



Metathesis of ethylene and 2-butene over $\text{MoO}_x/\text{Al}_2\text{O}_3\text{-SiO}_2$: Effect of MoO_x structure on formation of active sites and propene selectivity

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ABSTRACT

Catalyst characteristics affecting product selectivity and mechanistic aspects of formation of Mo-carbene species in the metathesis of ethylene and *trans*-2-butene to propylene over $\text{MoO}_x/\text{AlSiO}_x$ were elucidated by complementary techniques. Steady-state catalytic tests revealed that reaction pathways leading to propene formation depend on the kind (highly dispersed or polymerized) of MoO_x species, from which Mo-carbene species are formed in situ. C_3H_6 is produced directly through metathesis of C_2H_4 and *trans*-2- C_4H_8 on Mo-carbenes originated from polymerized MoO_x species, whereas the metathesis of 1- and 2-butenes plays an important role for propene formation on Mo-carbenes formed from highly dispersed MoO_x . In situ FTIR spectroscopy and kinetic analysis suggest that the pathways of propene formation and accordingly the selectivity are determined by the ability of C_2H_4 to react with oxidized MoO_x species and Mo-carbenes. This feed component interacts with highly dispersed MoO_x species more weakly than with polymerized ones. Moreover, C_2H_4 adsorbs more strongly on Mo-carbenes formed from highly dispersed MoO_x than on those originating from polymerized MoO_x species.

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1. Introduction

The metathesis of ethylene and 2-butene to propene represents an attractive technology to close the gap between supply and demand of this important building block in the chemical industry [1,2]. On a large scale, this reaction is performed over a WO_x/SiO_2 catalyst operating at temperatures above 573 K [3]. Supported Mo-containing catalysts are promising alternatives owing to the higher intrinsic activity of Mo sites compared with their W counterparts [4–8].

In order to improve performance of the known catalysts or to design new materials, it is important to identify selective and non-selective reaction pathways and to establish relationships between them and active sites. According to the commonly accepted mechanistic concept, olefin metathesis is catalyzed by metal carbene species [9]. These species are formed in situ under reaction conditions through a pseudo-Wittig mechanism [10–13]. The group of Bell showed that in comparison with air treatment, treatment of WO_x/SiO_2 in a flow of He results in a faster transformation of mono-oxo W(VI) species to dioxo W(VI) species [14]. The latter are converted into W-carbene upon their reaction with propene. Alternatively, treatment with organosilicon reductants

was recently reported to facilitate creation of carbene species over WO_x/SiO_2 or $\text{MoO}_x/\text{SiO}_2$ at low temperatures [15]. In addition to the treatment, the kind of supported ReO_4 species determines the activity of $\text{ReO}_x/\text{Al}_2\text{O}_3$ in propene metathesis [16]. In contrast to ReO_4 bounded to two more basic Al^{3+} sites, ReO_4 anchored at two more acidic Al^{3+} sites are the active sites for the target reaction. Another important activity-determining factor is the usage of metathesis-inactive co-catalysts such as MgO , $\text{Ca}(\text{OH})_2$, CaO , Y_2O_3 , NaOH , NaNO_3 , or KNO_3 [17–19]. It is assumed that such materials generate gas-phase species from 2-butene, which are responsible for formation/stabilization of Mo-carbenes.

The following four steps were suggested for transformation of MoO_x species into Mo-carbenes ($\text{Mo}=\text{CHR}$) in the course of propene metathesis over a $\text{MoO}_x/\text{SiO}_2$ catalyst: (i) protonation of propene on surface $\text{Mo}(\text{VI})\text{O}_x$ species possessing Brønsted acidity, (ii) oxidation of the adsorbed propene to acetone, (iii) desorption of acetone resulting in a reduction of $\text{Mo}(\text{VI})$ to $\text{Mo}(\text{IV})$, and (iv) oxidative addition of another propene molecule to the latter species yielding $\text{Mo}(\text{VI})$ -alkylidene ($\text{Mo}=\text{C}_3\text{H}_6$) species. [13] As shown in our recent study of the metathesis of ethylene and 2-butene to propene over $\text{MoO}_x/\text{SiAlO}_x$ ($\text{Si} = 0\text{--}100$ wt%) catalysts [7], no direct correlation between Mo loading and the rate was established, while the rate of propene formation increased with Brønsted acidity of MoO_x species. The latter result underlines the importance of step (i) for generation of active Mo-carbenes.

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In comparison with most previous studies dealt with elucidation of activity-determining factors in propene metathesis, investigations addressing selectivity in the metathesis of ethylene and 2-butene to propene are rather scarce. Hahn et al. [20] have recently demonstrated that propene selectivity over $\text{MoO}_x/\text{SiAlO}_x$ is strongly influenced by the kind of supported MoO_x species (highly dispersed vs. polymerized). However, no detailed mechanistic analysis was performed to identify the origins of the different catalytic behavior.

Against the above background, the objectives of the present contribution were (i) to investigate formation of $\text{Mo}=\text{CHR}$ from highly dispersed or polymerized MoO_x species supported on $\text{SiO}_2\text{-Al}_2\text{O}_3$ upon their reaction with ethylene, propene, and *trans*-2-butene and (ii) to elucidate primary and secondary reaction pathways of ethylene and *trans*-2-butene metathesis to propene over carbenes formed from the above species. To this end, we used several complementary techniques, such as in situ Fourier transform infrared (FTIR) spectroscopy, switch tests with ethylene or *trans*-2-butene, the temporal analysis of products (TAP) reactor, and steady-state catalytic experiments. The latter tests were applied for identifying primary and consecutive reaction pathways. The FTIR and switch tests enabled us to derive insights into the mechanism of Mo-carbenes formation, while the rate constants of adsorption and desorption of ethylene and *trans*-2-butene were obtained from TAP experiments.

2. Experimental

2.1. Catalyst preparation and their characterization

The catalysts were prepared by incipient wetness impregnation of commercial SiO_2 (Aldrich), Al_2O_3 (Chempur) and $\text{SiO}_2\text{-Al}_2\text{O}_3$ supports (Sasol) containing 1, 10, 40, or 70 wt% of SiO_2 . The supports were initially dried at 383 K for 24 h and then calcined at 773 K in static air for 8 h. Hereafter they were impregnated by adding dropwise aqueous solutions of ammonium heptamolybdate (Riedel-de Haen). The obtained catalyst precursors containing 0.15 or 1.5 $\text{Mo}\cdot\text{nm}^{-2}$ were treated at 383 K in static air under agitation for 10 h and then calcined in the same way as the supports. The most important characteristics of the catalysts tested in the present study are summarized in Table 1. Further detailed information about preparation, the kind of supported MoO_x species, their redox and acid-base properties as well as physico-chemical properties of the bare supports as determined from N_2 adsorption, ICP-OES, XRD, UV-Vis and Raman spectroscopy, H_2 -TPR, and FTIR pyridine adsorption can be found in our previous study [7]. For easier reading of the present manuscript, we, however, summarized the most important experimental data related to the assignment of the kind of surface MoO_x species in Figs. S1 and S2 in SI. In general, the catalysts with 0.15 $\text{Mo}\cdot\text{nm}^{-2}$ possess highly dispersed

MoO_x species, while their counterparts with 1.5 $\text{Mo}\cdot\text{nm}^{-2}$ contain mainly polymerized MoO_x species as well as MoO_3 , with the latter being present in the catalysts containing 40, 70, or 100 wt% SiO_2 . The catalysts on the basis of $\text{SiO}_2\text{-Al}_2\text{O}_3$ supports are abbreviated as XMoSY , where “X” stands for the nominal Mo loading ($\text{Mo}\cdot\text{nm}^{-2}$) and “Y” for the silica content (wt.%) in the bare support. XMoAl is used to abbreviate $\text{MoO}_x/\text{Al}_2\text{O}_3$ materials. The bare $\text{SiO}_2\text{-Al}_2\text{O}_3$ supports are labelled as Si(Y)AlO_x .

2.2. In situ FTIR spectroscopy

The FTIR spectra were recorded with a Tensor 27 spectrometer (Bruker) equipped with an in-house developed reaction cell with CaF_2 windows. The cell used for FTIR tests is like a continuous-flow reactor and is equipped with two open/close valves at the inlet and the outlet. The valves are used to interrupt the flow and to keep the catalyst under static conditions in the same feed mixture. In such way, the treated catalyst is not exposed to the ambient atmosphere. The cell was connected to the flow system of the reactor used for the catalytic tests described in Section 2.3. The catalysts (50 mg) were pressed into self-supporting wafers with a diameter of 20 mm and treated as follows:

- (i) Heating from room temperature to 663 K in a flow of nitrogen with $5\text{ K}\cdot\text{min}^{-1}$,
- (ii) oxidation in a flow of air at 663 K for approximately 2 h,
- (iii) cooling to 423 K in a flow of nitrogen with $5\text{ K}\cdot\text{min}^{-1}$,
- (iv) treating in an olefin/nitrogen = 1/17 flow (olefin: C_2H_4 , C_3H_6 , or *trans*- C_4H_8) for 60 min and then closing the cell for 30 min,
- (v) purging with nitrogen for 30 min,
- (vi) treating in a $\text{C}_2\text{H}_4/\text{trans}\text{-C}_4\text{H}_8/\text{N}_2 = 1/1/16$ flow for 60 min and then closing the cell for 30 min,
- (vii) purging with nitrogen for 30 min.

The FTIR spectra were recorded after steps (iii), (v), and (vii). To illustrate reaction-induced changes with respect to the kind and the concentration of adsorbates, the spectrum of fully oxidized sample (after step (iii)) was subtracted from the spectra obtained after steps (v) and (vii).

2.3. Catalytic tests

Catalytic tests were performed using an ethylene/*trans*-2-butene/nitrogen = 5/5/1 feed at 423 K and total pressure of 125 kPa in an in-house developed set-up. This set-up is equipped with 15 continuous-flow fixed-bed tubular ($d_{\text{in}} = 4\text{ mm}$, $L = 500\text{ mm}$) quartz reactors operating in parallel. To determine selectivity-conversion relationship, the modified contact time ($m_{\text{cat}}/F_{\text{total}}$) was varied from 0.03 to 1.10 $\text{s}\cdot\text{g}\cdot\text{mL}^{-1}$ by adjusting both catalyst amount (0.02–0.60 g) and total gas flow (11 or 22 $\text{mL}\cdot\text{min}^{-1}$).

Table 1
Selected physico-chemical properties of used Mo-containing catalysts.

Sample	Si/Al ^a	ω_{Mo} , $\text{Mo}\cdot\text{nm}^{-2}$	S_{BET} , $\text{m}^2\cdot\text{g}^{-1}$	Brønsted acidity ^b , 10^{-3}	Lewis acidity ^b , 10^{-3}
0.15MoS10	10/90	0.17	340	0.00	16.24
0.15MoS40	40/60	0.21	390	3.49	12.56
0.15MoS70	70/30	0.13	320	6.69	10.72
1.5MoAl	0/100	1.48	140	0.00	35.21
1.5MoS1	1/99	1.33	255	0.00	28.90
1.5MoS10	10/90	1.37	315	3.94	19.21
1.5MoS40	40/60	1.35	365	9.40	16.25

^a Ratio of wt.% of SiO_2 to Al_2O_3 .

^b The acidity values were calculated from IR spectra of adsorbed pyridine recorded at 423 K.

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