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SURFACE DESIGN AND CATALYTIC ACTIVITIES OF WELL DEFINED, FIXED "Mo_2" CATALYSTS—— ACTIVE STRUCTURES FOR C_3H_6 METATHESIS

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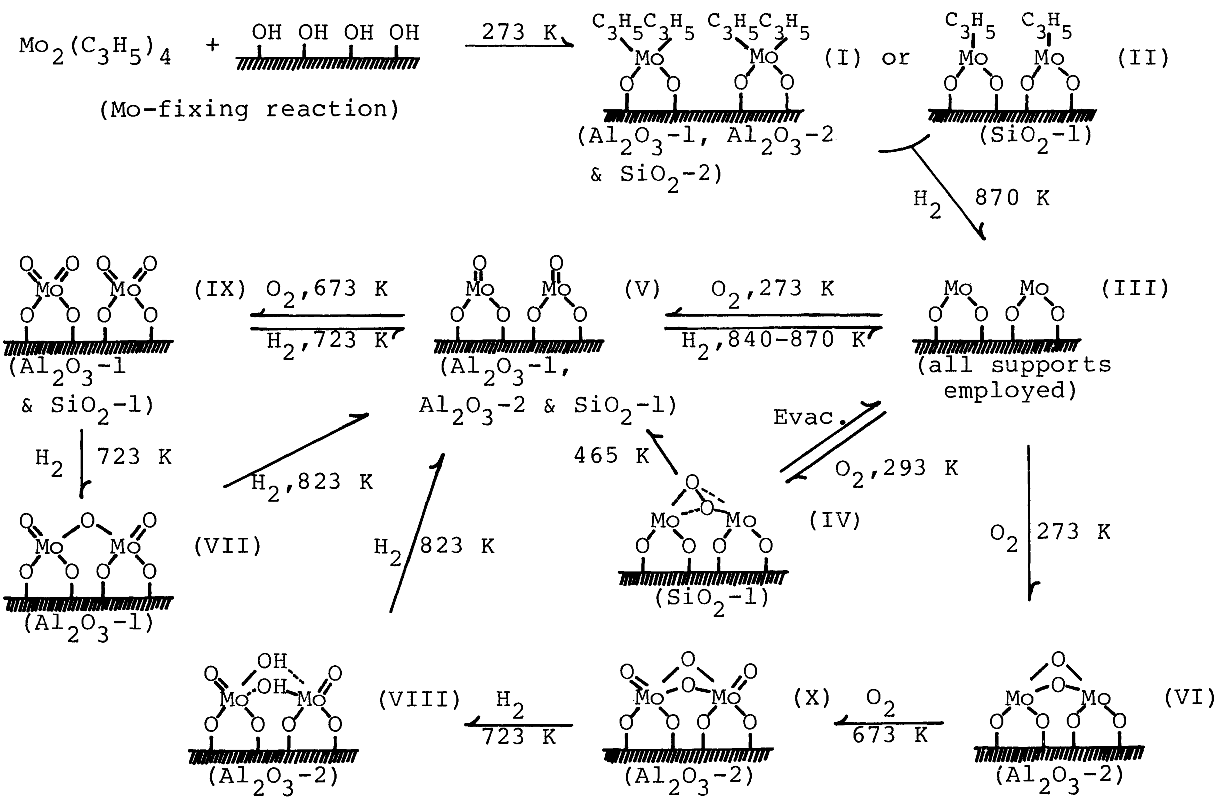
New fixed Mo_2 catalysts with "paired" molybdenum species were prepared using Al_2O_3 and SiO_2 supports to find the active structure for C_3H_6 metathesis and the following order of activity for surface structures was found in comparison with the activities of fixed "single" Mo catalysts; $>Mo^{4+}(C_3H_5)_2 \approx (>Mo^{4+}(C_3H_5)_2)_2 \gtrsim >Mo^{4+}=O > (>Mo^{4+}=O)_2 \gtrsim Mo^{4+}(-O-)_2Mo^{4+} > (>Mo^{3+}-C_3H_5)_2 \gg$ conventional Mo cat. $> O=Mo^{5+}-O-Mo^{5+}=O > (>Mo^{6+}(=O)_2)_2 \gtrsim O=Mo^{5+}(OH)_2Mo^{5+}=O \approx (>Mo^{2+})_2 \gtrsim >Mo^{2+} \approx O=Mo^{6+}(-O-)_2Mo^{6+}=O \approx >Mo^{6+}(=O)_2$.

It is generally difficult to create catalytically active molecular structures with well defined properties on ill defined, heterogeneous surfaces of inorganic oxides. However, it has been demonstrated by means of spectroscopies and volumetries, or from the behaviour of active sites during reactions, that the fixed "single" Mo catalysts acted as typical solid catalysts with well defined and uniform reaction sites.[1)] We wish to report the design of "paired" molybdenum structures on Al_2O_3 or SiO_2 and their catalytic activities for propene metathesis at 267-288 K to find the actual active structure for metathesis.

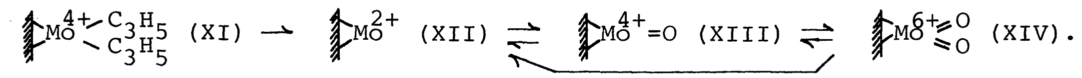
The fixed "paired" Mo_2 catalysts were prepared on the basis of the reaction[2)] between $Mo_2(\pi\text{-}C_3H_5)_4$ and surface OH groups of Al_2O_3 or SiO_2. The Mo-fixing reaction at 273 K was found, by the chemical analysis of Mo in a catalyst and the temperature programmed hydrogenolysis(TPH) of the allyl ligands on a Mo ion, to form the surface complex(I) in the synthesis scheme(supports: Al_2O_3-1(190 m^2/g), Al_2O_3-2 (385 m^2/g) & SiO_2-2(285 m^2/g)) or the complex(II)(SiO_2-1(120 m^2/g)) when the numbers of the OH groups of Al_2O_3-1, Al_2O_3-2, SiO_2-1 and SiO_2-2 were controlled to be 2.6, 4.5, 3.5 and 4.6 OH/100 $Å^2$, respectively. $Mo_2(\pi\text{-}C_3H_5)_4$ was purified by pentane extraction and recrystallization at 193 K under a high purity Ar(99.9995 %). The amounts of molybdenum thus fixed were determined to be 0.66 wt%(Mo/Al_2O_3-1), 0.56 wt%(Mo/Al_2O_3-2), 0.68 wt%(Mo/SiO_2-1) and 0.49 wt%(Mo/SiO_2-2).

$$C_3H_5Cl \; + \; Mg\text{(4.5 times excess)} \xrightarrow[\text{diethyl ether}]{\text{253 K, 10.5 h}} C_3H_5MgCl$$

$$C_3H_5MgCl \; + \; MoCl_5 \xrightarrow[\text{diethyl ether}]{\text{293 K, 6 h}} \xrightarrow[\text{pentane}]{\text{193 K \& 253 K}} Mo_2(\pi\text{-}C_3H_5)_4$$



The single Mo species could take only four types of surface structures as follows;



Although the characterization of the surface structures, (I)-(X), of the fixed Mo_2 catalysts by means of spectroscopies(UV diffuse reflection, photoluminescence, ESR and XPS), volumetries and TPH analyses, will be reported in detail in the following paper[3], the characteristic nature of the paired structures is briefly described. Both (I) and (II) were reduced with H_2 at 870 K to (III), when the allyl ligands were decomposed to C_1-C_4 hydrocarbons; the UV spectra of (III) suggested the formation of the δ-orbital by the pairing of adjacent Mo^{2+}. The (III) was converted to the spectroscopically different species, (V)(Al_2O_3-1), (IV)(SiO_2-1) or (VI)(Al_2O_3-2) by exposure to O_2 at 273 K, and at higher temperatures to the tetrahedral dioxo-Mo^{6+} structure(IX)(Al_2O_3-1 & SiO_2-1) or the bridged 5-coordinated structure(X)(Al_2O_3-2) with a CT band at 353 nm. It is noteworthy that the SiO_2-1-supported paired structure(III) of Mo^{2+} behaved as a reversible oxygen carrier under miled conditions. The SiO_2-1-supported Mo catalyst(XIV) with the mean Mo-Mo distance of ca.13 Å showed the strong photoluminescence($Mo^{6+}=O^{2-} \leftarrow Mo^{5+}-O^-$)[1)] at 22.9 $10^3 cm^{-1}$ whereas the corresponding paired structure(IX) gave no emission due to the interaction between two adjacent Mo ions. The bismolybdenyl(5+) structure(VII) with the characteristic UV peaks at 310 & 405 nm showed no ESR signal, indicating the interaction of a pair of Mo^{5+}.

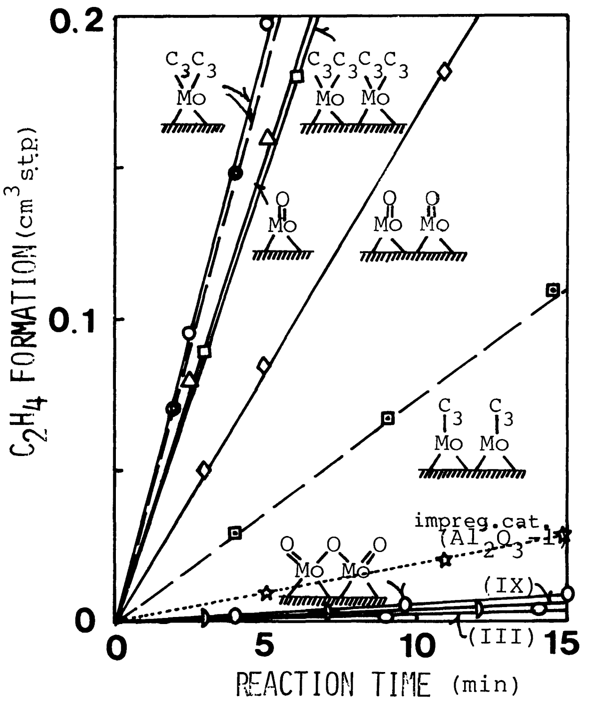


Fig.1 Metatheses over Fixed Catalysts with Various Surface Structures; C_3H_6: 18.6 Torr, React.Temp.: 273 K, catalyst: 87 mg, support: Al_2O_3-1(——) SiO_2-1 (– –)

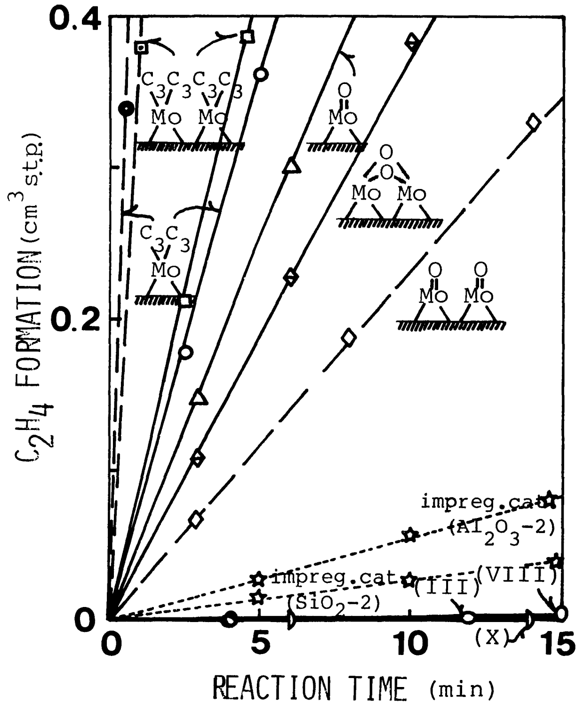


Fig.2 Metatheses over Various Surface Structures of Fixed Catalysts; C_3H_6: 19.3 Torr, React.Temp.: 273 K, catalyst: 90 mg, Support: Al_2O_3-2(——) SiO_2-2 (– –).

Figures 1 and 2 show the productive metathesis of propene over various surface structures at 273 K in a closed circulating system(190 cm^3). The structure and the oxidation state of Mo ions gave profound effects on metathesis activity. The activities of the fixed Mo_2 catalysts((I), (V) & (VI)) were found to be 7-147 times that of conventional Mo catalysts made by an impregnation method. The turnover frequencies(T.F.) for the metathesis on the allylic catalysts(I) at 273 K were 0.056 s^{-1}(SiO_2-2), 0.013 s^{-1}(Al_2O_3-2) or 0.0037 s^{-1}(Al_2O_3-1). Similarly the T.F. for the oxostructure(V) decreased in the following order for supports; SiO_2-2 > Al_2O_3-1 > SiO_2-1.

The paired(I) and single(XI) structures had similar activation energies;

8.4(Mo_2-Al_2O_3-1) & 7.9(Mo-Al_2O_3-1), or 7.5(Mo_2-Al_2O_3-2) & 6.3(Mo-Al_2O_3-2) kJ mol^{-1}. The activation energy(17.5 kJ mol^{-1}) for the paired oxo-species(V) was also similar in magnitude to that(16.3 kJ mol^{-1}) for the single species(XIII). The initial rates(r_o) of metathesis on the fixed catalysts at 273 K were always given by the equations, $r_o=k(C_3H_6)^{0.5}$ or equally $r_o=k'(C_3H_6)_{ad}$ in the range of (C_3H_6) of 6-150 Torr, where $(C_3H_6)_{ad}$ represents the amount of propene adsorbed on supports. The supports not only had large effects on catalytic activities and selectivities by the coordination to active Mo sites but also worked as a reservoir-supplier of reactants. The similarity of single and paired molybdenum catalysts in activation energies and reaction kinetics suggests that each Mo ion of the paired Mo_2 structure acted as a reaction site.

The oxygen bridged Mo_2 catalyst(VI) gave a larger activation energy(23.0 kJ mol^{-1}) than the paired oxostructure(V)(17.5 kJ mol^{-1}). The fixed Mo^{4+} ion(XI) showed a higher activity than the Mo^{3+} species by a factor of 5. The activity of the bismolybdenyl(5+) structure(VII) which was suggested to be an active species for metathesis[4)] was only three hundredth of the activity of the paired oxo-Mo^{4+} structure(V). Both single and paired structures of Mo^{2+} and Mo^{6+} were almost inactive. Thus the following order of activity of productive metathesis for structures of active sites was concluded on the basis of the relative activities of the fixed catalysts with well defined surface structures, the activation energies and the dependence of activity upon the nature of supports;

(XI) $\approx$ (I) $\gtrsim$ (XIII) $>$ (V) $\gtrsim$ (VI) $>$ (II) $\gg$ impreg.cat. $>$ (VII) $>$ (IX) $\gtrsim$ (VIII) $\approx$ (III) $\gtrsim$ (XII) $\approx$ (X) $\approx$ (XIV) = inactive.

References

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