CHEMISTRY LETTERS, pp. 1039-1042, 1978. Published by the Chemical Society of Japan

ACTIVE FIXED Mo CATALYSTS[1] FOR OLEFIN METATHESIS AND CHEMICAL STATE OF THE ACTIVE SITE

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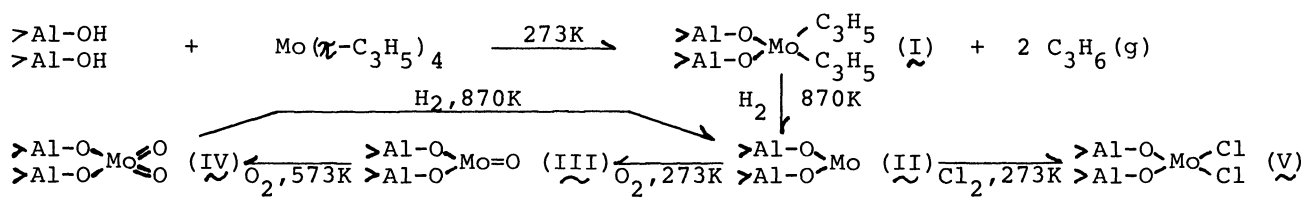
The fixed Mo catalysts with well-defined structures prepared by the facile reactions between $Mo(\pi\text{-}C_3H_5)_4$ and acidic OH groups of supports like γ-alumina, silica-alumina and silica, followed by the stoichiometric uptake of H_2, O_2 or Cl_2, were very active for olefin metathesis, where the coordinatively unsaturated tetravalent Mo uniformly populated on the surface was found to be the actual active site.

Although the properties of active sites of heterogeneous catalysts containing Mo, W or Re as active elements for olefin metathesis have extensively been studied[2], the active structure and the surface chemical state under a catalytic reaction condition are not well understood because of the heterogeneity of the catalyst surface, small number of active sites, etc.. For active species of Mo catalysts made by an impregnation method or by use of some complex, various oxidation states and structures involving Mo^{2+}-Mo^{5+} in their polymeric, dimeric or molecular forms[3] have been proposed. We report here active Mo catalysts with well-defined structures for olefin metathesis and clear evidence for the chemical state of the active site.



The active fixed Mo catalysts using γ-alumina and silica-alumina(Al_2O_3 content: 13 wt%) as supports were molecularly synthesized according to the scheme (as a typical example the alumina-fixed catalyst is shown), extending the preparation method described by Yermakov et al.[4] The facile reaction between $Mo(\pi\text{-}C_3H_5)_4$ and the surface OH groups of supports took place in the order of easiness, $SiO_2 \cdot Al_2O_3 \gtrsim Al_2O_3 \gg SiO_2$. Although the fixing pattern and the subsequent distribution of molybdenum on supports, and the individual step in the scheme will be described in detail elsewhere[5], the results are briefly summarized: (1) comparing our treating condition of supports and the number of OH groups with the results reported by Peri et al[6], the supports employed seem to largely hold the paired OH groups and hence the mean distance between the nearest-neighbour molybdenum ions at SiO_2 and Al_2O_3 surfaces could be estimated to be ca.20 Å and ca.13 Å, respectively, assuming the ideal distribution of the paired OH groups; (2) the Mo fixation takes place on acidic OH groups in contrast to the case of conventional impregnation catalysts[7]; (3) the surface complex(I) was found to have 2.1 C_3H_5-ligands per a Mo atom on average; (4) the stoichiometric uptakes of O_2, H_2 and Cl_2 in the formation of surface structures(III), (IV) and (V) were observed; (5) the alumina-fixed catalyst behaves in a different way from the silica-catalyst in the reduction of catalyst(IV) with H_2. Thus fixed Mo catalysts with three types of ligand using different supports were molecularly obtained under controlled preparation conditions. An active Mo catalyst with chlorine ligands is not known except for a $Mo(NO)_2Cl_2(PPh_3)_2\text{-}EtAlCl_2$ homogeneous system[8].

The reactions were carried out in a closed-circulating system(182 cm^3) using 50-100 mg of catalyst in the low temperature range 273-313K. The turnover numbers of the propene metathesis and the kinetic data at 273K are given in the Table. The fixed Mo catalysts with various ligands, prepared by the stepwise synthesis, were found to be much more active than the catalyst made by a conventional impregnation method: the propene metathesis(C_3H_6/Mo=100) on the catalyst(I) at 273K attained to the thermodynamic equilibrium within 1 hr. The selectivity towards 2-butene on the catalyst(I) was 99.8% and 99.5% for the catalyst(III). The ratios of the rates in

TABLE Turnover Numbers of C_3H_6 Metathesis and Kinetic Data at 273K

Active Structure	$>Mo<^{C_3H_5}_{C_3H_5}$	$>Mo<^{Cl}_{Cl}$	$>Mo=O$	$>Mo=O$	$>Mo=O$	$MoO_3 \cdot Al_2O_3$*** (impreg.cat.)
Supports	Al_2O_3	Al_2O_3	Al_2O_3	$SiO_2 \cdot Al_2O_3$	SiO_2	Al_2O_3
Turnover Number*	0.299	0.082	0.239	0.315	0.075	0.1(373K)
E_a(KJ/mol)	7.9	33.9	16.7	38.5	10.5	37.7
Reaction Order**	0.5	0.5	0.5	0.5	0.5	—— ***

* C_2H_4 molecules/min/Mo-atom, C_3H_6=21 torr., Mo/Al_2O_3=1.5-1.7wt% ** with respect to the C_3H_6 partial pressure *** ref.9), R.O. depends upon the C_3H_6 pressure

the metathesis reactions of propene and 1-butene depended upon the kind of ligands on a molybdenum ranging 1.4-7.8. The nature of the supports which coordinate to a molybdenum through oxygen atoms also affected the metathesis activity: the decreasing activity for supports was observed in the order, $SiO_2 \cdot Al_2O_3 > Al_2O_3 > SiO_2$. The correlation between the catalytic activity and the activation energy for the alumina-fixed catalysts was observed, but surface properties of supports give profound effects on the frequency factor. The same reaction order for the fixed catalysts suggests the similar reaction mechanism.

The Mo^{6+}(xps binding energy for Mo $3d_{5/2}$: 233.5±0.3 eV) and the Mo^{2+}(230±0.5 eV) species showed no catalytic activity under the experimental conditions. The amounts of Mo^{5+} ions contained in active fixed catalysts were only 0.5-3.4% of total molybdenum in terms of esr spectroscopy and they had no correlation with the activity. The xps spectra of molybdenum in the fixed catalysts which were taken by a Mcpherson ESCA-36 spectrometer after the reaction without contacting air are given in the Figure: the binding energies(±0.3 eV, referred to 83.7 eV for Au $4f_{7/2}$ level) for Mo $3d_{3/2}$ and $3d_{5/2}$ levels in catalysts(III) and(V) were observed to be 235.3 and 232.5 eV, and 235.4 and 232.6 eV, respectively. A variety of values for the difference between the Mo 3d binding energies of MoO_3(6+) and MoO_2(4+) have been reported in the range of 0.7-3.3 eV and also 0.3-1.7 eV for some Mo complexes, depending upon the kinds of ligand[10]. Comparing with the spectrum of Mo^{6+} catalyst(IV), the values indicate that the molybdenum atom is situated in a tetravalent state. The uptakes of 1.0-1.1 oxygen atoms per a Mo atom in the oxidation of the Mo^{2+} species with O_2 and 2.0 chlorine atoms/a Mo atom in the complexation of Mo^{2+} with Cl_2 also show the formation of the tetravalent oxo- and dichloromolybdenum structures which are very active for olefin metathesis. The catalytic acti-

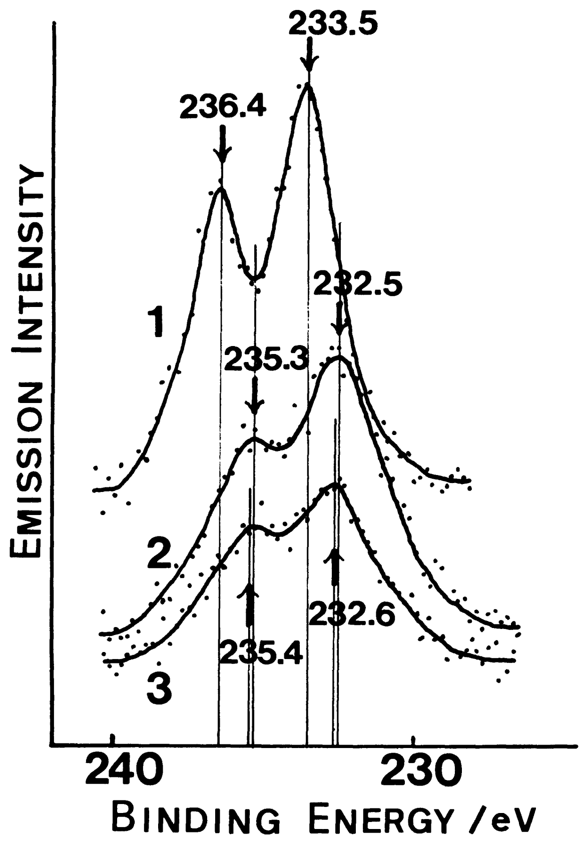
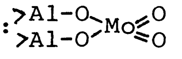
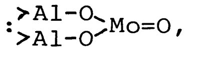
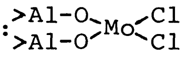


FIGURE Xps Emission Spectra of Fixed Catalysts(Mo/Al_2O_3=1.5 wt%);

1: 
$\begin{matrix}>Al-O\\>Al-O\end{matrix}Mo\begin{matrix}=O\\=O\end{matrix}$,

2: 
$\begin{matrix}>Al-O\\>Al-O\end{matrix}Mo=O$,

3: 
$\begin{matrix}>Al-O\\>Al-O\end{matrix}Mo\begin{matrix}Cl\\Cl\end{matrix}$

vity linearly increased with the amount of Mo^{4+} contained in the fixed catalyst, which indicates that each Mo^{4+} species uniformly populated on the support surface acts as an active site.

Thus it is evident from these results on the much more active fixed Mo catalysts with the well-defined structures than the conventional impregnation catalyst, that the coordinatively unsaturated tetravalent molybdenum molecularly fixed on originally acidic OH groups is the actual active species in olefin metathesis and that the natures of ligands as well as supports give the profound effects on the catalytic behaviour of the Mo^{4+} species.

A part of this work was financially supported by the Asahi Glass Foundation. Y.I. thanks the Sakko-kai Foundation for a subsidy.

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(Received July 31, 1978)