Reactions of propene on supported molybdenum and tungsten oxides

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Abstract

Alumina-supported tungsten and molybdenum oxide catalysts with a wide range of MO_3 loadings were studied in the metathesis of propene. The catalysts were activated by several procedures in order to correlate the oxidation state of Mo or W, as characterized by XPS, and the acidic character, as determined by IR of adsorbed pyridine, with the main metathesis reaction and side olefin reactions. The catalytic activity of the samples under standard conditions was found to be invariant with the pretreatment (air or He). This leads to the conclusion that the activation of catalysts takes place under the propene atmosphere during the first minutes of reaction. XPS studies of fresh and spent catalysts showed that the active sites for metathesis seem to be W(VI) or Mo(VI) species. Both MoO_3/Al_2O_3 and WO_3/Al_2O_3 catalysts are active in parallel reactions such as polymerization, isomerization and cracking. The product distribution for the metathesis reaction differed greatly from that expected. Thus, for all catalysts the ethene/butene ratio is lower than 1 and isobutene was the main component of the C_4 fraction, its proportion increasing with the metal oxide content. Studies by IR of adsorbed pyridine showed the Brønsted acid sites generated on MoO_3 or WO_3 in samples with high metal oxide content to be responsible for the lateral acid-catalyzed reactions.

Keywords: Metathesis; Molybdenum oxide; Propene reactions; Tungsten oxide

1. Introduction

Metathesis, isomerization, cyclopropanation and polymerization reactions are closely related alkene transformations. The metathesis of olefins has been a widely studied process due to its academic and industrial interest [1–5]. The metathesis technology affords interesting possibilities for the synthesis of valuable organic compounds which are difficult to obtain by other methods [6].

Tungsten oxide and molybdena based catalysts have received considerable attention due to their high metathesis activity and because they provide a close relation between heterogeneous and homogeneous catalysis. Most of the mechanistic studies of the reaction have been performed on homogeneous systems and have shown that metal carbene complexes are intermediates [7,8]. It has also been widely accepted that analogous metal carbene species are formed on the surface of heterogeneous oxidic catalysts [9,10]. However, extremely divergent conclusions have been drawn

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concerning the oxidation state of the metal which is part of the active carbene site. For supported MO_3 (M = Mo, W) catalysts, the oxidation states suggested are 0 [11], +2, +3 [12,13], +4 [14–18], +5 [19–21] and +6 [17,18,22–24]. Therefore, this is still a subject of debate which merits further clarification. On the other hand, olefin metathesis is usually accompanied by several competing parallel reactions involving the reacting olefins such as reduction, dehydrogenation, carbon deposition ... [25]. Few studies [21] dealing with this carbon deposition problem have been reported so far in the literature.

The present paper studies comparable series of alumina-supported Mo- and W-based catalysts with a wide range of MO_3 loadings in the metathesis of propene. The catalysts were activated by several procedures in order to correlate the oxidation state of Mo or W, as characterized by X-ray photoelectron spectroscopy (XPS), and the acidic character, as determined by IR of adsorbed pyridine, with the main metathesis reaction and side olefin reactions.

2. Experimental

2.1. Catalyst preparation

A Girdler γ-alumina with a low impurity content and a surface area of 188 $m^2 \cdot g^{-1}$ was used as support. Support was sieved between 0.4 and 0.75 mm and catalysts were then prepared by the incipient wetness method from neutral H_2O_2 solutions of $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ or $(NH_4)_2W_4O_{13} \cdot 8H_2O$. The solution concentrations were to have 3, 6, 10 and 15 nominal weight% on MO_3 (M = Mo, W). The impregnated samples were dried under air from room temperature up to 393 K for 24 h and then calcined in air at 50 $K \cdot h^{-1}$ up to 873 K for 3 h. Similarly, but using a D11-11 BASF silica as support, a sample with a nominal 15 wt% WO_3/SiO_2 was prepared for comparison. In Table 1, the MO_3 contents of the catalysts are resumed and the nomenclature of the samples is illustrated.

Table 1
Nomenclature and composition of MO_3 (M = W or Mo) / Al_2O_3 catalysts

Catalyst [a]	MO_3 content (%)	
	Nominal	Chemical analysis
3WA	3	3.2
6WA	6	6.2
10WA	10	10.1
15WA	15	15.0
3MoA	3	2.9
15MoA	15	13.7
15WS	15	14.6

[a] A = alumina support, S = silica support.

2.2. Catalytic activity

Catalytic tests were performed in a single-pass (differential) fixed-bed microreactor system at 101 kPa (1 atm) of total pressure. The operating mode was similar for all catalysts. A catalyst sample, 0.25–1 g was placed in the reactor and then pretreated under air or helium flow at temperatures between 873 K and 1073 K for 1 h. Once the catalyst was cooled to the reaction temperature, 573 K or 773 K, high purity propene was admitted at 20 $ml \cdot min^{-1}$. Reactant conversions were less than 3%, so mass and heat transfer limitations were avoided. The reactor effluent was analyzed by gas chromatography using a Varian 3400 GC equipped with an automated and heated on-line gas sampling valve. In all cases, a study of the activity and selectivity over the reaction time was done. Overall conversion is defined as the total amount of propene converted to other products, while metathesis conversion is defined as the amount of propene converted to C_2 and C_4 olefins. Ethene and butenes (1-C_4, i-C_4, t-C_4, c-C_4) selectivities are calculated as the amount of propene converted to the product divided by the total amount of propene converted to C_2 and C_4 olefins.

2.3. X-ray photoelectron spectroscopy (XPS)

The XP spectra were recorded with a Fisons ESCALAB MKII 200R spectrometer equipped with a Mg Kα X-ray excitation source

($h\nu = 1253.6$ eV) and hemispherical electron analyzer. The samples were turbopumped to ca. 10^{-3} N·m^{-2} and then moved into the analysis chamber. The residual pressure in this ion-pumped chamber was maintained below 2×10^{-7} Nm^{-2} during data acquisition. A 20 eV energy region of the photoelectrons of interest were signal-averaged for a number of scans in order to obtain good signal-to-noise ratios at reasonable acquisition times. Although surface charging was observed in all samples, accurate (± 0.2 eV) binding energies (BE) could be determined by charge referencing with a C 1s at 284.9 eV or a Au 4f$_{7/2}$ peak at 83.8 eV.

2.4. Infrared spectroscopy (IR)

The infrared spectra were recorded on a Nicolet 5ZDX Fourier transformed spectrophotometer with a resolution of 4 cm^{-1}. Self-supporting wafers of the samples with weight-to-surface ratios of about 10 mg·cm^{-2} were placed in a vacuum cell assembled with greaseless stopcocks and KBr windows. The adsorption of pyridine was effected after evacuation of materials at 723 K for 1.5 h. Subsequently, the samples were exposed to 2 Torr (1 Torr = 133.3 Pa) of pyridine vapour at room temperature for 5 min, and then outgassed at 473 K for 1 h. The IR spectra were recorded at room temperature.

3. Results and discussion

3.1. Catalytic activity

It is well known that activity of catalysts for metathesis reaction is sensitive to pretreatments with various gases under different operating conditions [26]. In Figs. 1A and 1B, the influence of the gas (air or He) for catalyst activation on the specific activity in the propene conversion under standard reaction condition is presented. Besides the transformation of propene to metathesis products (ethene and butenes), parallel reactions such as cracking, carbon deposition and polymerization
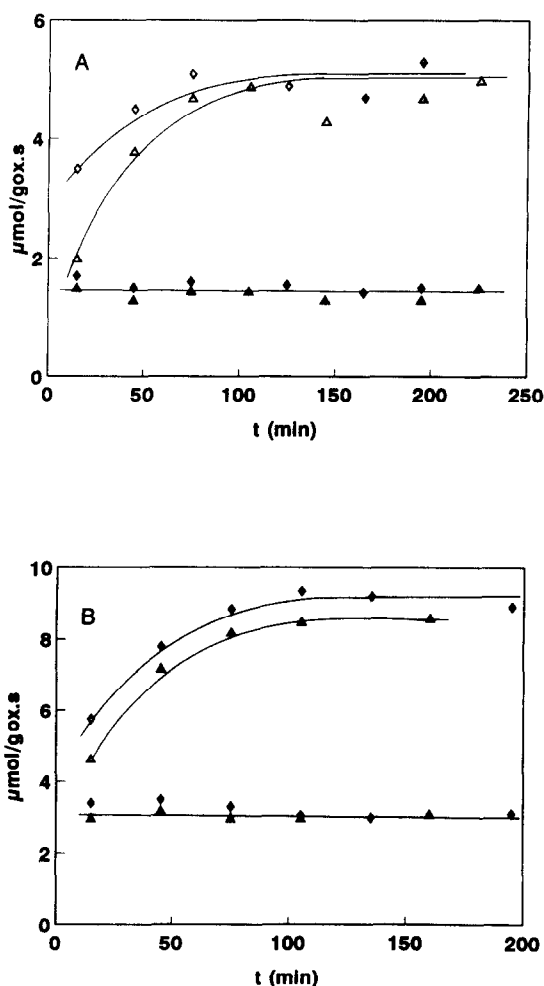

Fig. 1. Dependence of the total activity (open symbols) and metathesis activity (filled symbols) with the time on-stream for the 3WA (A) and 3MoA (B) catalysts subjected to pretreatment in air ($\Diamond$, $\blacklozenge$) or helium ($\triangle$, $\blacktriangle$).

are present. Then the overall activity (μmol of total propene converted per gram of metal oxide and per second) and metathesis activity (μmol of propene converted to C$_2$ and C$_4$ olefins per gram of metal oxide and per second) for 3WA (Fig. 1A) and 3MoA (Fig. 1B) catalysts are plotted as a function of time on-stream. It is seen that catalytic activities measured after air treatment at 773 K for 1 h are very similar to those resulting from the inert gas activation (He at 873 K for 1 h). The overall activities increase with the time on-stream and become constant after 2 h, whereas the metathesis activities are stable over time. 3WA
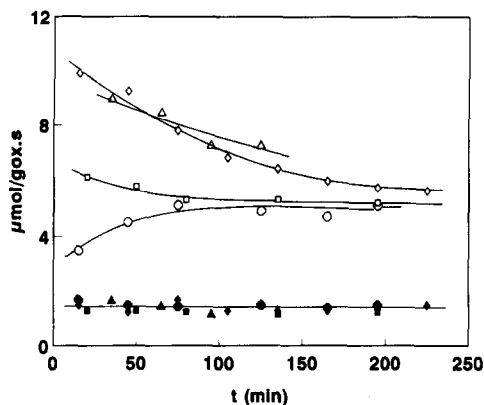
Fig. 2. Dependence of the total activity (open symbols) and metathesis activity (filled symbols) with the time on-stream for the WA catalysts with variable amount of WO_3: (○, ●) 3%; (□, ■) 6%; (△, ▲) 10%; (◇, ♦) 15%. Pretreatment in air at 773 K for 1 h was used.
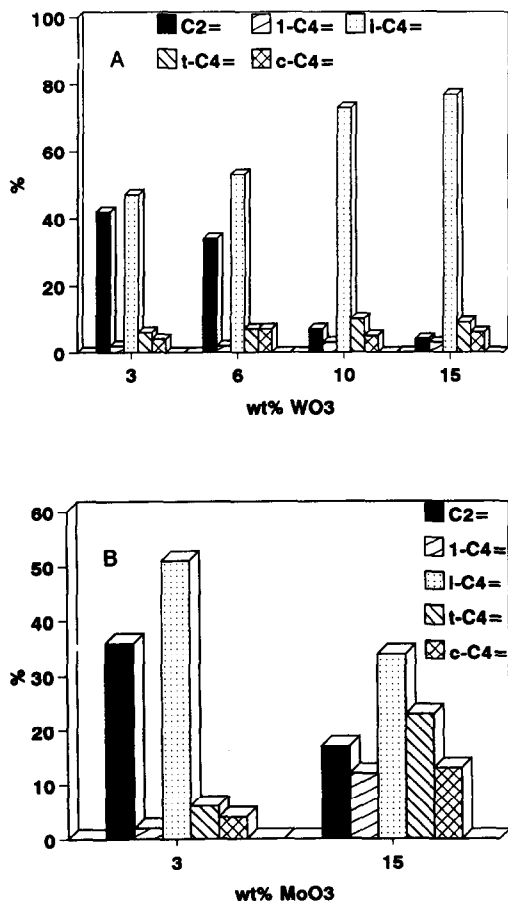

Fig. 3. Selectivity to metathesis products for WA (A) and MoA (B) catalysts as a function of the metal oxide content. The ethene and butenes are identified inside the figure.

and 3MoA catalysts display a very similar type of behaviour, although the latter shows a higher level of activity in the propene reaction and is invariant with the pretreatment (air or He). In principle, thermal treatment under He is expected to generate active sites in the metathesis reaction, especially for catalysts containing a greater amount of metal oxide, since they are more easily reduced [27,28]. However, this is not the case. It is concluded that the activation takes place under the propene atmosphere, and given that the metathesis activity is constant with the process time, the active sites are created during the very early time of reaction. These findings agree with those reported for MoO_3/Al_2O_3 catalysts where no influence of the reduction degree on the metathesis activity was detected [29]. In addition, on alumina-supported WO_3 or MoO_3 catalysts [17,18], it has been suggested that the active sites of metathesis can be formed starting from W(VI) or Mo(VI) species, probably in a tetrahedral coordination.

The influence of transition metal content on the stability of the catalyst with the time on-stream is shown for the WO_3 catalysts pretreated in air at 773 K for 2 h in Fig. 2. A similar picture can be obtained for the MoO_3 catalysts. The catalysts display a similar metathesis activity in spite of their very different WO_3 content. This indicates as has been established before that the portion of active sites for the metathesis reaction is low and occupies only a small fraction of the catalyst surface [29]. However, the overall catalytic activity increases with the metal oxide content, so the generated species in these samples catalyze other reactions such as polymerization and cracking. The coke formation, which produce a relatively strong coloration of the catalysts after reaction, leads to a decline in the overall activity. Fig. 2 shows that the higher the overall activity, the higher the deactivation of the catalyst. But active sites for metathesis are not destroyed by the coke deposition.

The selectivity to metathesis products for WO_3 and MoO_3 catalysts as a function of the metal oxide content is illustrated in Figs. 3A and 3B
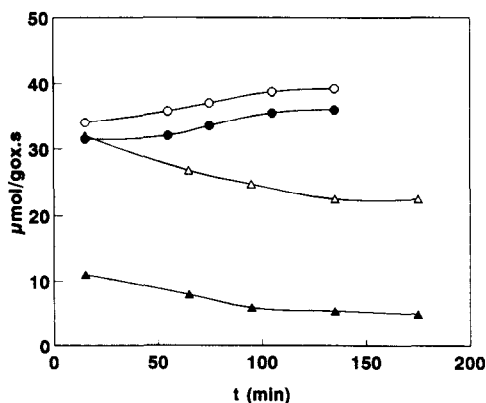
Fig. 4. Influence of the time on-stream on the total activity (open symbols) and metathesis activity (filled symbols) at reaction temperature 773 K on 15WS (O, ●) and 15WA (△, ▲) catalysts pretreated in a helium flow at 973 K for 1 h.

respectively. For all catalysts a ethene/butene ratio of less than 1 is always found. The 3MoA and 3WA catalysts show an ethene/butene ratio closer to that of propene metathesis. But this ratio decreases markedly with the increasing metal oxide content. This indicates that after metathesis reaction, dimerization of ethene may take place. Analysis of the butenes formed revealed that the isobutene is the main component of the C_4 fraction and the portion of isobutene increases with the metal oxide content. Besides isobutene, the 2-butenes (*trans* and *cis*) and 1-butene are present. For all catalysts the trans/cis 2-butene ratio corresponds to equilibrium [30]. It is known that acid centers of γ-alumina may be active in olefine polymerization and isomerization reactions. However, when γ-alumina was reacted with ethene under the experimental conditions used in the propene reaction, ethene was dimerized only in a minor extent and no isobutene was detected. Consequently, the polymerization, isomerization and cracking reactions must be catalyzed by acid sites generated on the tungsten oxide or molybdena in catalysts with high loading. Similar results have been reported by Tsuda et al. [31] who found that over unsupported WO_3 below about 600 K dimerization was the dominant reaction.

A completely different picture is found when WO_3 is supported on silica. In Fig. 4 the specific activity at 773 K of 15WSi and 15WA catalysts

pretreated in He at 973 K for 1 h is plotted as a function of the reaction time. The 15WSi catalyst has a high selectivity (≈ 92%) to metathesis reaction. The product distribution corresponds to that expected for metathesis. The ethene/butene ratio is equal to one and the butene distribution is as expected from thermodynamic considerations. Moreover, the 15WSi shows almost constant activity, while the 15WA deactivates over time. The inferior performance of WO_3 on alumina compared to silica may be due to the high interaction of the WO_3 with the alumina, which produces very different catalytic active species.

3.2. IR characterization

Studies by IR of pyridine adsorbed on the catalysts were performed in order to determine the nature (Brønsted or Lewis) and the strength of the acidic centers present. Fig. 5 displays the IR spectra of catalysts after adsorption of pyridine. The 3WA and 3MoA catalysts have Lewis (1455 cm^{-1}) acid sites, while both Brønsted (1545 cm^{-1}) and Lewis (1455 cm^{-1}) sites are present in 15MoA and 15WA catalysts. The presence of Brønsted acid sites in samples with high MoO_3 or WO_3 content is probably associated with the for-
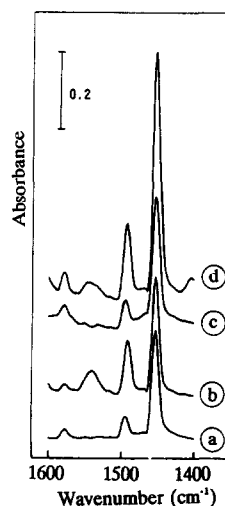

Fig. 5. FT infrared spectra of chemisorbed pyridine on outgassed catalysts at 723 K. (a) 3MoA; (b) 15MoA; (c) 3WA; (d) 15WA. Physically adsorbed pyridine was removed by outgassing at 473 K prior recording the spectra.
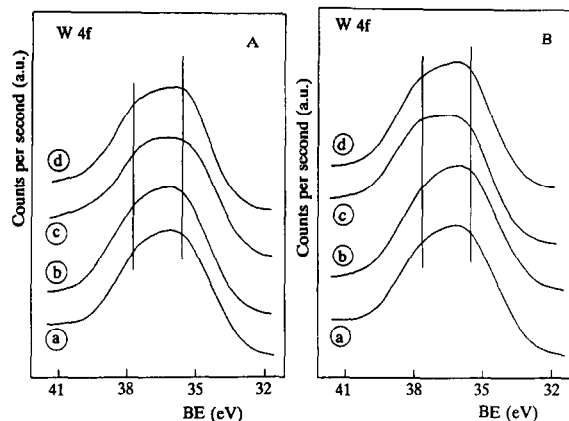
Fig. 6. W 4f core level spectra of fresh (A) and spent (B) WA catalysts with variable amount of WO_3: (a) 3%; (b) 6%; (c) 10%; (d) 15%.
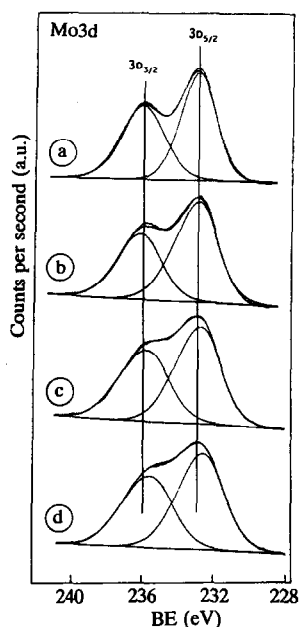

Fig. 7. Mo 3d core level spectra of fresh MoA catalysts with variable amount of MoO_3: (a) 3%; (b) 6%; (c) 10%; (d) 15%.

mation of octahedral polymeric tungstate (molybdate) structures characteristic of the bulk metal oxide. These octahedral structures easily trap the H_2O coming from the dehydroxylation of the alumina and form stable hydroxyl groups which remain after treatments in He at 973 and 1073 K. The hydroxyl groups likely block the active sites for metathesis and give reactions typical of acid sites, such as polymerization, isomerization and cracking.

3.3. XPS characterization

A study of the fresh and spent MoO_3 and WO_3 catalysts was done by XPS. In Fig. 6, XP spectra of the W 4f levels for fresh (Fig. 6A) and spent (Fig. 6B) catalysts are presented. For the MoO_3 catalysts the Fig. 7 summarizes the XP spectra of the Mo 3d level. The BE values are listed in Table 2. From the BEs of the principal W $4f_{7/2}$ (≈ 35.7 eV) and Mo $3d_{5/2}$ (≈ 232.8 eV) peaks, it can be deduced that all the samples, either fresh or spent, show only the presence of W(VI) or Mo(VI). These findings are in accordance with an early ESR and kinetic study on MoO_3/Al_2O_3 (24) in which the Mo(VI) sites are found to be the active species for the olefin disproportionation. These results also agree with those of Grünet et al. who proposed that the active sites for metathesis can be formed from W(VI) and Mo(VI) precursors [17,18]. Nevertheless, on the basis that only a fraction of the active component is involved in the catalytic sites of metathesis, the presence of other species such as W(V) or Mo(V) in a proportion below the limit of detection of the XPS cannot be excluded. However, the almost constant catalytic activity with the pretreatment (air or He) support the conclusion that the W(VI) or Mo(VI) species are the active sites for the metathesis activity.

In Fig. 8 the W 4f/Al 2p XPS intensity ratios are plotted versus the bulk atomic ratios and compared with the intensity ratios predicted for mon-

Table 2
Binding energies (eV) and XPS intensity ratios of fresh and spent catalysts

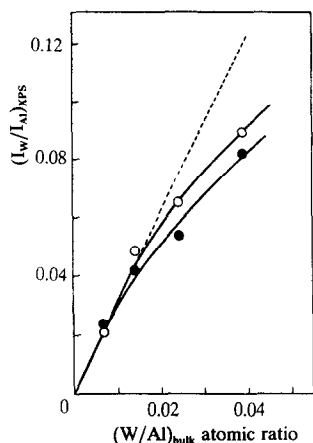| Catalyst	Pretreatment	Al 2p	Mo $3d_{5/2}$ or W $4f_{7/2}$
3WA	calcined	74.1	35.4
6WA	calcined	74.2	35.5
10WA	calcined	74.1	35.7
15WA	calcined	74.2	35.8
3WA	used	74.2	35.5
6WA	used	74.2	35.4
10WA	used	74.4	35.6
15WA	used	74.5	35.9
3MoA	calcined	74.3	232.6
15MoA	calcined	74.5	232.9
3MoA	used	74.2	232.4
15MoA	used	74.4	232.8

Fig. 8. Tungsten-to-aluminum XPS intensity ratios vs. the tungsten-to-aluminum bulk ratios in fresh (O) and used (●) WA catalysts. The theoretical intensity ratios predicted by the stacking sheet model is represented as a dashed line.

olayer coverage by the stacking sheet model [32]. It is seen that deviations from the monolayer prediction already occur below the theoretical monolayer coverage. In fact, for samples with higher metal oxide content, peaks corresponding to WO_3 were observed by X-ray diffraction. For the MoO_3 similar behaviour can be described.

4. Conclusions

Alumina-supported tungsten and molybdenum oxide catalysts were studied in propene metathesis. The catalytic activity of the samples under standard conditions is invariant with the pretreatment (air or He). This finding leads to the conclusion that the activation of catalysts takes place under the propene atmosphere during the first minutes of reaction. XPS studies of fresh and spent catalysts show that the active sites for metathesis seem to be W(VI) or Mo(VI) species.

Both MoO_3/Al_2O_3 and WO_3/Al_2O_3 catalysts are active in parallel reactions such as polymerization, isomerization and cracking. Therefore, the product distribution obtained was quite different from that of the metathesis reaction. For all catalysts the ethene/butene ratio was less than 1 (the expected value from the stoichiometric reaction: $2 C_3H_6 \rightarrow C_2H_4 + C_4H_8$) and isobutene was the

main component of the C_4 fraction, its proportion increasing with the metal oxide content. Studies by IR of adsorbed pyridine showed the Brønsted acid sites generated on MoO_3 or WO_3 in samples with high metal oxide content to be responsible for the lateral acid-catalyzed reactions.

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