Structure Sensitivity for Ethene Dimerization, Homologation and Metathesis on SiO_2-supported Catalysts derived from $Mo(NMe_2)_4$ and $Mo_2(NMe_2)_6$

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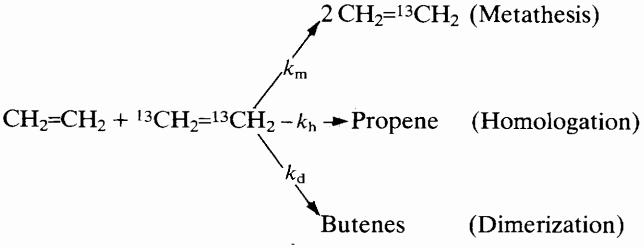
The SiO_2 grafted dimer precursor $(Me_2N)_3Mo{\equiv}Mo(NMe_2)_3$ specifically exhibited catalytic activity for ethene dimerization, whereas the monomer $Mo(NMe_2)_4$ derived catalyst showed high activity for ethene homologation, but was inactive for ethene dimerization.

Organometallic compounds, including metal clusters, grafted on the surface of supports have been widely used as catalyst precursors to provide a rational approach for the preparation of tailored metal catalysts.[1] It is known that ethene metathesis proceeds on both homogeneous and heterogeneous Mo catalysts,[2] while ethene homologation takes place on heterogeneous Mo catalysts.[3] Ethene dimerization has only been reported to occur when monomer Mo complexes were used in solution.[4] From the fundamental viewpoint of the relationship between homogeneous and heterogeneous catalysis, it is of interest to try to prepare tailored Mo catalysts by anchoring $Mo(NMe_2)_4$ and $Mo_2(NMe_2)_6$ complexes onto suitable supports to study their catalytic performance for these three different reactions of ethene.

The monomer $Mo(NMe_2)_4$ (purple) and dimer $Mo_2(NMe)_6$ (yellow) complexes were synthesized in an anaerobic atmosphere by the literature method.[5] Silica (Kiesel Gel 60, Merck, 487 $m^2\ g^{-1}$), dehydrated at 450 °C for 1 h in a vacuum, was soaked in a hexane solution of each complex for 12 h at room temperature. After the solvent had been removed by evacuation at the same temperature, $Mo(NMe_2)_4$–SiO_2 and $Mo_2(NMe_2)_6$–SiO_2 (1.29 wt% Mo) were obtained. A temperature programmed decomposition experiment (TPDE) on the $Mo(NMe_2)_4$–SiO_2 showed a desorption peak of $N(CH_3)_2^+$ (*m*/*z* 44) at 110 °C, whereas the $Mo_2(NMe_2)_6$–SiO_2 derived catalyst gave two distinct peaks at 110 and 280 °C as shown in Fig. 1. Consequently, it is suggested that $Mo(NMe_2)_4$ and $Mo_2(NMe_2)_6$ react with the silanol OH group on silica with evolution of dimethylamine in the gas phase at 110 °C, during the grafting process. The desorption peaks of dimethylamine were accompanied by peaks due to small amounts of CH_3, H_2 and NH_4 at 280 °C on the Mo dimer-derived catalyst, implying further decomposition of the dimer precursor.

The reaction of ethene was carried out at 110 °C using 0.3 g of catalyst and 10–20 torr of ethene in a closed circulation Pyrex glass reactor of *ca.* 260 ml. Products were analysed by gas chromatography with a flame ionization detector and the distributions of ^{13}C atoms in each product were determined by mass spectrometry using an ionization voltage of 10–15 V.

In the reaction of a 1:1 molar mixture of $[^{12}C_2]$- and $[^{13}C_2]$-ethene on a Mo catalyst, the activities for ethene metathesis, homologation and dimerization reactions can be evaluated in terms of the product formation as in Scheme 1.



Scheme 1

Table 1 summarizes the specific activities of the catalytic ethene dimerization, homologation and metathesis reactions based on the Mo atom as a unit in the catalysts. The precursors of the Mo complex catalysts were essentially inactive for the reaction of ethene before thermal activation on SiO_2. It is found that (*i*) ethene dimerization occurred only on the catalyst derived from $Mo_2(NMe_2)_6$–SiO_2 after being activated at 110 °C, but did not occur after activation at 280 °C. It is noteworthy that but-1-ene is selectively formed initially on $Mo_2(NMe_2)_6$–SiO_2 activated at 110 °C, followed by the formation of but-2-enes, plausibly due to butene isomerization. (*ii*) SiO_2-supported $Mo(NMe_2)_4$ after activation at 110 °C gave the highest activity for ethene homologation (about 10–50 times higher than the other catalysts). (*iii*) Ethene metathesis activities are independent of the type of Mo precursor.

To obtain further information about the mechanism of ethene dimerization and homologation, kinetic isotope effects

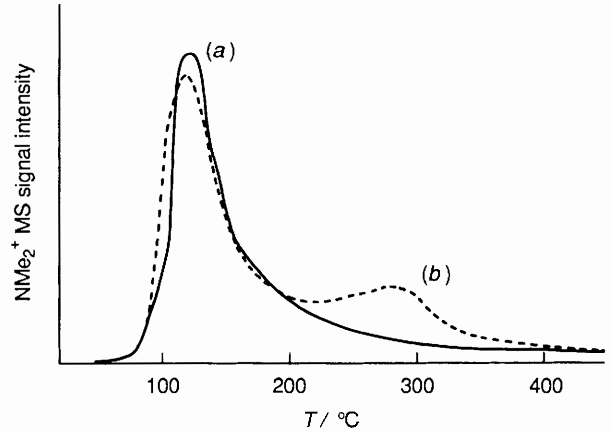


Fig. 1 TPDE Patterns of SiO_2-supported $Mo(NMe_2)_4$ (*a*) and $Mo_2(NMe_2)_6$ (*b*). Mo loading: 3.1 wt%, temperature-programmed heating rate: 5 °C min^{-1}, He flow rate: 100 ml min^{-1}

Table 1 Specific activity for ethene reactions at 110 °C on SiO_2-supported Mo catalysts derived from $Mo(NMe_2)_4$ and $Mo_2(NMe_2)_6$

Catalyst activation temp. (*T*/°C)	Specific activity/(product molecules $Mo^{-1}\ s^{-1}$)		
	Dimerization	Homologation	Metathesis
$Mo(NMe_2)_4$–SiO_2			
25	0	0	0
110	0	1.3×10^{-5}	2.8×10^{-3}
280	0	2.0×10^{-6}	7.1×10^{-3}
$Mo_2(NMe_2)_6$–SiO_2			
25	0	0	0
110	9.3×10^{-7}	6.9×10^{-7}	2.9×10^{-3}
280	0	8.0×10^{-7}	7.6×10^{-3}

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Table 2 ^{13}C Distributions in but-1-ene and propene formed in the reaction using a 1.04 : 1 ratio of [$^{12}C_2$]- and [$^{13}C_2$]-ethene with a 110 °C activated $Mo_2(NMe_2)_6$–SiO_2 catalyst

	Distribution of ^{13}C (%)					Isotope effect
Product	$^{13}C_0$	$^{13}C_1$	$^{13}C_2$	$^{13}C_3$	$^{13}C_4$	(^{12}C : ^{13}C)[a]
But-1-ene	7.3	19.4	46.1	21.7	5.4	0.98 ± 0.04
Propene	17.8	45.8	24.8	11.5	—	1.25 ± 0.04

[a] The value of isotope effect is normalized to the reactant mixture ($^{12}C_2H_4$: $^{13}C_2H_4$ = 1.04 : 1).

(KIE) for the products, *e.g.* but-1-ene and propene, were studied. After 6 h reaction at 110 °C using 18.2 torr of a labelled ethene mixture ($^{12}C_2H_4$: $^{13}C_2H_4$ = 1.04 : 1) on 110 °C-activated $Mo_2(NMe_2)_6$–SiO_2 (1.29 wt% Mo, 0.3 g of catalyst), 4.5×10^{-2} torr of but-1-ene and 3.2×10^{-2} torr of propene were formed. The ^{13}C distributions of but-1-ene and propene are shown in Table 2. The ^{12}C : ^{13}C ratio in but-1-ene is 0.98 ± 0.04 : 1, indicating no isotope effect for ethene dimerization. In contrast, the ratio shows a large isotopic effect for propene formation (^{12}C : ^{13}C = 1.25 ± 0.04 : 1). This seems to be related to the reaction intermediate, which consists of [CH_2] and C_2H_4 units in the rate-limiting step in ethene homologation to produce propene. The relatively larger isotope effect (^{12}C : ^{13}C) in propene, compared with the theoretical KIE value, possibly results from the initial contribution of the intermediate ^{12}C-carbene species (:$^{12}CH_2$) on Mo sites preformed from the dimethylamine ligand during the activation of the catalyst.

In conclusion, the catalytically inactive precursor complexes, $Mo(NMe_2)_4$ and $Mo_2(NMe_2)_6$, react with surface silyl OH on SiO_2 to eliminate the dimethylamine ligand at 110 °C, resulting in SiO_2-grafted species active for ethene reactions. The ethene dimerization and homologation are sensitive to the type of precursor Mo complex, while ethene metathesis is not. The SiO_2-grafted monomer complex catalyst exhibited quite high activity for ethene homologation relative to that derived from the Mo dimer. The ethene dimerization is likely to be associated with the active sites of two Mo atoms derived from the dimer precursor $(Me_2N)_3Mo{\equiv}Mo(NMe_2)_3$.

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