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SiO_2-grafted Dinuclear Molybdenum Catalyst Derived from $Mo_2(OAc)_4$; Highly Active for Alkene Metathesis Reaction

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SiO_2-grafted dinuclear molybdenum species derived from $Mo_2(OAc)_4$, *e.g.* $[Mo\overset{-\,-}{\equiv}Mo]^V$, which are characterized by ESR and EXAFS spectroscopy, exhibit marked catalytic activity for propene metathesis reaction, but are inactive for ethene homologation.

Organometallic compounds, including metal clusters, grafted onto the surface of a support have been widely used as catalyst precursors in order to provide a rational approach for the preparation of tailored metal catalysts.[1] Dinuclear organometallic compounds, such as $Mo_2(\pi\text{-allyl})_4$,[2] $Mo_2(NMe_2)_6$,[3] $[Rh(\mu\text{-}CH_2)_2(C_5Me_5)Me]_2$[4] and $[Nb(\eta^5\text{-}C_5H_5)H\text{-}\mu\text{-}(\eta^5,\eta^1\text{-}C_5H_4)]_2$,[5] can potentially be grafted onto different oxide supports, such as SiO_2 and Al_2O_3. Recently we reported that the SiO_2-grafted catalyst derived from $Mo_2(NMe_2)_6$ exhibits remarkable activity for the ethene dimerization reaction, whereas the monomer $Mo(NMe_2)_4$-derived catalyst is inactive.[3] Some dinuclear oxide species of Mo on Al_2O_3 derived from $Mo_2(\pi\text{-allyl})_4$[2] and of Nb on SiO_2 from $[Nb(\eta^5\text{-}C_5H_5)H\text{-}\mu\text{-}(\eta^5,\eta^1\text{-}C_5H_4)]_2$[5] have been characterized by EXAFS, which showed that no metal–metal bonding is retained. Here we use $Mo_2(OAc)_4$ with a quadruple Mo–Mo bond as the precursor to graft Mo_2 species uniformly onto SiO_2. On appropriate thermal activation, the $Mo_2(OAc)_4/SiO_2$ showed a strikingly high activity for propene metathesis. ESR and EXAFS spectroscopic studies suggest that the SiO_2-grafted dinuclear $(Mo\overset{-\,-}{\equiv}Mo)^V$ species is formed by thermal activation of $Mo_2(OAc)_4/SiO_2$ at below 350 °C, which is specifically active for propene metathesis.

The $Mo_2(OAc)_4$ (99% purity, Strem Chemicals) was used without further purification. The $Mo_2(OAc)_4$ crystals were dry-mixed with the silica support (Kieselgel 60, Merck, 487 m^2/g) previously evacuated at 450 °C for 30 min. The mixture was ground under a dry nitrogen atmosphere in a glovebox (Shimadzu G 12) to give the 4.1 wt% (Mo) loading $Mo_2(OAc)_4/SiO_2$. It was sealed in a glass tube after evacuation. All experimental procedures were carried out either in a vacuum or under an argon atmosphere using the Schlenk technique to prevent O_2 and H_2O exposure. A Varian E-4 ESR spectrometer was used to characterize the catalyst at 60–300 K. The microwave power and frequency was 20 mW and *ca.* 9.5 GHz, respectively. The *g*-value of the sample was determined by using Strong Pitch (*g* 2.0028), and $CuSO_4$ was used to calibrate the spin concentration.

$Mo_2(OAc)_4$ consists of a $(Mo\overset{-\,-}{\equiv}Mo)$ bond having the electron configuration of $\sigma^2\pi^4\delta^2$. The $Mo_2(OAc)_4/SiO_2$ was originally diamagnetic and showed no ESR signal. The thermal activation of $Mo_2(OAc)_4/SiO_2$ under vacuum resulted in the formation of a paramagnetic species, which showed an intense and symmetrical ESR signal with $g_\perp = g_\parallel = 1.928$, and a narrow line width of 12 G (Fig. 1). The observed ESR spectrum is identical with that of the one-electron oxidized species of $Mo_2(C_3H_7CO_2)_4$ in solution.[6] The oxidition of $Mo_2(OAc)_4$ proceeds as $[\sigma^2\pi^4\delta^2] \rightarrow [\sigma^2\pi^4\delta^1]$ to give $[Mo\overset{-\,-}{\equiv}Mo)^V$, where the Mo–Mo bond order is changed from 4 to 3.5. Owing to the natural abundance of ^{95}Mo and ^{97}Mo, the total nuclear spin of the Mo_2 pair is $J = I^1 + I^2 = 0, 5/2, 5$. Thus, based on the nuclear-spin coupling, the corresponding eleven ESR signals of hyperfine structure were observed (Fig. 1). After activation at 350 °C the catalyst showed the highest spin concentration, the ratio of spin number to the number of paired molybdenum (Mo_2) is 0.83. This result suggests that about 83% of the $Mo_2(OAc)_4$ precursor was uniformly converted to the one-electron oxidized species $(Mo\overset{-\,-}{\equiv}Mo]^V$ grafted onto SiO_2. The oxidition may proceed *via* the partial loss of acetate ligands from $Mo_2(OAc)_4/SiO_2$ by reaction with surface OH groups on the SiO_2, which is similar to results revealed by TPD–FTIR.[3] By evacuating the sample at higher temperature up to 450 °C, the species was gradually converted into Mo^V as revealed by ESR, possibly owing to the cleavage of the $Mo\overset{-\,-}{\equiv}Mo$.

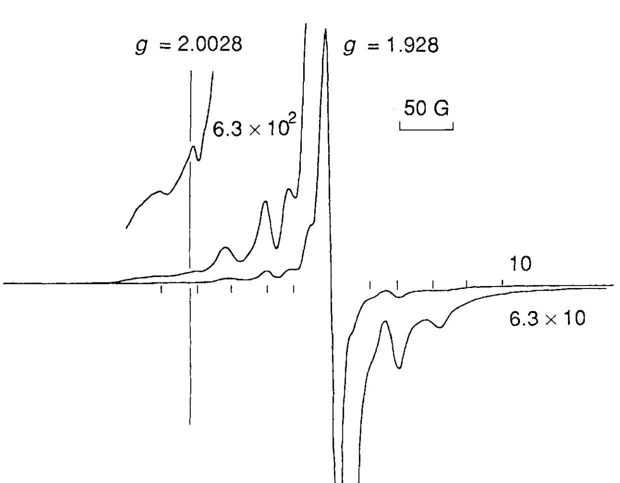

Fig. 1 ESR spectrum of $Mo_2(OAc)_4/SiO_2$ (4.1 wt% Mo, 0.3 g) measured at 25 °C after evacuation (10^{-4} Torr) at 350 °C for 30 min

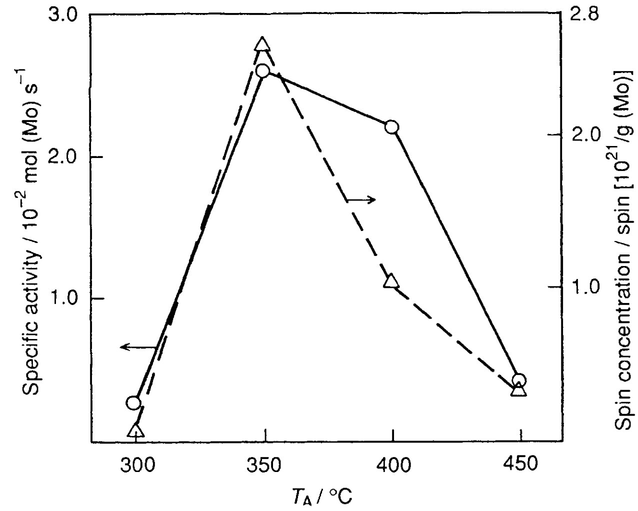

Fig. 2 Dependency of specific activities for propene metathesis and spin concentration of $Mo_2(OAc)_4/SiO_2$ on the activation temperature (T_A). *Reaction conditions* for propene metathesis: 0.008 g $Mo_2(OAc)_4/SiO_2$, 15 Torr of propene at 25 °C.

EXAFS measurements were conducted in transmission mode at the Mo-Kα absorption edge using the synchrotron radiation source at the Photon Factory, National Laboratory for High Energy Physics.[2,4,5] Pure samples were sealed under Ar in glass cells of 7 mm thick fitted with Kapton windows. Mo foil, $Mo_2(OAc)_4$, MoO_3 and K_2MoO_4 were used as reference compounds for the EXAFS measurement. The EXAFS data suggested that after activation at 350 °C the catalyst had a Mo–Mo distance (R_{Mo-Mo} = 2.13 Å) similar to that of the precursor (R_{Mo-Mo} = 2.09 Å), implying that multiple bonding of Mo–Mo is retained after thermal activation. The catalyst activated at 450 °C had R_{Mo-Mo} = 2.80 Å, which is fairly lengthened compared with $Mo_2(OAc)_4$, indicative of cleavage of the Mo≡Mo bonding.

The reactions of propene and ethene ($^{12}C_2H_4$ + $^{13}C_2H_4$; 10–16 Torr) were carried out on the resulting catalyst by using a closed circulating reactor with a volume of 150 ml.[3,7] The amount of catalyst was 0.005–0.3 g. The $Mo_2(OAc)_4/SiO_2$ was completely inactive for propene metathesis and alkene homologation until activated at 100 °C. After thermal activation of $Mo_2(OAc)_4/SiO_2$ at 100–450 °C, the resulting catalyst gave remarkable activity for propene metathesis at the reaction temperature of 0–27 °C. Fig. 2 shows the specific activities for propene metathesis to give but-2-enes (Z : E = *ca.* 0.5) as a function of the activation temperature for $Mo_2(OAc)_4/SiO_2$. It is of interest to find that $Mo_2(OAc)_4/SiO_2$ activated at 350 °C exhibited the maximum activity for the propene metathesis reaction, whereas it was inactive for the ethene homologation reaction even at 110 °C. After being activated at 450 °C, the specific activity of the catalyst for propene metathesis markedly decreased. In contrast, the 450 °C-activated catalyst showed appreciable activity for ethene homologation, as with conventional molybdenum catalysts.[7] The trend of catalytic performance in propene metathesis on the thermally activated $Mo_2(OAc)_4$ parallelled the change in ESR signal intensity owing to the formation of $[Mo{\equiv}Mo]^V$ as depicted in Fig. 1. It is also noteworthy that NO as a one-electron donating molecule efficiently poisons the metathesis activity upon exposure to 350 °C-activated $Mo_2(OAc)_4/SiO_2$.

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