shows the XRD patterns for the alumina supports and the catalysts on the basis thereof. Analysis of the XRD data shows that there is a crystalline phase of $\gamma$-$\text{Al}_2\text{O}_3$ in all support samples. The corresponding reflections in the XRD patterns are strongly widened that evidences the presence of low-crystalline phase. The crystalline phases of $\text{ZrO}_2$ in the modified supports were not detected that indicates their presence in a highly dispersed or X-ray amorphous state.

Figure 1. XRD patterns for the supports and catalysts.

The XRD patterns for the catalysts do not show the reflections of the crystalline phase of active component $\text{MoO}_3$. However, the XRD images of the samples obtained using the ammonium
heptamolybdate with citric acid as well as for the MoPOx/ZrO2/Al2O3 sample in the range of 20–30° (2θ) there are additional wide reflections that can be connected with the presence of highly dispersed X-ray amorphous phases of active component.

Figure 2 shows the UV-vis spectra for the prepared catalysts samples after drying in air at 110 °C. Independently on the support used, the spectra for the catalysts prepared using the citric acid solution of ammonium heptamolybdate are characterized by the absorption band with a maximum at 255 nm corresponding to the O2− → Mo6+ charge transfer in the isolated MoO6 structures [22 – 23]. The spectra for the catalysts prepared using the heteropolyacid solution contain a shoulder at ~350 nm (along with the one at 255 nm) characteristic for the O2− → Mo6+ charge transfer in the MoO6 structures [22 – 24]. The intensity of the band at ~350 nm in the spectra of the catalysts prepared over the zirconia-modified supports is higher than for those prepared over the unmodified alumina. The presence of the band at 255 nm in the catalyst samples prepared using the heteropoly acid solution evidences a partial destruction of the heteropoly ion that can be connected with the interaction of the Mo precursor with the support surface. Modification of the Al2O3 surface with zirconium oxide preserves the structure of the anion in heteropoly acid in the dried samples that evidences the increase of the intensity of the band at 350 nm in the corresponding spectra.

The subsequent calcination of the dried samples at 500 °C results in changing of the spectra (Figure 3). Independently on the precursor used and the modification of the support, the spectra of all calcined samples are characterized by the absorption in the range of 200–400 nm with a maximum at 253-257 nm and a shoulder at 295-302 nm. The observed absorption bands are caused by the O2− → Mo6+ charge transfer in the isolated MoO6 species and those bound in short chains with tetrahedral (250–290 nm) and octahedral (300–320 nm) oxygen surrounding of molybdenum [22 – 23].

All catalysts prepared on the basis of ZrO2-Al2O3 support are characterized by the increase of the absorption background (Figure 2c and Figure 3c). We suppose that application of wet mixing using the reprecipitated aluminum hydroxide of type C (γ-Al2O3) and citric acid solution of ZrO(NO3)2 at the stage of preparation of ZrO2-Al2O3 support leads to the formation of high concentration of surface defects. Such a defective surface increases the dispersion in UV-vis spectra in the range of 400-700 nm.

![Figure 2. UV-ViS spectra for the catalysts after drying at 110 °C.](image-url)
Figure 4 shows the Raman spectra of the synthesized catalysts obtained under the specific conditions at an excitation wavelength of 785 nm. The spectra of all samples do not contain the bands characteristic for crystalline molybdenum oxide (820, 996 cm\(^{-1}\)) that is consistent with the XRD data. The absence of the characteristic bands for phosphomolybdic acid at 883 and 983 cm\(^{-1}\) [25] in the spectra of the samples MoPO\(_4\)/Al\(_2\)O\(_3\), MoPO\(_4\)/ZrO\(_2\)/Al\(_2\)O\(_3\) and MoPO\(_4\)/ZrO\(_2\)-Al\(_2\)O\(_3\) indicates a complete decomposition of the Mo precursor. The absorption band in the range of 900-1000 cm\(^{-1}\) with a maximum at ~970 cm\(^{-1}\) in the spectra of the samples MoPO\(_4\)/Al\(_2\)O\(_3\), MoPO\(_4\)/ZrO\(_2\)-Al\(_2\)O\(_3\) and MoPO\(_4\)/ZrO\(_2\)-Al\(_2\)O\(_3\) correspond to the surface molybdate structures formed by (O=)\(_2\)MoO\(_2\) dioxy species [26 – 27]. A shifting of the maximum of this band to the range of larger wavenumbers in the spectrum for the MoO\(_3\)/Al\(_2\)O\(_3\) sample can be connected with the presence of Mo in the O=MoO\(_2\) monooxo species along with the (O=)\(_2\)MoO\(_2\) dioxy species [26 – 27]. The absence of the bands in the spectra taken in air for the samples prepared on ZrO\(_2\)/Al\(_2\)O\(_3\) support can be caused by the presence of Mo predominantly as the surface O=MoO\(_2\) monooxo species that do not show bands in the Raman spectra in a hydrated state.

Figure 5 shows TPR profiles for the catalyst samples. Analysis of the state of active surface of the synthesized catalyst samples shows that the method of introduction of ZrO\(_2\) modifier into the support as well as the Mo precursor used significantly influences the state of the active component.

For the MoO\(_3\)/Al\(_2\)O\(_3\) sample, prepared from the AHM a maximum of reduction is observed at 462 °C. According to Ref. [28], a reduction of octahedral species Mo\(^{6+}\) to Mo\(^{4+}\) occurs in this range. For Mo\(^{6+}\) in a tetrahedral coordination of oxygen, a stronger interaction with the support surface is observed, thus, its reduction occurs at higher temperatures [29]. For the sample MoPO\(_4\)/Al\(_2\)O\(_3\), hydrogen consumption with a maximum at 523 °C takes place. The observed shifting of the maximum of hydrogen consumption corresponds to the reduction of Mo\(^{6+}\) in a tetrahedral oxygen coordination into Mo\(^{4+}\). This can be caused by different interaction of the used Mo precursors with the support surface at the stages of impregnation and subsequent calcination of the samples that results in the formation of different surface phases. One cannot also exclude the effect of phosphorus in the MoPO\(_4\)/Al\(_2\)O\(_3\) sample on the reduction temperature of MoO\(_3\) species.

In case of the samples prepared over the modified ZrO\(_2\)/Al\(_2\)O\(_3\) support, the reduction profile contains one peak in the range of 530-550°C that can be connected with the reduction of the tetrahedral Mo\(^{6+}\) to Mo\(^{4+}\) as well as with the effect of zirconium oxide. With that, no significant difference is observed in the reduction behavior of Mo(VI) oxide species on the precursor used. Given the Raman spectroscopy data, the observed shifting of the reduction maximum in comparison with the samples prepared using the unmodified Al\(_2\)O\(_3\) is connected with effect of the modifier that changes the reaction ability of the O=MoO\(_2\) monooxo species in the MoO\(_3\) phases.

For the samples prepared over ZrO\(_2\)-Al\(_2\)O\(_3\) support, there are two reduction peaks in a high-temperature range. For the MoO\(_3\)/ZrO\(_2\)-Al\(_2\)O\(_3\) and MoPO\(_4\)/ZrO\(_2\)-Al\(_2\)O\(_3\) samples, the peaks with the maxima at 532 and 608 °C and at 518 and 715 °C, respectively, are observed. In case of MoO\(_3\)/ZrO\(_2\)-
Figure 4. Raman spectra of the investigated catalysts calcined at 500 °C.

Figure 5. TPR H₂ profiles for the Mo-containing catalysts prepared with unmodified and Zr-modified Al₂O₃ supports calcined at 500 °C.

Al₂O₃ sample, the first peak at 532°C is similar to the one for the reduction of the MoO₃/ZrO₂/Al₂O₃ sample and can be attributed to the reduction of Mo⁶⁺ in octahedral coordination to Mo⁴⁺ over zirconia. The second peak at 608 °C can be assigned to reduction of Mo⁶⁺ in a tetrahedral coordination to Mo⁴⁺ over zirconia. For the MoPO₅/ZrO₂-Al₂O₃ sample, the first peak is similar to the one observed at the reduction of the MoPO₅/Al₂O₃ sample and can be attributed to the reduction of Mo⁶⁺ in a tetrahedral coordination to Mo⁴⁺ over the alumina surface. The peak at 715 °C can be connected with the reduction of highly dispersed MoO₃ and MoO₂ phases [30]. The observed difference in the TPR profiles of the samples prepared over the ZrO₂/Al₂O₃ and ZrO₂-Al₂O₃ samples, is probably connected with different distribution of the modifier in the support, which result in different distribution and state of the active component.

4. Conclusion
Thus, based on the XRD, UV-vis, Raman and TPR data it is possible to conclude that all catalyst samples are characterized by the presence of highly dispersed X-ray amorphous molybdenum phases. With that, the modification of the support by ZrO₂ results in the changing of the state of surface MoO₃ phases in the samples. Introduction of ZrO₂ modifier into alumina support by impregnation leads to more homogeneous distribution of the modifier in a porous space of the support that provides the formation of surface MoO₃ phases predominantly as O=MoO₄ monooxo species independently on the nature of the Mo precursor. The use of the wet mixing method to introduce the modifier results in the formation of separate particles of aluminum and zirconium oxides that is accompanied by different distribution of active component in the catalysts prepared with different precursors.
Acknowledgements
Financial support by the Ministry of Science and Higher Education of the Russian Federation is acknowledged. Unique project identifier RFMEFI60717X0169.

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