New SiO_2-Bound Mo Dimers: Active Catalysts for Selective Oxidation of Propene to Acrylaldehyde

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SiO_2-bound molybdenum(VI) dimers (Mo–Mo 0.330 nm) with bridging oxygen atoms (Mo–O 0.194 nm), prepared from $Mo_2(\eta^3\text{-}C_3H_5)_4\text{–}SiO_2$ followed by treatment with H_2 or O_2, showed high activity in the selective oxidation of propene to acrylaldehyde.

Selective oxidation of propene to acrylaldehyde has been carried out on mixed metal oxide catalysts having easily diffusible lattice oxygen atoms.[1] The product distribution in alkene oxidation is in general markedly affected by the electronic character of the active oxygen atoms as well as their environment on the catalyst surface. This communication reports a new molybdenum dimer supported catalyst with bridging oxygen atoms which selectively oxidised propene at the SiO_2 surface.

The SiO_2-bound Mo dimer catalysts (**1**)—(**5**) were prepared by attaching $Mo_2(\eta^3\text{-}C_3H_5)_4$ onto a SiO_2 surface followed by treatment with H_2 or O_2 as shown in Scheme 1. The reaction between $Mo_2(\eta^3\text{-}C_3H_5)_4$ and SiO_2 (Nishio Industry Ltd.) pretreated at 773 K (specific surface area: 510 $m^2\,g^{-1}$; average surface OH number: 2 OH nm^{-2}) to form the surface complex (**1**) was rapid and completed within 10 min at 273 K. The molybdenum species were characterised by EXAFS (extended *X*-ray absorption fine structure), u.v.-visible DRS (diffuse reflectance spectroscopy), TPDE (temperature programmed decomposition), and chemical titration.

The initial molybdenum complex (**1**) with two C_3H_5 ligands on each Mo atom was bonded to the SiO_2 surface in a bidentate form *via* oxygen atoms. The TPDE chromatogram of (**1**) showed a two peak pattern similar to the SiO_2- or Al_2O_3-attached Mo dimers previously reported.[2] However, their peaks were observed at much lower temperatures. The surface complex (**1**) was reduced to the Mo^{II} dimer (**2**) with H_2 at 853 K. The Mo^{II} dimer was oxidized in a stepwise manner to the oxo Mo^{IV} species (**3**) at 273 K and to the dioxo molybdenum(VI) species (**5**) at 673 K, with the uptake of stoicheiometric amounts of oxygen, as shown in Scheme 1. The Mo^{VI} dimer (**5**) with a charge transfer band assigned to Mo=O at 310 nm was reduced with H_2 first to the Mo^{V} dimer (**4**) at 773 K for 1.5 h, then after 2.5 h at 813 K (**3**) and then at 853 K for 7 h to give (**2**) again, with the evolution of quantitative amounts of H_2O. The species (**3**) obtained by reduction of (**4**) with H_2 showed the same DRS spectrum as the oxo Mo^{IV} structure (**3**) obtained by oxidation of (**2**) with O_2.

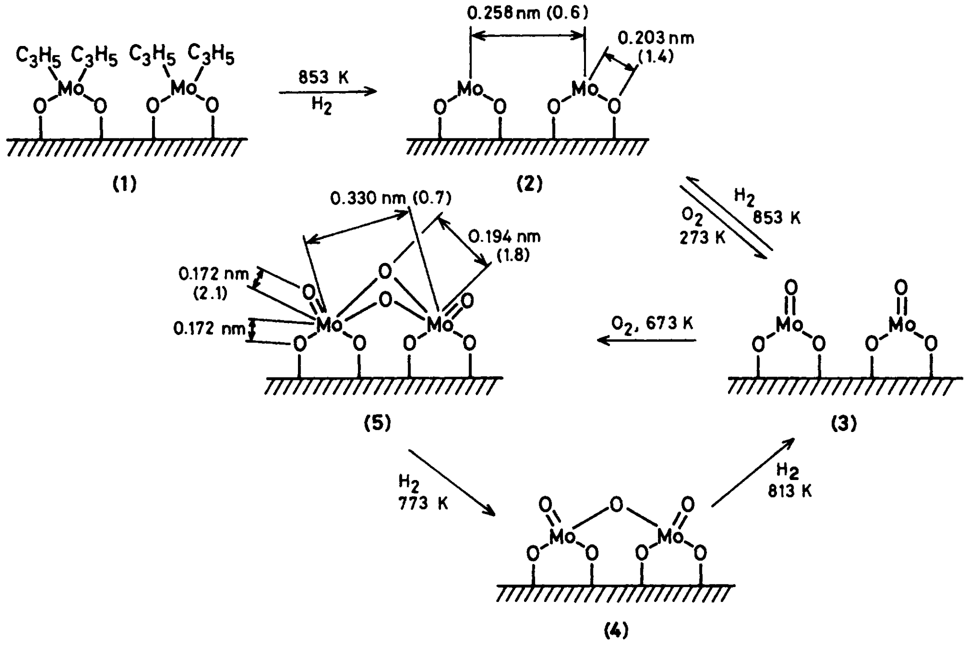
The Mo–Mo and Mo–O bond distances in the Mo^{II} dimer (**2**) were determined to be 0.258 nm and 0.203 nm, respectively, by the analysis of the Mo-*K*-edge EXAFS data obtained by use of synchrotron radiation. The Mo–Mo separation of the surface Mo^{II} dimeric species is elongated compared with 0.218(3) nm in the original $Mo^{II}_2(C_3H_5)_4$ complex,[3] but the bond is still strong. The Mo–O (surface) single bond was shortened by 0.031 nm with an increase in the oxidation state from Mo^{II} to Mo^{VI}. The Mo–Mo-bond length of the species (**5**) was found to be 0.330 nm. This observation is due to the fixation of the Mo–Mo separation by bridging oxygen atoms since no direct bonding has been observed for two adjacent Mo^{VI} ions of dioxomolybdenum(VI) dimers attached to SiO_2 or Al_2O_3.

It was found that these μ-type oxygen atoms were very active and selective for partial propene oxidation as shown in Table 1. Dioxomolybdenum monomers (**6**) showed *ca.* one order of magnitude higher activity than a conventional

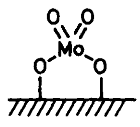
Table 1. Catalytic activity and selectivity of SiO_2-bound Mo dimers in propene oxidation.[a]

Catalyst	SiO_2 Support[b]	Reaction temperature/K	Turnover frequency $/10^{-3} min^{-1c}$	Selectivity Acrylaldehyde	Acetaldehyde	Propionaldehyde
(**6**)	A	673	7.9	32.3	67.7	0
		641	3.0	25.0	75.0	0
(**5**)	A	673	68.9	84.6	15.4	0
		642	27.9	78.6	21.4	0
(**6**)	B	673	9.1	33.3	61.1	5.6
		643	3.8	26.7	73.3	0
(**7**)	B	673	8.1	37.5	62.5	0

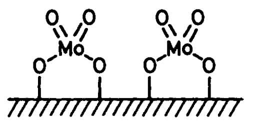
[a] C_3H_6, 25 Torr; O_2, 50 Torr; catalyst, 0.11—0.27 g; Mo, 0.38—0.85 wt%. [b] Surface area: A, 510 $m^2 g^{-1}$; B, 285 $m^2 g^{-1}$. [c] Propene molecule consumed min^{-1} Mo $atom^{-1}$.



Scheme 1. Surface transformations of SiO_2-bound molybdenum dimers. Values in parentheses are the co-ordination numbers of the molybdenum or oxygen atoms.



(**6**)



(**7**)

impregnation Mo catalyst, but the selectivity towards acrylaldehyde was only 25—33%.[4] The values are independent of the type of SiO_2 used as support. Dioxomolybdenum dimers (**7**) also showed similar results. However, the oxygen-bridged molybdenum dimers (**5**) were *ca.* 100 times more active and the acrylaldehyde selectivity (79—85%) was found to be remarkably high, in comparison with conventional SiO_2-supported molybdenum catalysts. Judging from the Mo–Mo separation of 0.330 nm and the Mo–O bond length of 0.194 nm, the two μ-oxygen atoms seem to be located too close to each other. This structural hindrance may activate the μ-oxygen atoms towards the substrate. The reaction between the molybdenum atoms of $Mo_2(\eta^3\text{-}C_3H_5)_4$ and surface oxygen atoms of the silanols retains the active molybdenum dimer structure without redistribution of molybdenum ions during catalyst preparation and catalysis.

Received, 18th January 1985; Com. 080

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