

Metathesis of 1-octene over MoO_3 supported on mesoporous molecular sieves: The influence of the support architecture

Pavel Topka^a, Hynek Balcar^a, Jiří Rathouský^a, Naděžda Žilková^a,
Francis Verpoort^b, Jiří Čejka^{a,*}

^a *J. Heyrovský Institute of Physical Chemistry, Academy of Sciences of the Czech Republic, Dolejškova 3,
CZ-182 23 Prague 8, Czech Republic*

^b *Department of Inorganic and Physical Chemistry, Division Organometallic Chemistry and Catalysis, Ghent University,
Krijgslaan 281 (S-3), B-9000 Ghent, Belgium*

Received 28 March 2006; received in revised form 8 June 2006; accepted 10 June 2006
Available online 25 July 2006

Abstract

New types of heterogeneous catalysts for alkene metathesis based on molybdenum oxide supported on mesoporous molecular sieves MCM-41, MCM-48 and SBA-15 were developed. These new systems represent inexpensive, easy-to-prepare and highly active and selective heterogeneous catalysts for metathesis of linear alkenes applicable under mild reaction conditions without the necessity of solvent or co-catalyst presence in the reaction mixture. In metathesis of 1-octene, these catalysts showed considerably higher activity compared with MoO_3 supported on conventional silica with selectivity to 7-tetradecene being in the range between 60% and 95%. The highest activity exhibited $\text{MoO}_3/\text{MCM-41}$ with 6 wt.% of Mo (75% conversion after 6 h at 40 °C with selectivity to 7-tetradecene 84%). The turn-over-frequency of the catalysts loaded with 8 wt.% of Mo decreased in the order MCM-41 > MCM-48 > SBA-15, while the selectivity slightly increased in the same order. Using Raman spectroscopy, the differences in the catalytic activity were elucidated as a result of different dispersion of the active phase over the supports.

© 2006 Elsevier Inc. All rights reserved.

Keywords: Metathesis; 1-Octene; Mesoporous molecular sieves; Molybdenum oxide; Raman spectroscopy

1. Introduction

The metathesis of alkenes is at present one of the most frequently used transformations in modern chemical synthesis. It is an attractive reaction for the conversion of low value feedstocks into useful chemical products as important petrochemicals, polymers, oleochemicals and specialty chemicals. The most important applications of alkene metathesis in the field of petrochemicals are the Olefin conversion technology process (originally the Phillips triolefin process) and the Shell higher olefins process, both upgrading less valuable alkenes into the desired products

[1]. Tungsten, molybdenum and rhenium oxides supported on high surface area silica and alumina were used as catalysts in these processes and also in other industrial applications of alkene metathesis [2].

Tungsten and molybdenum oxide catalysts require higher reaction temperatures, at which side reactions (isomerization and oligomerization) decreasing metathesis selectivity occur. Tungsten oxide on silica operates at temperatures ranging from 300 to 500 °C, and molybdenum oxide on alumina or silica is active usually at temperatures from 100 to 200 °C. Only high-priced rhenium oxide catalysts exhibit a high activity and selectivity at temperatures below 100 °C [1–3].

From the practical point of view, catalysts based on molybdenum oxide have attracted the most attention and were thoroughly investigated. Their catalytic activity was

* Corresponding author. Fax: +420 286582307.
E-mail address: jiri.cejka@jh-inst.cas.cz (J. Čejka).

found to depend particularly on (i) the properties of the support, (ii) the content of molybdenum oxide, (iii) activation conditions, and (iv) the oxidation state of molybdenum species. As concerns the support, the activity was found to decrease in the order of decreasing Brønsted acidity of the support, i.e. silica–alumina > alumina > silica [4]. Specific activity of such catalysts was found to pass a maximum for Mo content corresponding approximately to the formation of monolayer of Mo species on the surface [1]. At higher Mo concentrations specific activity decreases due to the formation of catalytically inactive bulk MoO_3 [5]. According to the well-known mechanism of alkene metathesis [1], active centers represent molybdenum carbenes bound to the support surface. High dispersity of molybdenum oxide species on the support surface and a slight reduction of Mo^{VI} to a lower oxidation state (Mo^{IV} or Mo^{V} [5,6]) are prerequisites for the formation of sufficiently active and stable Mo carbene species. The concentration of carbene species on the catalyst surface is rather low, usually only a small fraction of the total amount of molybdenum is converted into the catalytically active species (e.g. about 1% [7]). Up to now, the investigation of molybdenum oxide based metathesis catalysts has been centered on their application in low alkene metathesis in gaseous phase. However, the importance of higher linear alkene metathesis in liquid phase is growing in connection with new demands of feeds for detergent production [8]. Therefore, new efficient catalysts for metathesis of higher alkenes as 1-octene are desired and were developed [9,10]. Key improvement in increasing selectivity of molybdenum oxide catalysts was connected with the introduction of alkali metals on the catalyst surface to poison the acid sites. Thus, while the first metathesis catalyst for 1-octene metathesis ($\text{CoO}/\text{MoO}_3/\text{Al}_2\text{O}_3$) operated at 163 °C allowing to achieve more than 70% conversion but only 3% selectivity to tetradecene [11], the system $\text{K}_2\text{O}/\text{MoO}_3/\text{Al}_2\text{O}_3$ reached 82% conversion and 81% selectivity to 7-tetradecene at 178 °C [12]. The application of $\text{MoO}_3/\text{SiO}_2$ system in metathesis of higher alkenes was not yet reported, although low acidity of SiO_2 support promises an increased selectivity of this catalyst.

In 1992, successful synthesis of MCM-41, the first member of a new family of mesoporous molecular sieves, opened a new area in the research of porous materials [13]. These new types of silica and alumina possess high surface areas, regular structure and mesopores of narrow pore size distribution, which make them ideal for catalysts supporting [14,15]. As concerns the alkene metathesis, siliceous MCM-41 has been used as a support for anchoring of homogeneous Mo and Ru-based metathesis catalysts [16,17]. It was also recently reported that rhenium oxide supported on organized mesoporous alumina (OMA) exhibited more than one order of magnitude higher activity in metathesis of higher alkenes than similar catalysts based on conventional γ -alumina [18–20]. Pore size of OMA was found to influence both the catalyst activity and selectivity [21]. In spite of some hypotheses [19,20,22] the reason for

enhanced activity of these catalysts on OMA is not yet completely understood. According to our best knowledge, only a short communication dealing with application of mesoporous silica as a support for molybdenum oxide metathesis catalyst has been published [23]. Hexagonal mesoporous silica (HMS) was prepared and impregnated with molybdate solution and tested in 1-octene metathesis at 50 °C. The catalyst activity depended strongly on the support structure. Three HMS samples were prepared using three alkylamines with different alkyl chain length (C_8 , C_{12} and C_{16}) as templating agents. Nevertheless, only HMS prepared with octylamine provided the extraordinary high activity in comparison with catalyst prepared using conventional silica as a support (more than ten times higher). However, this study lacks detailed characterization of HMS support and prepared catalysts. In our preliminary communication we have shown that siliceous mesoporous molecular sieve of ordinary MCM-41 type can be effectively used as a support for molybdenum oxide to catalyze 1-alkene metathesis at low reaction temperatures [24].

The objective of this contribution was to utilize the advantages of mesoporous molecular sieves in the preparation of new types of molybdenum oxide catalysts for metathesis of higher alkenes. Three all-siliceous supports with different pore sizes and architectures have been employed in this study: (i) MCM-41 with hexagonal array of one-dimensional channels, (ii) SBA-15 also of hexagonal structure but with approximately two times larger channel diameter, and (iii) cubic MCM-48 with three-dimensional intersecting channels. By supporting MoO_3 on these supports new metathesis catalysts were prepared. As commonly used impregnation with ammonium heptamolybdate aqueous solution was reported to destroy a hexagonal mesoporous structure of MCM-41 [25], we used the thermal spreading for supporting of MoO_3 . This relatively new approach represents an easy and low-cost method, which has been recently used in the preparation of various Mo oxide catalysts [26–28]. The catalysts prepared were characterized by nitrogen adsorption, X-ray diffraction, scanning electron microscopy and Raman spectroscopy and tested in the metathesis of 1-octene, which was chosen as a model substrate. The effect of support architecture and concentration of the active phase on catalyst activity and selectivity was investigated. The catalytic activity of all these catalysts was compared with that of MoO_3 supported on conventional silica.

2. Experimental

2.1. Catalyst preparation

MCM-41 was synthesized by the homogeneous precipitation method, described in a detail in Ref. [24]. Hexadecyltrimethylammonium bromide (CTABr) was used as a template and sodium silicate as a silicon source; pH of the synthesis mixture was controlled by the addition of ethyl acetate. The molar composition of the reaction

Download English Version:

<https://daneshyari.com/en/article/76898>

Download Persian Version:

<https://daneshyari.com/article/76898>

[Daneshyari.com](https://daneshyari.com)