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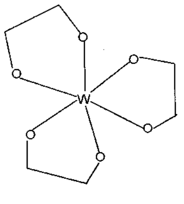
NOTE

Preparation and Activity of Heterogeneous Metathesis Catalysts Based on Trisdiolatotungsten(VI) Complexes as Precursors

Tungsten-based catalysts are well known for the metathesis of olefins (1). In heterogeneous catalysis the active metal compound is usually deposited on an oxidic support, typically SiO_2 or Al_2O_3. The coordination sphere of the tungsten atom in the catalyst is generally formed by oxygen atoms. The alkene metathesis reaction in the homogeneous case includes formation of metal carbene and metallacyclobutane complexes (2). It is widely accepted that the heterogeneous catalysis follows a comparable mechanism, and carbene species which are the key intermediates are produced from alkenes and metal oxide on the surface in the initial stage of the reaction (3, 4). A typical olefin metathesis catalyst is prepared by impregnating alumina or silica with an aqueous solution of ammonium molybdate, tungstate, or perrhenate, drying, and calcining the product in the presence of a stream of dry air or nitrogen (1). Another approach for dispersing active oxides on an oxidic support is by the reaction of hydroxyl groups on the support (e.g., silica) surface with a metal precursor, such as an alcoholato complex (5, 6). Tungsten complexes, e.g., carbonyls, allyls, and alkyls, all form active catalysts when supported on silica. However, these catalysts show no real advantages over tungsten oxide catalysts, especially as they are air-sensitive and difficult to handle (7). Monomeric trisdiolatotungsten(VI) complexes [W(eg)$_3$] **(1)**, [W(eg)(pin)$_2$] **(2)**, and [W(pin)$_3$] **(3)** (H_2eg = 1,2-ethanediol, H_2pin = 2,3-dimethylbutane-2,3-diol) on the other hand, are stable in air and soluble in common organic solvents.



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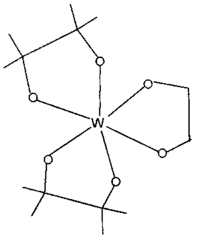

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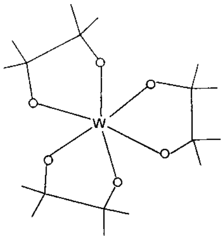

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We have investigated these three complexes as precursors for silica-supported tungsten oxide catalysts and report here their use in propene metathesis. Comparison is made with reference catalysts prepared from $(NH_4)_2WO_4$ and $WOCl_4$, respectively.

Catalyst precursors were prepared as described previously (8). SiO_2 (Aldrich, grade 951, BET surface area 600 m^2/g, average pore size 42–48 μm) was kept in vacuum for 1 h at room temperature before impregnation. Catalysts I–III were prepared by depositing trisdiolatotungsten(VI) complexes from organic solvents onto silica (Table 1). Only a sufficient amount of solution was used to enable the silica particles to be stuck together (ca. 1.5 ml/g (SiO_2)). The mixture was allowed to stand for 1 h at room temperature, and volatiles were then removed by vacuum. Catalysts IV and V were prepared similarly using aqueous $(NH_4)_2WO_4$ (Aldrich) and $WOCl_4$ (Aldrich) in tetrahydrofuran, respectively.

The propene metathesis reaction was studied in a single-pass continuous-flow system using a tubular quartz reactor of 5.0 mm inner diameter. The reactor was mounted with a coaxial thermowell to monitor temperature along the length of the catalyst bed. The propene feed was dried over activated molecular sieves and deoxygenated by BASF Deoxo catalyst. A sample of catalyst (150–250 mg) was first calcined by heating to 600°C for 1 h under an air flow (3 liters/h). The sample was then cooled to 400°C under N_2 (3 liters/h) and a propene flow was introduced into the reactor (Table 2). The propene flow was adjusted to be high enough that the equilibrium composition of reactant and metathesis products was not reached . The outcoming gas flow containing ethene, propene, and *cis*- and *trans*-butenes was analyzed by a gas chromatograph (CE instruments, GC 8000) fitted with a Chrompack-fused silica column and a FID detector. The catalytic activity for

TABLE 1

Preparation of Trisdiolatotungsten(VI)-Based Catalysts

Catalyst	Precursor	Solvent	wt% of tungsten	Weight of sample (mg)
I	W(eg)$_3$ **(1)**	MeOH	3.6	250
II	W(eg)(pin)$_2$ **(2)**	THF	2.5	150
III	W(pin)$_3$ **(3)**	THF	3.1	180
IV	$(NH_4)_2WO_4$	H_2O	2.8	225
V	$WOCl_4$	THF	2.8	210

Note. eg = 1,2-ethanediolato; pin = 2,3-dimethylbutane-2,3-diolato.

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TABLE 2

Reaction Conditions for Activity Tests

Catalyst	WHSV (propene) (h^{-1})	Flow rate (propene) ($g\ h^{-1}$)
I	22–68	5.6–17
II	30–45	4.5–6.8
III	25–44	4.7–7.9
IV	6.7–8.4	1.6–1.9
V	8.8–53	1.9–11.3

the propene metathesis reaction was calculated as turnover frequency (N_t):

$$N_t = \frac{\text{(number of reacted propene molecules/s)}}{\text{(total number of tungsten atoms in catalyst)}}.$$

The reaction of propene over the studied catalysts leads to a mixture of ethene, propene, and *cis*- and *trans*-butenes. No isomerization or polymerization products were found. The activities of the studied catalysts are shown in Fig. 1. It is clearly seen that catalysts **I** and **II** are more active than either of the reference catalysts, **IV** and **V**, and **III** is nearly as active as the catalyst prepared from $WOCl_4$.

As thermal decomposition of the alcoholato complexes leads to oxides (9), the calcination of the catalysts at 600°C in an air flow presumably produces silica-supported WO_3. Exposure to propene leads to the active catalyst. It is known that in the activation of WO_3/SiO_2 catalyst by propene, trace amounts of acetaldehyde and acetone are formed (10). This is possibly due to formation of the metal carbene (Scheme 1).

Since the activity of a catalyst depends in general on the number of active sites, the number of tungsten species suitable for carbene formation determines the activity. Distribution of the tungsten atoms on the surface of the support is also a crucial step in the formation of the active sites. The conventional impregnation method followed by calcination and catalyst activation has been employed extensively in the preparation of supported catalysts. For silica-supported tungsten oxide catalyst ammonium tungstates are generally used as precursors (10–12). Oxotungstic species in aqueous solutions are in equilibrium between WO_4^{2-} and polynuclear clusters, depending upon the pH and concentration (13). Consequently, a nonuniform distribution of the active sites may be produced in the catalyst surface during the immersion and calcination.

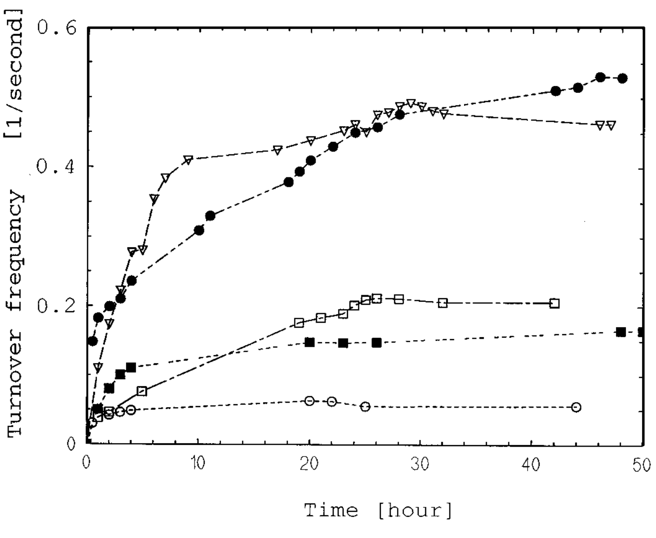
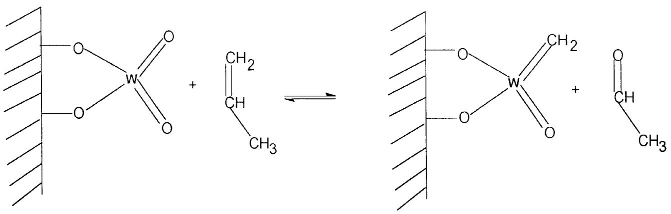
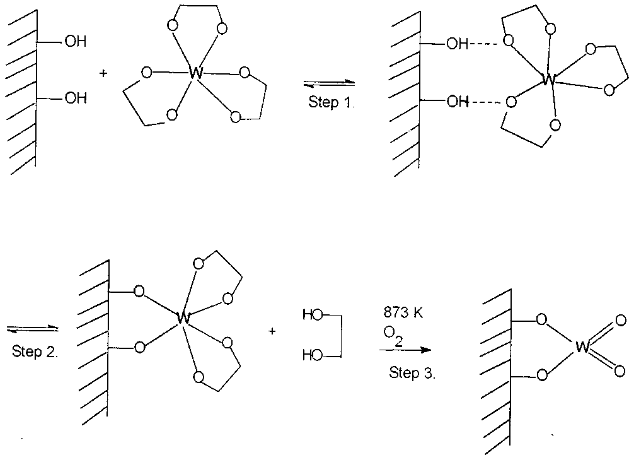


FIG. 1. Catalytic activities of catalysts for propene metathesis. Catalyst I, (▽); catalyst II, (●); catalyst III, (■); catalyst IV, (⊙); catalyst V, (□).



SCHEME 1

The suggested reaction mechanism is shown in Scheme 2. The first step is the formation of hydrogen bonds between surface OH groups and alcoholato oxygen atoms, similar to those found to form between complex **2** and phenol or aniline (14). The second step involves the releasing of the diol and as a result the tungsten compound becomes tightly anchored on the silica surface. These surface reactions can lead to an even distribution of the tungsten atoms on the surface of silica. Complex **2** is more readily hydrolyzed than complex **3** (14). Also in complexes **1** and **2** the diolato ligand exchange reaction occurs easily (8). Thus it is possible that **3** has lower reactivity with surface hydroxyls, which can explain the lower activity of catalyst **III**. The activities of catalysts **I** and **II** do not differ significantly. It follows



SCHEME 2

that only one labile ligand is necessary for good activity. However, catalyst **II** is easier to prepare, because precursor **2** is more soluble in common solvents than **1**. $WOCl_4$ is also soluble in organic solvents, but it is more difficult to handle due to its sensitivity to air and moisture. It may also be too reactive, forming polynuclear species.

The following conclusions may be drawn. Compounds **1**, **2**, and **3** can be converted to heterogeneous catalysts which are more active in olefin metathesis reaction than traditional ammonium tungstate-based catalysts. These catalysts are also easy to prepare, because precursors are soluble in organic solvents and stable in air. The reason for higher activities is considered to be the even distribution of the precursor molecules on the silica support before the calcination step due to hydrogen bonds forming between the alcoholato oxygens and the OH groups of the silica support.

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