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STRUCTURES OF RHENIUM(VII) OXIDES ON ALUMINA AND THEIR CATALYTIC ACTIVITIES FOR METATHESIS OF OLEFINS

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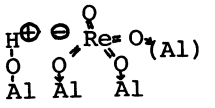
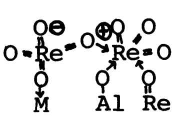
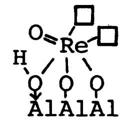
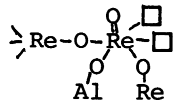
IR studies revealed that the Re_2O_7/Al_2O_3 metathesis catalyst has two different surface rhenium species, $[ReO_4]^-_{ads}$ and $[Re_2O_7]_{ads}$, which are similar in both structure and behavior to those in the aqueous solution of Re_2O_7. $[Re_2O_7]_{ads}$, which is present only in high loading catalysts, should be responsible for their high catalytic activity for the metathesis of olefins.

Our previous works have shown that the catalytic activity of a Re_2O_7/Al_2O_3 system for the metathesis of olefins markedly depends on its composition.[1,2] The catalytic behavior of the system is characterized by the big difference in catalytic activity among three different ranges of Re_2O_7 loading, which ranges were dessignated by K-region, L-region, and M-region, respectively, as shown in Table 1. In particular, the distinct difference between M-region catalysts and the others is abnormal and suggests the difference in the properties of rhenium oxide on alumina between them. A few studies on some physicochemical properties of rhenium oxide in the Re_2O_7/Al_2O_3 system have been reported; however, its structure is still unknown.[1-4] The present work on the structures of rhenium oxides on alumina was done mostly by comparing the IR spectra of the catalysts with those of some known rhenium compounds. The interactions between surface rhenium oxide species and the support were presumed on the analogy of the structures of rhenium oxide species in a Re_2O_7 crystal and its aqueous solution. The dependence of the catalytic activity on the structure of rhenium oxide species on the support was discussed mostly in the light of the results in our previous works.

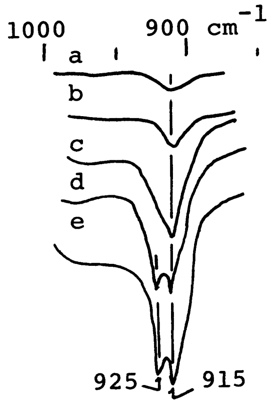
The Re_2O_7/Al_2O_3 catalysts were prepared by impregnating γ-alumina(from Nissan Chemical Industry Co., Ltd., $200 m^2 g^{-1}$) or ALON-C alumina(from Strem Chemicals) with an aqueous solution of Re_2O_7(from Mitsuwa Chemicals, 99.99%) and drying at 120°C for 18 hours followed by air calcination at 500°C for two hours. More details on the experimental methods and conditions were described in our previous works.[1,2] Two different methods were employed for IR studies; one is a conventional KBr method and the other is a vacuum cell method, in which a disk of the catalyst itself is placed. In both cases, IR spectra were recorded at room temperature by placing a catalyst or catalyst/KBr disk in one side of a double beam IR spectrometer and an alumina or alumina/KBr disk in the other.

Fig. 1 shows the IR spectra of the rhenium oxides in the different rhenium

Table 1 Structures and properties of Re oxides in the different Re_2O_7/Al_2O_3 catalysts

		K-region	L-region		M-region	
Loading of	Re/Al[a)]	1/199	1/99	3/97	4/96	5/95
Re_2O_7	wt% of Re_2O_7	2.3	4.6	12.8	16.5	20.0
Catalytic	I[b)]	0.1-0.2	1.5	4.5	32	35
Activity	II[c)]	0.2-0.3	1.2	5.5	20	23
Principle Surface Rhenium Species[d)]		$[ReO_4]^-_{ads}$			$[Re_2O_7]_{ads}$	
Probable Structures of Re Species on Support[d)e)]					 M=Al or Re	
Extraction of the Re Species		Hardly extrated by hot water	Extractable with hot water[f)]		Extractable with cold water[g)]	
The Ratio of O_2[h)] to Re		$\sim 10^{-4}$	$10^{-4} \sim 10^{-3}$		$10^{-3} \sim 10^{-2}$	
Possible Structures of Active Sites[i)]						

a) atomic ratio b) initial rate of the metathesis of propene at 50°C and at 0.1 atm ,[mol $hr^{-1}g^{-1}$] c) % yield of 3-hexene obtained by the metathesis of 2-pentene in chlorobenzene at 25°C, catalyst: 0.2g, 2-pentene in (1 mol dm^{-3}), solvent:2.25 cm^3, after 5 min.[2)] d) by IR studies e) on the analogy of the Re species in Re_2O_7 crystal and its aqueous solution f) The extraction changed it to a K-region -catalyst. g) The extraction changed it to an L-region-catalyst. h) a cumulated amount of oxygen liberated from the catalyst up to 500°C during a temperature programmed desorption experiment i) on the analogy of the active sites on supported MoO_3 catalyst[9)] and that of the result in our previous work[10)] b)c);The catalysts were activated in vacuum at 500°C for one hour.



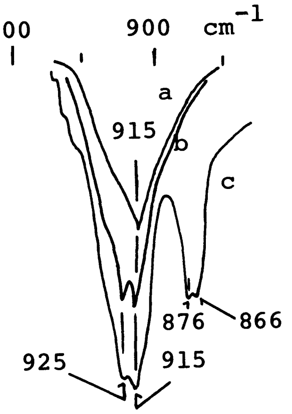


Fig. 1 (left) IR spectra of different loading Re2O7/Al2O3 catalysts, a Re/Al= 1/199 b 1/99, c 3/97, d 4/96, e 5/95: by KBr method (Similar but weaker spectra were obtained by the vacuum cell method.)

Fig. 2 (right) IR spectra of NH_4ReO_4(a), Re_2O_7(b), and $Re_2{}^{16}O_{7-x}{}^{18}O_x$(c) which was prepared by oxidation of partially reduced rhenium oxide ($Re^{16}O_y$) at 400°C in $^{18}O_2$.

oxide loading catalysts. The low loading catalyst in either K- or L-region has a single principle band at about 915 cm^{-1}, while the high loading one in M-region has two bands at about 915 and 925 cm^{-1}, respectively. Fig. 2 shows the IR spectra of two different rhenium compounds, NH_4ReO_4 and Re_2O_7. The former has a single principle band at 915 cm^{-1}, which is due to the Re=O stretching vibration of $[ReO_4]^-$ in NH_4ReO_4 crystal.$^{5)}$ The latter has a couple of bands at 915 and 925 cm^{-1}, respectively. Re_2O_7 crystal has a ligated Re_2O_7 unit which consists of two different groups, a distorted octahedral group, $[ReO_3]^+$, and an approximately tetrahedral $[ReO_4]^-$ group as shown in Fig.3.$^{6)}$ The structure of Re_2O_7 crystal and the isotopic effect shown in Fig. 2 suggest that a couple of the absorption bands at 915 and 925 cm^{-1} are assignable to the Re=O stretching vibration of the $[ReO_4]^-$ and $[ReO_3]^+$ groups, respectively.

A comparison among the IR spectra in Fig. 1 and Fig. 2 led us to a conclusion that the lower loading catalyst in K- and L-region has surface $[ReO_4]^-$, while the higher loading one in M-region does surface dirhenium species, ligated Re_2O_7 units, of which structure should be closely similar to that of Re_2O_7 crystal. However, X-ray studies showed the absence of Re_2O_7 crystal even in M-region-catalysts. This evidence and the fact that the Re_2O_7 species in the catalysts hardly sublime even at 510°C in vacuum or in a stream of oxygen in spite of a fairly high volatility of Re_2O_7 crystal (bp 350°C) suggest that the Re_2O_7 species interacts with aluminum ions and oxide ions of the support.

An aqueous solution of Re_2O_7 has two different rhenium species, monorhenium species, $[ReO_4]^-$, and dirhenium species, Re_2O_7 molecule having a couple of water ligands, as shown by (1).$^{7)}$ The ratio of their concentrations depends not only on the acidity of the solution but also on the concentration of rhenium oxide in the solution. By comparison among the IR spectra in Fig. 1 and Fig. 2 and on the analogy of the structure of the rhenium oxide species in Re_2O_7 crystal and its aqueous solution, probable structures of the rhenium oxide species in the catalysts were presumed and illustrated in Table 1. One can find the similarity in structure between rhenium oxide species on alumina and in crystal or in solution and recognize the similarity between the behaviors of rhenium oxide species on alumina and in solution, and may regard an alumina support as an "immobile solvent".

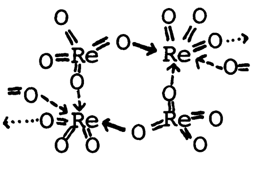
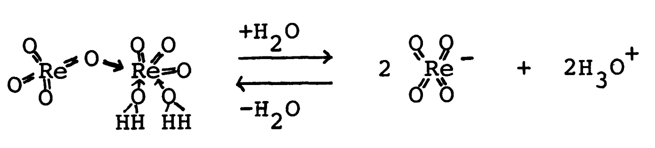


Fig.3. An Asymmetrical Unit of Re_2O_7 Crystal Structure (from reference 6)



(1)

$[ReO_4]^{\ominus}[ReO_3(H_2O)_2]^{\oplus}$ (in concentrated or acidic solution)

$[ReO_4]^-$ (in dilute or basic solution)

Two different rhenium species in solution

A distinct correspondence between the structure of the surface rhenium species and their catalytic activity for the metathesis of olefins, which are shown in Table 1, indicates that the catalysts having the Re_2O_7 species on their surface are definitely more active than the others. The IR studies showed no difference in structure between the surface rhenium species in K-region and L-region. However, they are different in the strength of the interaction with the support: most of the rhenium species in L-region was easily extracted by hot water, while that in K-region was hardly done even by boiling water; presumbly the adsorption sites of them are different each other and the rhenium species in K-region mostly interacts with stronger Lewis acid-Lewis base sites on alumina.

However, we do not believe that the surface Re_2O_7 and $[ReO_4]^-$ species are active for the reaction but we do believe that they are precursors of the active sites, because the liberation of oxygen from the catalysts was observed during the activation process, which is necessary to get the catalytic activity, and the catalysts which had been used for the reaction had weaker Re-O stretching bands than the corresponding fresh catalysts. In fact, the catalytic activity was found to be approximately proportionl to the amounts of oxygen reliesed from the catalyst during the activation at different temperatures. EPR studies also showed that the activated catalysts have medium valent Re ions such as Re^{6+} or Re^{4+}, of which concentrations depend on the activation temperature and the structure of the surface rhenium species.[1,2] The oxygen liberation experiments and EPR studies indicate that the ratio of the medium valent Re ions, one of which has been assumed to be the active sites for the reaction [1,3], to Re^{VII} in all catalysts used in the present work is very low and the tendency to reliese oxygen markedly depends on the structure of the rhenium oxide species as shown in Table 1.

Consequently, the big difference in the catalytic activity between M-region catalysts and the others should be attributable to two different effects; not only the promotion effect of the Re^{VII} oxide ligands to the active sites in M-region, which effect has been reported in our previous works[1,2,8], but also the difference in the concentrations of the active sites. The difference in the structure of the surface rhenium oxide species should be responsible for both effects.

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