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ISOMERIZATION OF ALKANES OVER A PALLADIUM SALT OF HETEROPOLYACID

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Palladium dodecatungstophosphate ($Pd_3(PW_{12}O_{40})_2$) supported on silica is an active and selective catalyst for the isomerization of pentane and hexane in the presence of hydrogen. Thus, hexane could be isomerized in a flow system under atmospheric pressure over 90% selectivity at 483 K. The reaction proceeds in a dual-dunctional mechanism; palladium metal formed by the reduction of palladium(II), and protons, act as a hydrogenation-dehydrogenation catalyst and an olefin-isomerization catalyst, respectively.

Heteropolyacids like dodecatungstophosphoric acid are strong acids and are very active catalysts for many acid-catalyzed reactions proceeding both in liquid phase and vapor phase.1-6) It is also known that some metal salts of heteropolyacids are also effective as solid-acid catalysts.7-13) For example, silver salts of heteropolyacids are much more effective catalysts for the conversion of methanol into hydrocarbons.9-11) The development of the acid sites in the silver salts were found to be accompanied by the reduction of silver(I) cation.11,14) Enhancement of the catalytic activity by the presence of hydrogen was observed in the conversion of methanol11) and the synthesis of methyl t-butyl ether from isobutene and methanol over the silver salts.

Isomerization of alkanes is an industrial process, which uses platinum in combination with acidic carriers such as fluorided alumina and zeolites.15-17) As the reaction mechanism, the dual functionality is generally accepted. Thus, the isomerization proceeds via the dehydrogenation of a n-alkane to n-alkene. This is isomerized to the olefin-isomers, which are in turn hydrogenated to the corresponding alkane. The hydrogenation-dehydrogenation steps proceed on the platinum sites, the isomerization on acidic sites. As for the acidic component, high acid strength is usually necessitated and the isomerization step is considered to be rate-determining.

We have attepmted the isomerization of alkanes by using palladium dodecatungstophosphate [$Pd_3(PW_{12}O_{40})_2$, PdTP] supported on silica-gel. Prior to the reaction, the salt was heated in a hydrogen stream at the reaction temperature (443 - 523 K). By this treatment, Pd(II) cations are reduced to Pd(0) and protons are created by the reaction,

$$\mathrm{Pd(II)} + H_2 \longrightarrow \mathrm{Pd(0)} + 2\,H^+$$

It is noted that PdTP are active for acid-catalyzed reactions such as the ester-forming reaction from acetic acid and ethanol even without hydrogen pretreatment, indicating that there is another way of the acid-site formation, as will be discussed elsewhere. Irrespective of the way of the acid-site formation, PdTP after the reduction is expected to be a potential catalyst for the isomerization, since it would contain both metallic sites (Pd(0)) and acidic sites (H^+).

PdTP was prepared as follows. To an aqueous solution of dodecatungstophosphoric acid, the solution containing the stoichiometric amount of palladium nitrate was added, and then heated over a water-bath until the part of the solute was deposited as precipitate. The precipitate was then dried at 373 K and stored. The precipitate was dissolved in water and then silica-gel was added to the solution. The suspension was kept overnight, and then heated over a water-bath to dryness. The silica-gel was offered by Fuji-Davison Chemical Ltd. and had the average pore diameter of 30.8 nm and the particle size of 0.13 - 0.85 mm.

The reaction was carried out with a continuous flow reactor operating at atmospheric pressure. The catalyst was packed in a reactor of silica-tubing (12 mm i.d.) placed in a vertical furnace and then heated in a hydrogen stream at the reaction temperature for 1 h. Alkanes was delivered by a motor driven syringe to be vaporized in the preheating zone of the reactor, containing 10 cm^3 of quartz. Hydrogen or nitrogen was fed through a flow-meter. The gas from the outlet of the reactor was analyzed by gas-chromatography with a 10-m column of sebaconitrile-Uniport C.

Figure 1 shows a typical time course of the conversion of hexane over PdTP (50%)-SiO_2 under the reaction conditions of 483 K, W/F = 100 $g \cdot h \cdot mol^{-1}$ and hexane/hydrogen ratio of 3 to 7. The total conversion of hexane decreased as time on stream; thus, it was 61.0% and 43.2% at the time on stream of 1 h and 6 h, respectively. The result shows that PdTP is effective for the isomerization. When hydrogen in the feed was replaced by nitrogen at 2 h after starting the reaction, the conversion dropped sharply as shown in Fig. 1(B). Thus, the presence of hydrogen is essential for the catalysis, indicating the dual functional character of the catalysis. The catalytic activities of various salts of dodecatungstophosphoric acid (30 wt%) supported on silica were compared at 523 K. As is shown in Table 1, the palladium salt is the most active among the salts studied. It is worthy of note that dodecatungstophosphoric acid gives the very low conversion. This indicates the essential role of the palladium component. This is confirmed by a following experiment. Dodecatungstophosphoric acid (101 wt%) was supported on Pd (5 wt%)-C, which was obtained from Engelhard. The catalyst

Table 1. Catalytic activities of metal dodecatungstophosphate

Cation	Conversion/%	Selectivity/%
Pd	33.7	84.4
Ag	7.6	75.9
Ni	5.8	72.5
Al	3.7	63.1
Cu	2.8	47.5
H	1.5	64.8

Reaction temperature 523 K, W/F = 100 $g \cdot h \cdot mol^{-1}$, hexane 30 kPa, hydrogen 71 kPa, catalysts were pretreated by hydrogen at 573 K for 1 h.

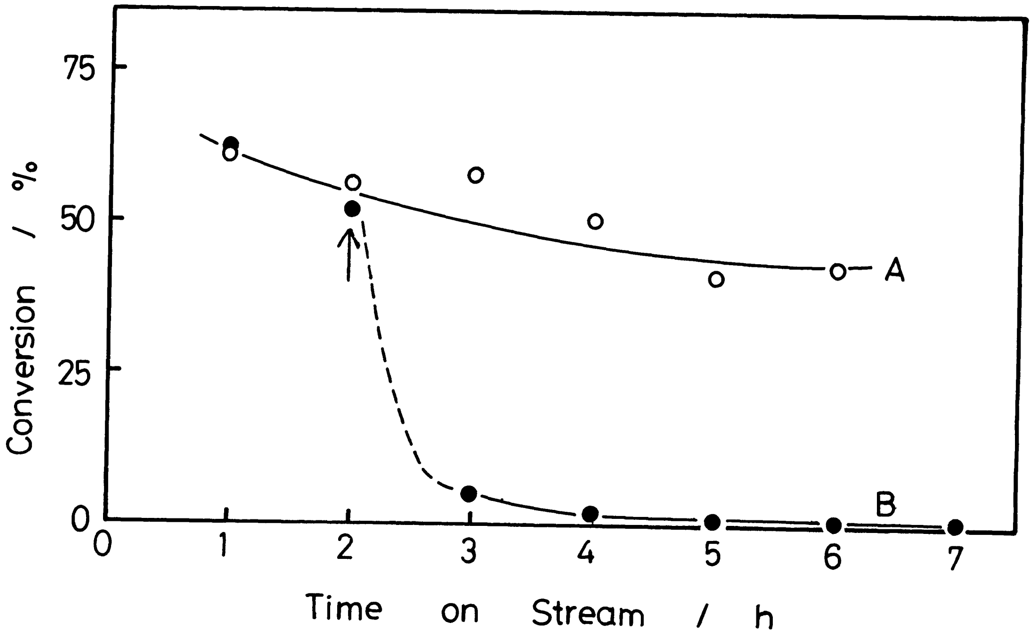

Fig. 1. Change in the conversion of hexane with time on stream.
Reaction conditions; 483 K, hexane pressure, 30 kPa,
Run A (○), hydrogen pressure; 71 kPa,
Run B (●), hydrogen was replaced by nitrogen at 2 h of time on stream.

Table 2. Product distribution in hexane isomerization over palladium dodecatungstophosphate supported on silica

Reaction temperature / K	443	483	523
Conversion / %	27.1	53.0	53.8
Selectivity to isomers / %	94.2	89.8	78.5
Product distribution / %			
Methane	0.0	0.0	0.1
Ethane	0.0	0.1	0.3
Propane	0.3	1.7	6.1
Butanes	1.1	4.2	9.6
Pentanes	0.6	3.4	5.1
2,2-Dimethylbutane	2.7	4.3	3.1
2,3-Dimethylbutane 2-Methylpentane	63.7	59.1	51.5
3-Methylpentane	27.8	26.4	23.9
Methylcyclopentane	1.6	0.5	0.2
Cyclohexane	2.2	0.2	0.1
Heptanes	0.0	0.1	0.0

Hexane 30 kPa, Hydrogen 71 kPa, W/F = 100 g·h·mol^{-1}.

is also active at 483 K in the presence of hydrogen, giving the hexane conversion of 27.1% together with the selectivity to the isomers of 97.9%.

The distribution of the reaction products in hexane isomerization at three different temperatures is given in Table 2. The conversion increased with increasing the reaction temperature, while the selectivity to the isomers was higher at lower temperatures. Thus, the selectivity of 94.2% was obtained at 443 K. Aromatic compounds were not detected under the reaction conditions.

Pentane can be also isomerized to isopentane under the similar conditions. At 453 K and pentane pressure of 30 kPa with hydrogen pressure of 71 kPa, the selectivity was 96.8% at the conversion of 39.5%.

As described above, the palladium salt of heteropolyacids or the combination of palladium metal and heteropolyacids is an active catalyst for the isomerization of alkanes, heteropolyacids being a very effective component in the dual functional catalysts.

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