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PREPARATIONS OF TiO_2-ATTACHED Rh CATALYSTS AND THEIR CATALYSIS

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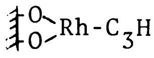
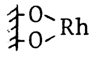
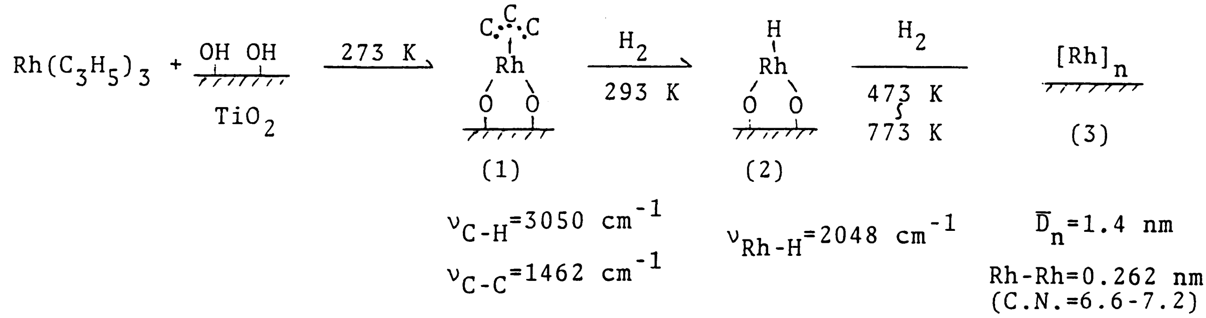
New TiO_2-attached Rh catalysts with the surface structures,  $\begin{array}{l}O\\O\end{array}\!\!>\!Rh\text{-}C_3H_5$ (ν_{C-H}=3050 cm^{-1}, ν_{C-C}=1462 cm^{-1}),  $\begin{array}{l}O\\O\end{array}\!\!>\!Rh\text{-}H$ (ν_{Rh-H}=2048 cm^{-1}) and $[Rh]_n$ ($\bar{D}_n$=1.4 nm, Rh-Rh=0.262 nm), were prepared by the reaction between $Rh(\eta^3\text{-}C_3H_5)_3$ and surface OH groups of TiO_2, followed by chemical treatments with H_2. These catalysts showed higher activities for ethane hydrogenolysis and ethene hydrogenation than a conventional impregnation Rh catalyst.

The chemical design of catalytically active sites with well defined properties on solid surfaces is one of current topics in the research boundary between homogeneous and heterogeneous catalytic systems as well as in surface science. A class of inorganic oxide-attached metal catalysts obtained by using metal-η^3-allyl complexes and metal carbonyls has been demonstrated to provide a new way of preparations of distinct solid catalysts and to be of great advantage to a molecular-scale study of catalysis.[1)] In the present article the preparations of TiO_2-attached Rh catalysts and their catalytic properties are reported.

$Rh(\eta^3\text{-}C_3H_5)_3$ was synthesized from $[RhCl(C_3H_5)_2]_2$ and C_3H_5MgCl according to the previous report.[2)] The attachment of $Rh(\eta^3\text{-}C_3H_5)_3$ onto TiO_2 surface was conducted in a specially devised Pyrex-glass reactor equipped with several U-shaped glass tubes with breakseals. TiO_2(P-25)(decarbonated) was treated at 473 K in the reactor in situ before the rhodium-attaching. The attaching reaction at 273 K was completed within 20 min to give the TiO_2-attached Rh catalyst(1) with Rh/TiO_2=2.0

wt%. A conventional supported Rh catalyst(Rh/TiO_2=2.0 wt%) was obtained by an impregnation method using aqueous $RhCl_3$ solution.



Scheme 1. The Attachment of $Rh(\eta^3-C_3H_5)_3$ onto TiO_2 and Surface Transformations.

The temperature programmed decomposition(TPDE) products of the surface complex (1) were mainly propene and ethene, each exhibiting a single peak. The amount of allyl ligands coordinated to a Rh atom in the species(1) was determined to be unity from the TPDE analysis as given in Table 1. This implies that two C_3H_5 groups of $Rh(\eta^3-C_3H_5)_3$ were lost by the attaching reaction with two surface OH groups. The characteristic absorption bands of (1), 3050 and 1462 cm^{-1} for ν_{C-H} and ν_{C-C}, respectively, indicate that the C_3H_5 ligand of the surface complex is still of π-allyl-type. The Rh-allyl species(1) reacted with H_2 at 293 K to form the Rh-hydride(2) with concomitant evolution of propane. The composition(H/Rh) of the structure(2) was estimated from the amount of H_2 consumed in the reduction step(Table 1). The IR bands for the allyl groups disappeared by exposure to hydrogen(70 Torr, 1 Torr =133.3 Pa) for 1 h at 293 K to be replaced by a new peak at 2048 cm^{-1}. The peak shifted to 1495 cm^{-1} by exchange with D_2. The 2048 cm^{-1} peak also disappeared with contact with ethene: two peaks at 2970 and 2916 cm^{-1} with shoulders which are assigned to the C-H stretching vibrations of C_2H_5 groups were observed. Reversely, the ν_{C-H} peaks were replaced by the 2048 cm^{-1} peak by introducing H_2 again. The ratio, H/Rh, was also determined from the amounts of C_2H_6 evolved and H_2 consumed in the step, $\Big\}{}^{O}_{O}{>}Rh-C_2H_5(4) \longrightarrow \Big\}{}^{O}_{O}{>}Rh-H(2)$, as given in Table 1.

Thus the peak of 2048 cm^{-1} was assigned to the mononuclear rhodium-monohydride species(2). When $Rh(\eta^3-C_3H_5)_3$ was supported into zeolite cavities followed by HCl or H_2 treatments, Schwartz et al[3)] observed twin peaks at 2098 and 2029 cm^{-1} which were assigned to $\Big\}O-Rh{<}^{H}_{H}$ unidentately linked to the surface. They also claimed the formation of unidentate Rh-hydride species situated in heterogeneous

Table 1. Compositions of Species(1) and (2) Determined by Gas Phase Analyses

Amount of Rh Attached, Rh/TiO_2 (wt%)	2.0
Amount of Allyl Ligands per Rh Atom in Species(1)	0.98
Amount of Hydrides per Rh Atom in Species(2)	
from H_2 Consumption in the Step, Rh-allyl $\longrightarrow$ Rh-H	1.10
from C_2H_6 Evolution and H_2 Consumption in the Step, Rh-ethyl $\longrightarrow$ Rh-H	0.85

environments on TiO_2.[4)] The present TiO_2-attached Rh-H structure(2) in a bidentate form showed neither twin nor bridged-type ν_{Rh-H} peaks in the range of H_2 pressure 10-400 Torr. On the contrary, Gates et al[5)] suggested that the SiO_2-attached $\nmid$O-Rh(allyl)$_2$ did not react with molecular H_2.

The Rh-H species(2) was converted to TiO_2-attached $[Rh]_n$ assembly(3) by reduction with H_2 at temperatures 473-773 K. The mean particle size($\bar{D}_n$) was determined to be 1.4 and 1.5 nm for the samples reduced at 473 K and 773 K, respectively, by TEM studies. These $[Rh]_n$ particles were much smaller than the Rh particles($\bar{D}_n$= 3.2 nm by TEM, 6.0 nm by H_2 titration) of the traditional impregnation catalysts. The large difference of both types of catalysts was also seen in Rh-Rh bond length and Rh coordination number(C.N.) determined by EXAFS analysis.[6)] The Rh-Rh bond distances and the C.N. of Rh of (3) and the impregnation catalyst were 0.262 nm and 6.6-7.2(varied with reduction temperatures), and 0.266 nm and 12, respectively. These results together with a remarkably large shift of X-ray absorption edge(ΔE= 3.1 eV) demonstrate that small thin $[Rh]_n$ clusters(3) with stronger Rh-Rh bonding and cationic character were prepared via the Rh-hydride structure(2) chemically bonded to the TiO_2 surface, whereas the physical parameters of Rh particles of the impregnation catalyst were similar to those of Rh metal.

The TiO_2-attached Rh-hydrides(2) and Rh-thin particles(3) showed high catalytic activities compared with the impregnation Rh catalysts for ethene hydrogenation and ethane hydrogenolysis as shown in Fig.1. The catalytic activity of the impregnation catalyst markedly decreased by the prereduction at 773 K owing to a strong metal-support interaction(SMSI) effect, but the corresponding attached Rh catalyst retained the high activity. The attached catalysts obeyed no SMSIpoisoning in H_2 or CO chemisorption in the range of the prereduction temperatures 403-773 K unlikely usual TiO_2-supported Rh catalysts. In general, ethane hydrogenolysis requires multi-metal atoms for reaction. It may be noted that the most active catalyst was the mononuclear Rh-hydride species(2) with the smallest activation energy (30 kJ mol^{-1}) in Fig.1.

We have been preparing the surface structures with no analogues with homogeneous and conventional heterogeneous catalysts; the present specific TiO_2-attached Rh catalysts may be typical examples of a new class of catalysts.

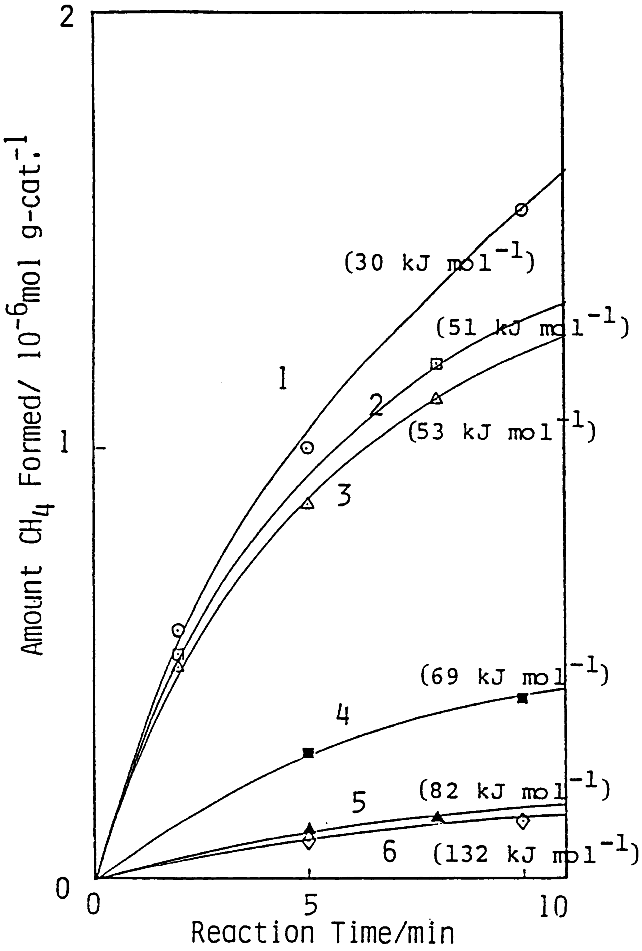


Fig.1. Ethane Hydrogenolysis on Rh/TiO_2 Catalysts; catalyst : 0.33 g (Rh/TiO_2=2.0 wt%), react.temp. : 373 K, C_2H_6 = 20 Torr, H_2 = 40 Torr, 1: attached Rh-H, 2: attached Rh(473 K redn.), 3: attached Rh(773 K redn.), 4: impreg.Rh(473 K redn.), 5: impreg.Rh (773 K redn.), 6: attached Rh(863 K redn.). The activation energies are also shown in ( ).

References

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