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ISOMERIZATION OF OLEFINS CATALYZED BY SILICA-POLYALUMAZINE-PALLADIUM COMPLEXES

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ABSTRACT

A silica-supported polyalumazane-palladium complex (abbreviated Al-N-Pd) has been found to be an effective isomerization catalyst for olefins. It can catalyze pentene-1 to pentene-2 in 72% yield and hexene-1 to hexene-2 and hexene-3 in yields of 88 and 12%, respectively, at 0°C and under atmospheric pressure. In investigating the solvent effects on the isomerization of hexene-1 catalyzed by Al-N-Pd, it was found that alcohol probably plays a role as promoter. Kinetic studies on the isomerization of hexene-1 indicate that the rate equation is $r = k C_{\text{Pd}} C_{\text{hexene-1}}$, where $k = 0.82 \pm 0.07$ (mol Pd•min)$^{-1}$. Al-N-Pd is very stable in air and relatively stable during the reaction. The turnover numbers in the isomerization of hexene-1 amount to above 1 000. These results show that the inorganic polymer-supported metal complex Al-N-Pd is more active, selective, and stable than other catalysts for isomerization of α-olefins.

INTRODUCTION

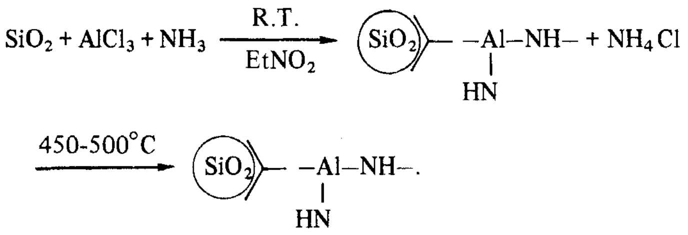
Until now, although many catalysts for the isomerization of α-olefin to β-olefin are known, most of them have some disadvantages. For example, alumina-supported palladium or palladium halide was used at 60-150°C and under 20-68 kg/cm^2 pressure, but the yield of β-olefin was only 32% [1]. When $H_2Os_3(CO)_{10}$ was used, the reaction could be carried out at room temperature and under atmospheric pressure, but it was unstable [2]. If $H_2Os_3(CO)_{10}$ was anchored to a polymer ligand with diphenylphosphino groups, it could also catalyze the isomerization of α-olefin, but the reaction had to be carried out under nitrogen [3]. Zeolite-supported palladium carbonate could also be used at 10-40°C under atmospheric hydrogen pressure, but hydrochloric acid or sulfuric acid had to be added as a promoter, and the yield of β-olefins was about 80% [4].

We reported in a previous paper that silica-supported polyalumazane-palladium complex (abbreviated Al-N-Pd) is an effective hydrogenation catalyst for olefins, nitro compounds, aldehydes, and ketones [5]. We recently found Al-N-Pd to also be an effective isomerization catalyst for olefins.

EXPERIMENTAL

Preparation of Silica-Polyalumazane

Silica-polyalumazane was prepared by the following method:



(Al-N)

Aluminum chloride (40 g) was dissolved in nitroethane (500 mL) in a 1 000-mL three-necked flask, and silica gel (surface area 370 m/g, 20 g) was added. The mixture was stirred, and then ammonia was passed into the reactor to react with the $AlCl_3$ at room temperature until the mixture became alkaline. The mixture was filtered and dried at 100°C for 8 h, then heated at 450°C to sublimate out the ammonium chloride.

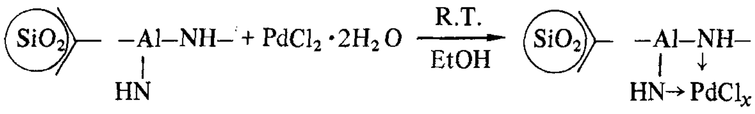
Preparation of the Palladium Complex of Polyalumazane

$PdCl_2 \cdot 2H_2O$ (85.2 mg) was dissolved in ethanol (25 mL) in a 50-mL flask, then polyalumazane (4 g) was added to react with $PdCl_2$ for 1 h at room tem-

TABLE 1. XPS Data for Al-N-Pd, Al-N, and $PdCl_2$

	Binding energy, eV		
XPS peak	Al-N-Pd	Al-N	$PdCl_2$
$Pd_{3d\ 5/2}$	335.8		338.4
N_{1s}	402.2	400.8	
Cl_{2p}	199.4		199.2
Si_{2p}	103.3	103.4	
O_{1s}	533.2	533.3	
Al_{2p}	74.8	74.9	

perature. The mixture was filtered and dried in a dessicator at room temperature.



(Al-N-Pd)

Characterization of Al-N-Pd by XPS

The XPS data for Al-N-Pd, Al-N, and $PdCl_2$ are shown in Table 1. It can be seen that the binding energies of Cl_{2p}, O_{1s}, Si_{2p}, and Al_{2p} for Al-N-Pd are similar to those for Al-N. However, the difference in N_{1s} binding energies between Al-N-Pd and Al-N is 1.4 eV, and the difference of $Pd_{3d\ 5/2}$ binding energies between Al-N-Pd and $PdCl_2$ is 2.6 eV. These results show that coordinate bonds are formed between the palladium atom and the two nitrogen atoms in the complex.

RESULTS AND DISCUSSION

Isomerization

The isomerization of pentene-1 and hexene-1 catalyzed by Al-N-Pd at 0°C at atmospheric pressure are shown in Figs. 1 and 2, respectively. It can be seen

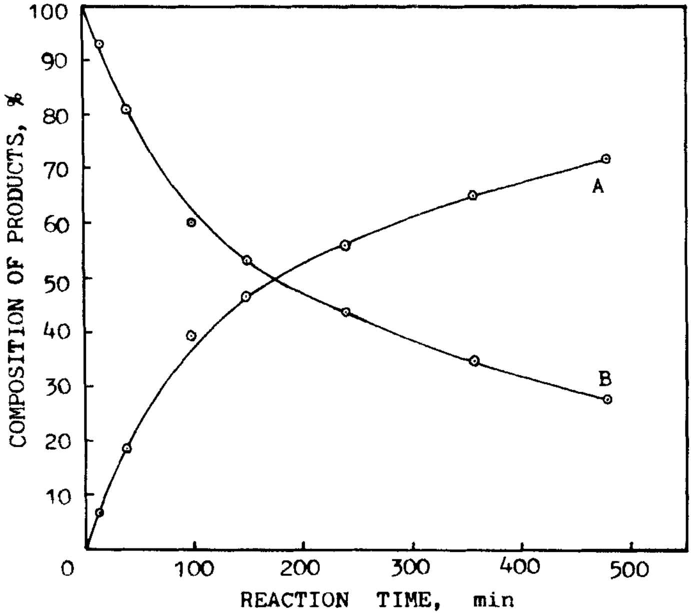


FIG. 1. Isomerization of pentene-1 catalyzed by Al-N-Pd. (A) Pentene-2, (B) pentene-1. Pd, 0.05 mg atom; pentene-1, 10 mmol; solvent, ethanol, 5 mL; 0°C; 1 atm.

that, in the isomerization of pentene-1, the yield of pentene-2 is 72%, and in the isomerization of hexene-1, hexene-2, and hexene-3 are produced in 88 and 12% yields, respectively, the total yield amounting to 100%.

In comparison with the catalysts mentioned above, Al-N-Pd has some evident advantages for it can catalyze hexene-1 entirely to hexene-2 and hexene-3 at 0°C under atmospheric pressure in the absence of any promoter, yielding 88% β-hexene.

Effect of Solvent

The results of isomerization of hexene-1 catalyzed by Al-N-Pd in different solvents are shown in Table 2. It can be seen that isomerization takes place only in the alcoholic solutions. The hydroxy proton of the alcohol probably plays the role of promoter. The promotion effects depend on the kind of alcohol according to the following order: $CH_3OH > CH_3CH_2OH > (CH_3)_3COH$.

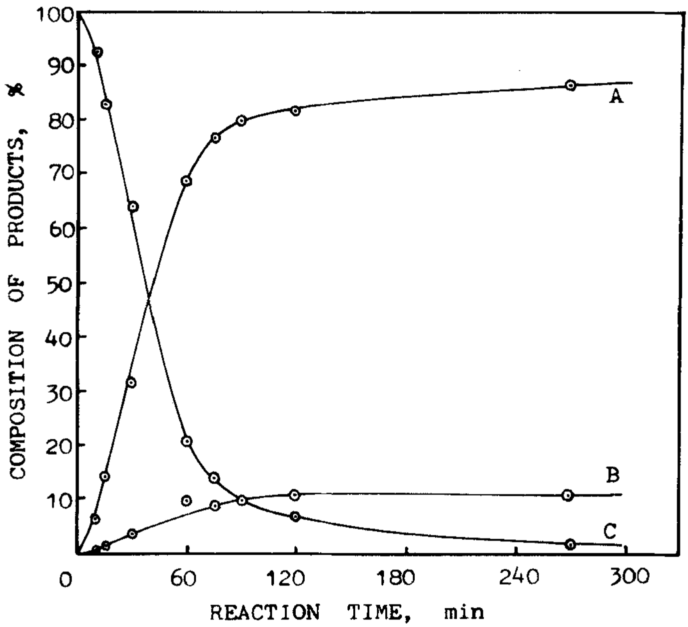


FIG. 2. Isomerization of hexene-1 catalyzed by Al-N-Pd. (A) Hexene-2, (B) hexene-1, (C) hexene-3. Pd, 0.02 mg atom; hexene-1, 5 mmol; solvent, ethanol, 5 mL; 0°C; 1 atm.

TABLE 2. Effects of Solvents on the Isomerization of Hexene-1 Catalyzed by Al-N-Pd[a]

Solvent	mL	Reaction temperature, °C	Conversion, %
Methanol	5	0	99
Ethanol	5	0	79
t-Butanol	5	27	1
THF	5	0	0
Hexene-1	2	0	0
Cyclohexane	5	0	0

[a] Pd, 0.02 mg atom; hexene-1, 5 mmol; 0°C; 1 atm; 1 h.

TABLE 3. The Relationship between Initial Concentration and ln C_0/C at Constant Reaction Time[a]

Serial number	C_0, mol/L	C, mol/L	ln C_0/C
1	0.47	0.31	0.42
2	0.89	0.57	0.45
3	1.61	0.98	0.49
4	2.19	1.49	0.39

[a] Pd, 0.02 mg atom; solvent, ethanol; 30 min; 0°C; 1 atm.

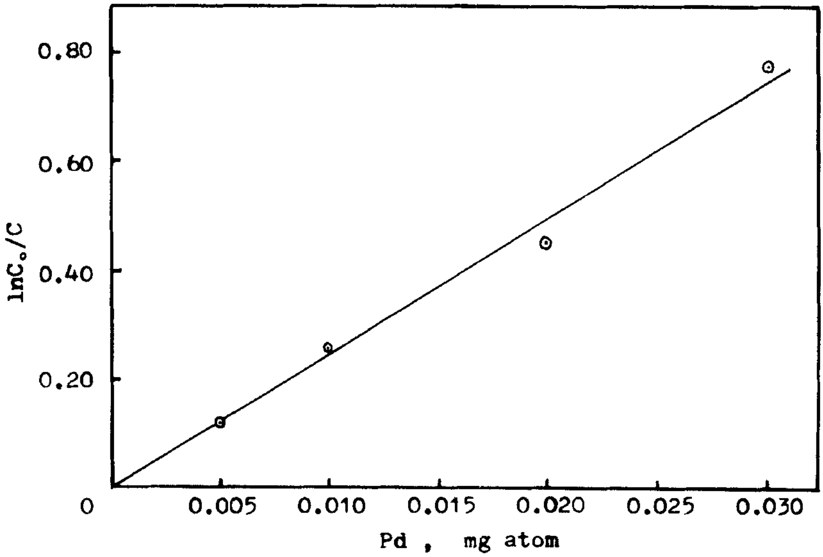


FIG. 3. The relationship between ln C_0/C and amount of the catalyst Al-N-Pd. Hexene-1, 5 mmol; solvent, ethanol, 5 mL; 30 min; 0°C; 1 atm.

Although the promotion effect of methanol is larger than that of ethanol, ethanol is a more suitable solvent for this reaction because Al-N-Pd loses its catalytic activity more easily in methanol solution. Possibly Al-N-Pd is more easily reduced in methanol solution and liberates palladium metal.

Kinetic Studies on the Isomerization of Hexene-1

The results of isomerization of different initial concentrations of hexene-1 at constant reaction time are shown in Table 3. Since ln C_0/C is constant, the reaction is first-order with respect to hexene-1, with rate constant

$$k_1 = \frac{1}{t} \ln C_0/C = 0.015 \pm 0.002 \text{ min}^{-1}.$$

The results of isomerization of hexene-1 catalyzed by different amounts of Al-N-Pd at constant reaction time are shown in Fig. 3. It can be seen that ln C_0/C is proportional to the amount of catalyst Al-N-Pd; that is, $\ln C_0/C = k\,(C_{\text{Pd}})\,t$, thus $k = 0.82 \pm 0.07$ (mol Pd·min)$^{-1}$.

Stability of Al-N-Pd

Al-N-Pd is very stable in air and relatively stable in the reaction. The turnover numbers in the isomerization of hexene-1 amount to over 1 000. These results show that the inorganic polymer-supported metal complex Al-N-Pd is more active, selective, and stable than any other catalysts for the isomerization of α-olefins.

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