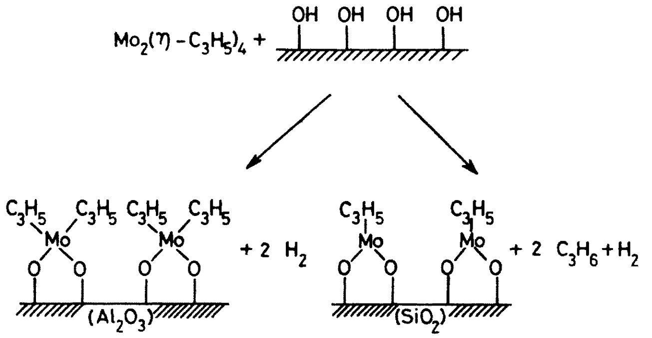
Highly Active 'Paired' Mo^{2+} Structure of Well Defined Supported Catalysts for Ethene Hydrogenation at Low Temperatures

By YASUHIRO IWASAWA,* MASAHIKO YAMAGISHI, and SADAO OGASAWARA
(*Department of Applied Chemistry, Faculty of Engineering, Yokohama National University, Tokiwadai, Hodogaya-ku, Yokohama 240, Japan*)

Summary Chemically well defined, 'paired' divalent molybdenum species supported on alumina or silica, acted as excellent catalysts with high activities for ethene hydrogenation at 200—293 K.

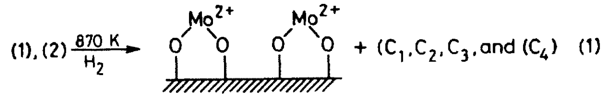
ALTHOUGH much attention has been paid to the preparation or design of solid catalysts with high activities and selectivities and to the elucidation of the essential factors for catalysis such as surface structure, and the environment and oxidation state of the active sites, these major questions remain unresolved. We report here a highly active, 'paired' molybdenum catalyst with well defined properties for ethene hydrogenation at 200—293 K, supported on alumina or silica surfaces.



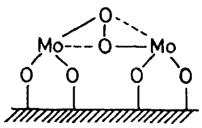
(1) (2)

SCHEME

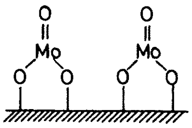
The reactions between $Mo_2(\eta-C_3H_5)_4$ and supports like Al_2O_3 and SiO_2 described by Candlin and Thomas[1] proceeded easily and exclusively at 273 K in the stoicheiometries given in the Scheme when the numbers of surface OH groups of an active alumina (surface area 190 m^2/g) and a silica gel (120 m^2/g) were controlled at 2·6 OH/100 Å^2 and 3·5 OH/100 Å^2, respectively. Both (**1**) and (**2**) were reduced with H_2 at 870 K to give (**3**), releasing the allyl ligands, as in reaction (1). The diffuse reflectance u.v. spectra of (**3**) suggested δ-orbital participation by the pairing of adjacent Mo^{2+} atoms. The species (**3**) were converted into the spectroscopically distinguishable species (**4**) (SiO_2) and (**5**) (Al_2O_3) on exposure to O_2 at 273 K, and at higher temperatures into the tetrahedral dioxo-Mo^{6+} structure (**6**) with a charge-transfer band at 282 (Al_2O_3) or 290 nm (SiO_2). The SiO_2-supported Mo_2 catalyst (**3**) with paired molybdenum ions behaved as a reversible oxygen



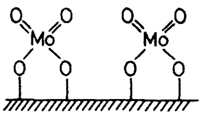
(3)



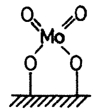
(4)



(5)



(6)



(7)

carrier at 273—430 K. The previously reported SiO_2-supported single Mo^{6+} catalyst (7)[2] with a mean Mo–Mo distance of *ca.* 13 Å showed strong photoluminescence from the T_1 state at 22,900 cm^{-1} whereas the corresponding paired structure (6) showed no emission owing to the interaction between the two adjacent Mo ions. The fixed Mo_2 catalysts were considerably different in spectroscopic properties, temperature-programmed hydrogenolysis (t.p.h.) curves, adsorptions, and reactivities, from the fixed Mo catalysts[2] which were synthesized readily by the reaction[3] between mononuclear $Mo(\eta\text{-}C_3H_5)_4$ and surface OH groups of Al_2O_3 (2·2 OH/100 $Å^2$) or SiO_2 (1·3 OH/100 $Å^2$). The characterization of the surface structures of the fixed Mo_2 catalysts by spectroscopy (diffuse reflectance u.v., photoluminescence, e.s.r., and *X*-ray photoelectron), volumetric adsorption measurements, and t.p.h. analysis, will be reported in detail elsewhere.[4] The quantity of molybdenum thus fixed was determined by chemical analysis to be 0·66 wt% (Mo/Al_2O_3) or 0·68 wt% (Mo/SiO_2).

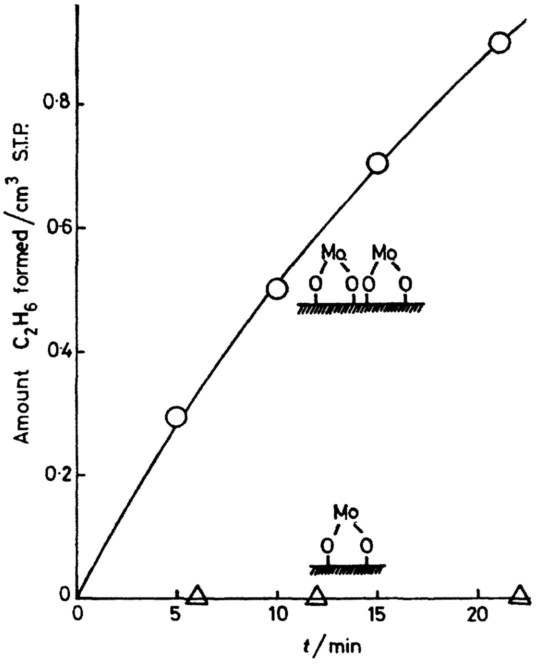


Figure 1. Ethene hydrogenation over fixed Mo and Mo_2 catalysts at 293 K; catalyst, 0·28 g; support, SiO_2; $P(C_2H_4)$, 12 Torr; $P(H_2)$, 48 Torr.

The paired divalent molybdenum species (3) on a silica surface showed much higher activity than the corresponding single isolated species for ethene hydrogenation at 293 K, as shown in Figure 1, where the activity of the latter was negligible although isolated molybdenum ions fixed on a different silica (510 m^2/g) catalysed the reaction. No side reactions occurred. The initial rates (r_0) of hydrogenation at 273 K over the fixed paired molybdenum catalyst (f), compared with a conventional impregnation catalyst (i) are as follows: $r_0 = k_f(H_2)$ and $r_0 = k_i(C_2H_4)^{0{\cdot}1}(H_2)$, respectively. The surface of the impregnation catalysts required reconstitution by repeated reduction with H_2 at 830 K, and small amounts of metallic molybdenum were formed as shown by *X*-ray photoelectron spectroscopy; the fixed catalysts were stable.

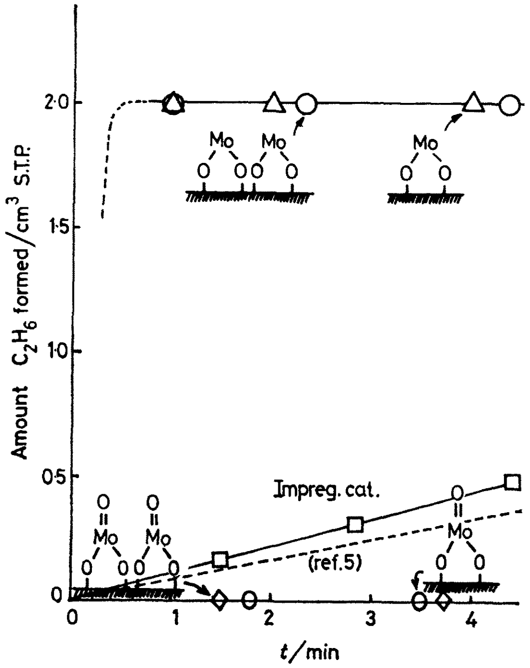


Figure 2. Ethene hydrogenation over fixed Mo and Mo_2 catalysts and an impregnation catalyst at 200 K; catalyst, 0·10 g; support, Al_2O_3; $P(C_2H_4)$, 12 Torr; $P(H_2)$, 48 Torr.

Figure 2 shows results for ethene hydrogenation at 200 K over the three types of catalyst in a closed circulating system (136 cm^3). The fixed catalysts were found to be much more active than the impregnation catalyst; the reaction was completed within 30 s, indicating that the reaction rate was limited by the rate of circulation of the reactants in the system used. Brenner reported a turnover frequency (T.F.) of 5 s^{-1} (H_2/C_3H_6 = 4, total pressure = 1 atm) for hydrogenation of propene at 298 K on a supported Mo catalyst obtained from $Mo(CO)_6$ and Al_2O_3.[6] A molybdenum film gave a T.F. of 0·1 s^{-1} at 298 K.[7] The T.F. for ethene hydrogenation over the fixed single Mo^{2+} and paired $(Mo^{2+})_2$ catalysts was estimated to exceed 0·4 s^{-1}

(P 60 Torr) or 5 s^{-1} (P 1 atm) at 200 K. Figure 2 also shows that the fixed catalysts containing Mo^{4+} ions had no significant activity at 200 K.

Consequently, it has been demonstrated that divalent molybdenum is the active species for ethene hydrogenation at low temperatures and that the paired Mo^{2+} structure is remarkably active irrespective of the support. The hydrogenation over the co-ordinatively unsaturated Mo^{2+} species may proceed by a similar mechanism to that for propene hydrogenation at 195—257 K over an alumina-supported fixed Cr^{2+} catalyst involving the oxidative addition of H_2 to Cr^{2+} with three vacant sites.[8]

(*Received, 28th May* 1980; *Com.* 561.)

---

[1] J. P. Candlin and H. Thomas, *Adv. Chem. Ser.*, 1974, **132**, 212.

[2] Y. Iwasawa and S. Ogasawara, *J. Chem. Soc., Faraday Trans.* 1, 1979, **75**, 1465; Y. Iwasawa, Y. Nakano, and S. Ogasawara, *ibid.*, 1978, **74**, 2968; Y. Iwasawa, S. Ogasawara, and M. Soma, *Chem Lett*, 1978, 1039.

[3] Yu. I. Yermakov, *Catal. Rev.*, 1976, **13**, 77; Yu. I. Yermakov, B. N. Kuznetsov, and Yu. A. Ryndin, *J. Catal.*, 1976, **42**, 73.

[4] Y. Iwasawa, M. Yamagishi, and S. Ogasawara, to be published.

[5] E. A. Lombardo, M. Houalla, and W. K. Hall, *J. Catal.*, 1978, **51**, 256.

[6] A. Brenner, *J. Mol. Catal.*, 1979, **5**, 157.

[7] A. Kouskova, J. Adamek, and V. Ponec, *Coll. Czech. Chem. Commun.*, 1970, **35**, 2538.

[8] Y. Iwasawa and S. Ogasawara, *Chem. Lett.*, 1980, 127.