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New Inorganic Oxide-attached Nb Catalysts Active for Propene Metathesis

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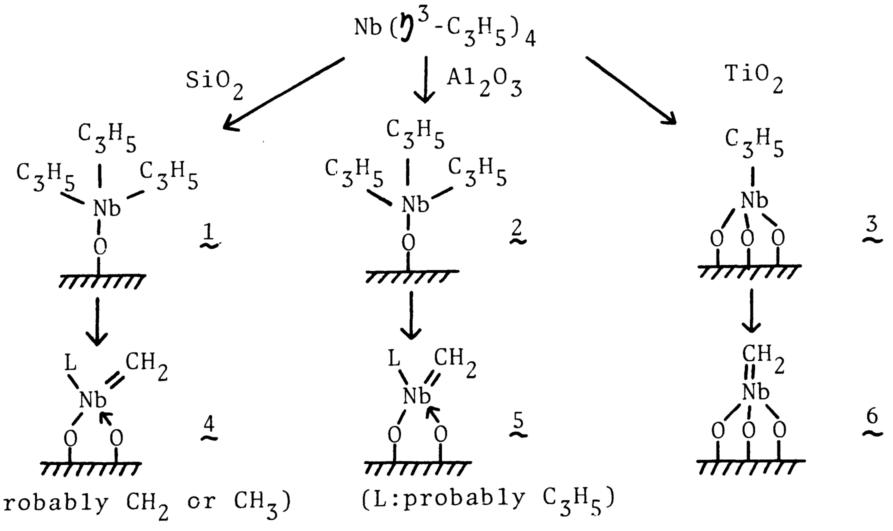
SiO_2-, Al_2O_3-, and TiO_2-attached Nb-monomer catalysts were prepared by the reactions between $Nb(\eta^3-C_3H_5)_4$ and surface OH groups of SiO_2, Al_2O_3, or TiO_2, followed by the treatments with H_2 in the temperature range 323-673 K. These catalysts showed high activities for propene metathesis at the low temperatures 273-310 K, in contrast to the known fact that traditional supported Nb catalysts show almost no activities.

A class of inorganic oxide-attached metal catalysts obtained by reactions between metal-η^3-allyl complexes and surface OH groups of inorganic oxides has been demonstrated to provide a new way of preparations of active supported metal catalysts or active precursor species which may be unstable in solution.[1)] A similar approach may also serve to develop new surface chemistry techniques. We report results for active attached-Nb catalysts for propene metathesis.

The SiO_2-, Al_2O_3-, and TiO_2-attached Nb complexes(**1** - **3**) were prepared by the reactions between $Nb(\eta^3-C_3H_5)_4$ (in pentane) and surface OH groups of SiO_2, Al_2O_3, or TiO_2 at 233-273 K. $Nb(\eta^3-C_3H_5)_4$ was synthesized in a similar way to that previously reported under Ar(99.9995%) atmosphere or vacuum.[2)] SiO_2(Aerosil-200), Al_2O_3 (Alon-C), and TiO_2(P-25) were evacuated for 2 h at 673 K, 773 K, and 473 K, respectively, in situ before use as supports. The amounts of Nb bound to SiO_2, Al_2O_3, and TiO_2 were determined by chemical analysis to be 2.0, 2.3, and 2.1 wt% as Nb/support, respectively. Conventional supported Nb catalysts with the same Nb-loadings as those of the attached catalysts were obtained by an impregnation method using an aqueous $NbCl_5$ solution, followed by calcination at 773 K.

The absorption bands of the OH groups of SiO_2(3741 cm^{-1}) and Al_2O_3(3793 cm^{-1}) decreased in intensity after the attachment reaction with $Nb(\eta^3-C_3H_5)_4$. The



Scheme 1. The attachment of $Nb(\eta^3-C_3H_5)_4$ onto SiO_2, Al_2O_3, and TiO_2, and proposed structures.

numbers of C_3H_5 ligands per Nb atom in **1**, **2**, and **3** were determined to be 3.0, 2.8, and 0.9, respectively, in a similar manner to that previously described.[3] These results indicate that the attaching reactions stoichiometrically proceeded to form the surface complexes as shown in Scheme 1. The temperature programmed decomposition (TPDE) patterns of **1**-**3** in the presence of H_2(13.3 kPa) in Fig.1 were almost unchanged in the range of Nb-loadings 0.5-2.3 wt%, suggesting that the majority of the Nb species was uniformly distributed on the pretreated inorganic oxides. The TPDE chromatogram of **1** depicted the peaks for ethane (main) and propane evolution at 523 K and the subsequent methane peak from residual C_1-ligands. The Nb species **2** on Al_2O_3 showed a different decomposition pattern. One of the three C_3H_5 ligands was desorbed as propane at 373 K, while the rest of the ligands gave the decomposition peaks (ethane and methane products) at 573 K. The C_3H_5 ligand of **3** on TiO_2 was most easily eliminated among **1**-**3**, evolving mainly propane. $Nb(\eta^3-C_3H_5)_4$ in solution is decomposed at 233 K, whereas the attached Nb complexes were much more stable thermally. The IR spectra of **1**-**3** were taken in a quartz-cell with two NaCl-windows which was specially devised to avoid the decompositions by temperature (pure complex), and oxygen and moisture (pure and attached complexes). The absorption bands of 3078-3084 and 1641 cm^{-1} assignable to ν_{C-H} and ν_{C-C}, respectively, were observed with **1**-**3**. These values indicate that the C_3H_5 ligands of the surface complexes are of σ-allyl-character. ESR spectra of **1** and **2** exhibited characteristic 10-line hyperfine structures derived

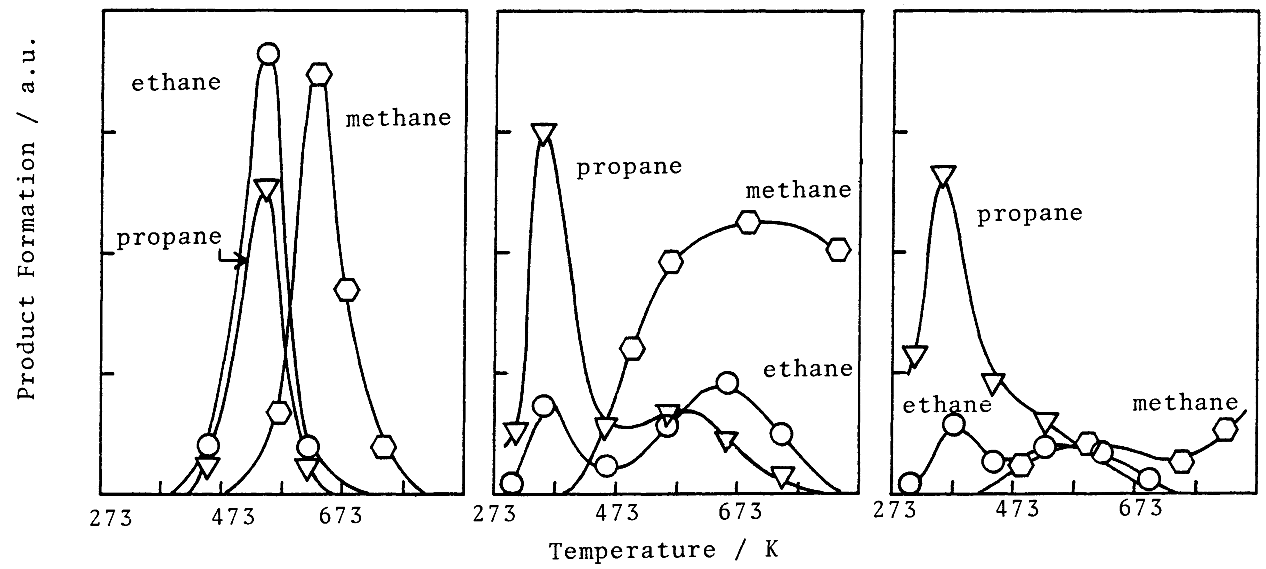


Fig.1. Temperature programmed decomposition chromatograms of 1, 2, and 3 at heating rate of 4 K^{-1} in the presence of H_2.

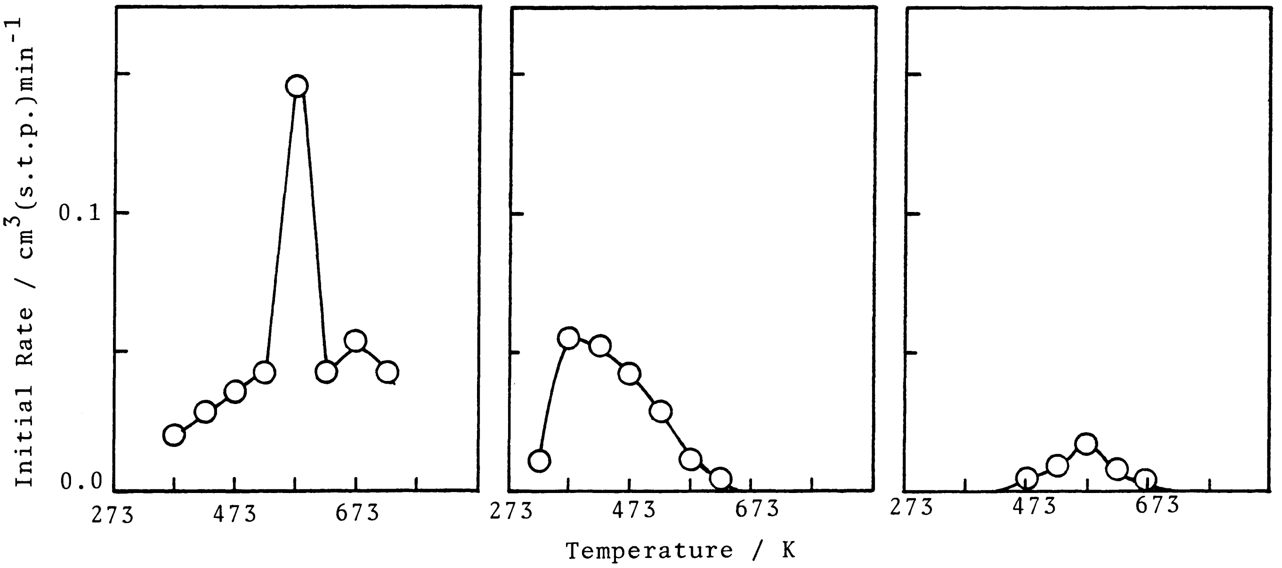


Fig.2. The variation of metathesis activities with temperature; 1, 2, or 3 was treated in the presence of H_2.

from Nb(IV) (9/2 spin) similarly to the ESR spectrum of Nb(η^3-C_3H_5)$_4$;[2] $g_{//}=2.01$ ($A_{//}=210$ G) and $g_{\perp}=1.98$ ($A_{\perp}=50$ G) for SiO_2 support and $g=1.99$ ($A=220$ G) for Al_2O_3. The analyses of the EXAFS (Extended X-ray Absorption Fine Structure) of 1-3 showed no Nb-Nb bond, suggesting that the Nb species are distributed in a monomer form.[4]

The surface Nb complexes were found to be converted to highly active species for propene metathesis by the treatments under vacuum or in the presence of H_2 at 323-673 K as shown in Fig.2. It can be seen from the comparison of Fig.1 and Fig.2 that each catalyst reached the highest activity after the elimination of a C_3H_5 ligand which provides a coordinatively vacant site on a Nb atom, and also after the decomposition of C_3H_5 ligands to ethane which may leave active carbene (propably $Nb=CH_2$) behind as proposed in Scheme 1; for example, the TPDE of **1** up to 523 K produced 0.9 molecules of propane and two molecules of ethane per Nb atom. The bidentate and terdentate structures of **4**, **5**, and **6** in Scheme 1 were inferred from Nb(V) structures obtained by the oxidation of **4**, **5**, and **6**, which were determined by means of EXAFS, Raman, and UV/VIS diffuse reflectance spectroscopies.4) These active carbenes appeared to be unstable or easily removable as methane by H_2 at elevated temperatures as shown in Fig.1, hence the maximum activity in Fig.2 was observed. The most active catalyst among the three catalysts was **4** attached on SiO_2, as shown in Fig.3. The low activity of the TiO_2-attached Nb species may be due to a low probability of the decomposition of **3** to form **6**. The activity of the SiO_2-attached Nb catalyst was comparable to that of a SiO_2-attached Mo-allyl catalyst which has been reported to be among the most active metathesis catalysts(Fig.3).5) In contrast, the conventional impregnation Nb catalysts, even if they were treated with H_2, showed no activity under similar conditions. Thus, Nb is suggested to be an active element which is capable of providing new active metathesis catalysts.

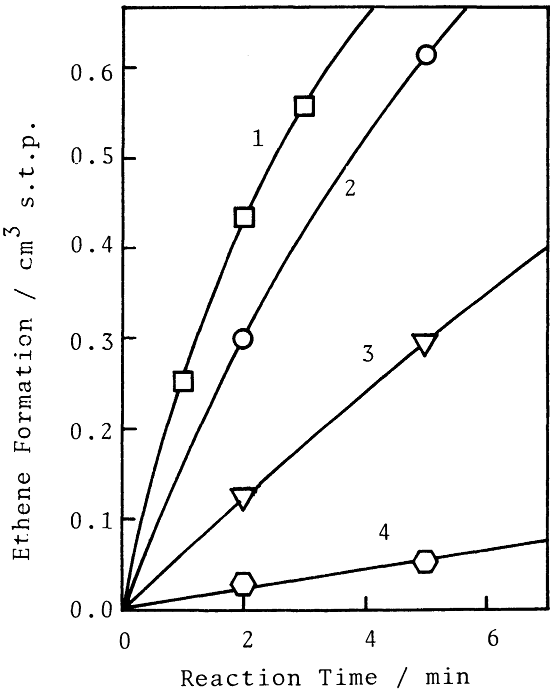


Fig.3. Metathesis reaction at 298 K;
1:attached Mo/SiO_2,
2:attached Nb/SiO_2 **4**,
3:attached Nb/Al_2O_3 **5**,
4:attached Nb/TiO_2 **6**.
(Catalyst:0.310 g)

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