

Hydrogenation catalyzed by silica-supported polystannazane-palladium and platinum complexes

S. K. Cao, M. Y. Huang, and Y. Y. Jiang

Institute of Chemistry, Academia Sinica, Zhongguancun, Beijing 100080, Peoples Republic of China

Summary

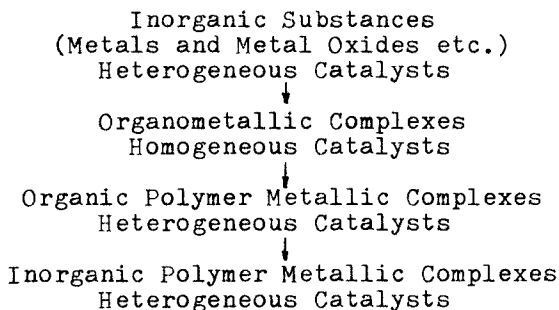
A new kind of inorganic polymer containing no organic groups, silica-supported polystannazane (abbr. as Sn-N), and its Pd and Pt complexes (abbr. as Sn-N-Pd and Sn-N-Pt respectively) were synthesized. When these two complexes were used to catalyze the hydrogenation of nitro- and carbonyl-compounds and the compounds containing C=C double bond, it was found that they have higher catalytic activity at room temperature and under atmospheric hydrogen pressure. The hydrogenation of carbonyl-compounds can be controlled in the alcohol stage, no further hydrogenation happened.

Introduction

Up to now, catalysts used in industry are mostly metals and metal oxides. They are stable and easy to be recovered. But in general, they have lower catalytic activity and selectivity, and need high temperature and high pressure. Different from these heterogeneous catalysts, in about late 20 years, many homogeneous catalysts have appeared. They are organometallic complexes having higher catalytic activity and selectivity. But they are poor in stability and not easy to be recovered. In order to resolve these problems, some polymer metallic complexes that can be used as heterogeneous catalysts have been studied (1,2). Many research works have proved that this kind of polymeric catalysts has higher catalytic activity and selectivity for many reactions. But in some cases, the stability of them is not as good as that of inorganic catalysts. For example, when it was used to catalyze oxidation reactions, the polymer itself may also be oxidized.

We have tried to explore new kinds of catalysts, inorganic polymer catalysts, that may have all of the advantages of the three kinds of catalysts mentioned above. Scheme 1 shows clearly that how this idea comes.

Silica-supported polyalumazane (abbr. as Al-N) and polysilazane (abbr. as Si-N), two inorganic polymers, and their complexes with Pd or Pt have been synthesized in our laboratory. It was found that they have higher catalytic activities for hydrogenation (3), isomerization (4) and oxidation (5) reactions. In this paper, we would like to show another inorganic polymer, polystannazane, and its complexes with palladium and platinum, and their use in catalytic hydrogenation of



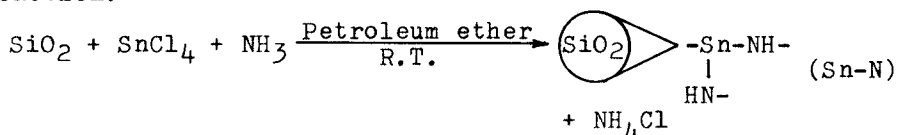
Scheme 1, Developments in Catalysts Study

nitro- and carbonyl-compounds and the compounds containing C=C double bond.

Experimental

Preparation of Silica-supported Polystannazane (Sn-N)

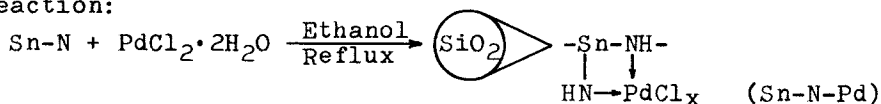
Reaction:



Petroleum ether (400ml), silica (5g, specific surface area: 370 m²/g) and stannic chloride (13g) were placed in a three-necked flask equipped with a gas inlet tube and a gas outlet tube. After stirring for 10 minutes, gaseous ammonia was introduced to the flask to react with stannic chloride. This is an exothermic reaction, so the flask must be cooled by a water bath during the reaction. After reacting for about 4 hours, the reaction mixture changed from acidic to basic. The product was filtered, and the by-product ammonium chloride was removed through washing with ethanol-water solution. Then the product was dried at 120°C.

Preparation of Silica-supported Polystannazane-Palladium Complexes (Sn-N-Pd)

Reaction:

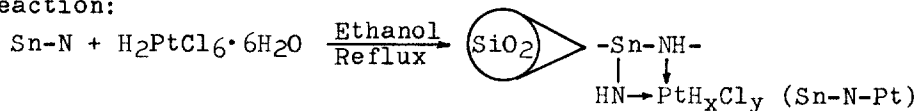


Several Sn-N-Pd complexes with different N/Pd molar ratios were prepared. For example, 1.00g (8.0 mmol of nitrogen contained) of silica-supported polystannazane (N wt%=11), 0.107g (0.5 mmol) of PdCl₂·2H₂O and 20ml of ethanol were placed in a three-necked flask (50-ml) equipped with a stirrer, a reflux condenser and a gas inlet tube. The mixture was stirred and refluxed under nitrogen for five hours. The white solid particles became grey and the dark brown solution turned into colorless and transparent. The product was filtered and dried

at 100°C, then kept in a dessicator. The N/Pd molar ratio of the product was 16 (calculated from the amounts of PdCl₂·2H₂O and Sn-N used). The ESCA datas show that the product was a palladium complex (see Table 1).

Preparation of Silica-supported Polystannazane-Platinum Complexes (Sn-N-Pt)

Reaction:



The preparation method of Sn-N-Pt was similar to that of Sn-N-Pd. The difference is that H₂PtCl₆·6H₂O was used instead of PdCl₂·2H₂O.

Hydrogenation

Sn-N-Pd (0.04 mmol of Pd) or Sn-N-Pt (0.04 mmol of Pt), solvent (20 ml) and substrate (10 mmol) were placed in a glass reactor equipped with a gas inlet tube and a magnetic stirring bar. The gas inlet tube was connected to a hydrogen storage bottle. The reactor was fixed on a magnetic stirrer and the reaction temperature was controlled in 30°C through a temperature controller. The reaction system was alternately evacuated and flushed with hydrogen for several times, and the hydrogen pressure was kept at near 1 atm (atmospheric pressure). The mixture was stirred and then the volume of hydrogen uptake was measured. Most of the reaction products were analyzed using gas chromatography. The remains, which have high boiling point, were separated, purified and analyzed by proton-NMR.

Results and Discussion

It was found that the hydrogenation reaction rate catalyzed by Sn-N-Pd or Sn-N-Pt was greatly affected by N/Pd or N/Pt molar ratio. As the examples shown in Fig.1 and Fig.2, the initial hydrogen uptake in the hydrogenation of p-nitroaniline changed with the N/Pd and N/Pt molar ratio respectively. An optimum hydrogenation rate appeared when the N/Pd molar ratio was about 32 for Sn-N-Pd, and when the N/Pt molar ratio was about 16 for Sn-N-Pt.

Table 1, ESCA Datas of Sn-N and Its Pd and Pt Complexes

Orbitals	Electron Binding Energy (ev)				
	PdCl ₂	H ₂ PtCl ₆	Sn-N	Sn-N-Pd	Sn-N-Pt
O _{1s}			532.4	532.4	532.2
Sn _{3d} 5/2			487.5	487.4	487.4
N _{1s}			400.0	401.0	401.9
Cl _{2p}	199.2	199.4		199.1	199.2
Pd _{3d} 5/2	338.4			335.5	
Pt _{4f} 7/2		75.5			71.5

The effect of solvents on the hydrogenation of nitrobenzene catalyzed by Sn-N-Pd is shown in Table 2. Generally speaking, alcohols are desirable solvents, but along with the alkyl group in the alcohol grows larger, the initial hydrogen uptake becomes slower. The polar solvents, diethylamine and tetrahydrofuran, are not suitable for the hydrogenation. Perhaps they have strong interaction with the active center in the Sn-N-Pd catalyst.

Hydrogenations of various kinds of unsaturated organic compounds were studied by using Sn-N-Pd and Sn-N-Pt respectively. As can be seen in Table 3, the catalytic activities of these two complexes for most of the hydrogenations are similar to each other. The difference is that the Sn-N-Pd has no catalytic activity for the hydrogenation of aliphatic carbonyl compounds. Different from Al-N-Pt (3), neither Sn-N-Pd nor Sn-N-Pt has catalytic activity for the benzene ring. All of the hydrogenation products of the carbonyl compounds listed in Table 3 are the corresponding alcohols. There was no further hydrogenation occurred. But in the hydrogenations of carbonyl compounds catalyzed by Al-N-Pd and Al-N-Pt, alcohol products were firstly formed, and then further hydrogenated to form corresponding hydrocarbons. Therefore, we can conclude from the above that the catalytic activity and selectivity of an in-

The legend for Table 2:
Sn-N-Pd: N/Pd=32, 0.04 mmol Pd, 10mmol of nitrobenzene. 30°C, 1 atm of hydrogen.

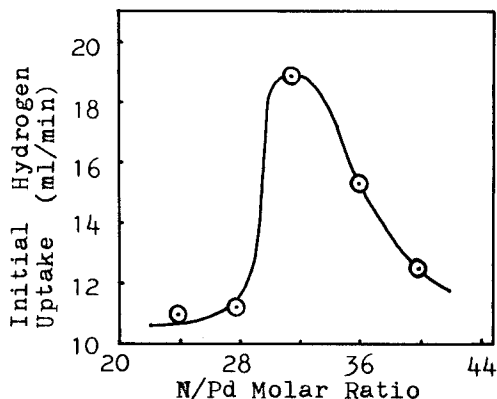


Fig.1, Relationship between the Initial hydrogen uptake and N/Pd molar ratio in Sn-N-Pd.

10 mmol of p-nitroaniline and 20 ml of methanol, 0.04 mmol Pd 30°C, 1 atm of hydrogen.

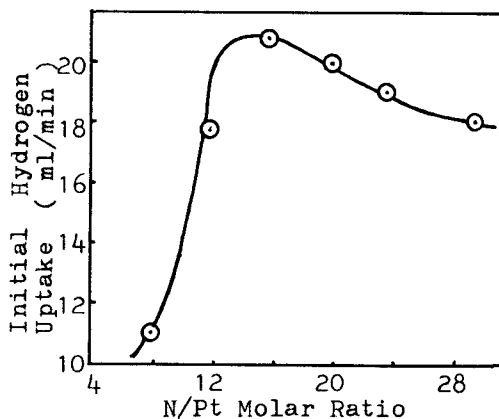


Fig.2, Relationship between the initial hydrogen uptake and N/Pt molar ratio in Sn-N-Pt.

10 mmol of p-nitroaniline and 20 ml of methanol, 0.04 mmol Pt, 30°C, 1 atm of hydrogen.

Table 2, Solvent Effect on the Initial Hydrogen Uptake

Solvent (20 ml)	Initial Hydrogen Uptake (ml/min)
methanol	20.0
ethanol	16.7
isopropanol	11.8
n-hexane	13.0
tetrahydrofuran	6.9
diethylamine	7.7

organic polymer catalyst varies with the composition of the inorganic polymer supports.

Table 3, Hydrogenations of Various Kinds of Unsaturated Organic Compounds Catalyzed by Sn-N-Pd and Sn-N-Pt

Substrates (10 mmol)	Initial Hydrogen Uptake (ml/min)		Products
	Sn-N-Pd	Sn-N-Pt	
p-nitroaniline	19.4	20.7	p-phenylenediamine
hexene-1	14.3	20.0	n-hexane
benzaldehyde	10.0	12.5	benzyl alcohol
acetophenone	4.4	4.2	@-phenyl ethanol
n-hexanal	0	4.6	n-hexanol
cyclohexanone	0	4.2	cyclohexanol
acetone	0	5.0	iso-propanol
benzene	0	0	—

Sn-N-Pd: 0.04 mmol Pd, N/Pd molar ratio=32;

Sn-N-Pt: 0.04 mmol Pt, N/Pt molar ratio=16;

20 ml of methanol as solvent; 30°C, 1 atm of hydrogen.

The hydrogenation results of various kinds of nitro-compounds are listed in Table 4. It can be seen that the Sn-N-Pd catalyst has high catalytic activity not only for aromatic but also for aliphatic nitro-compounds. The hydrogenation rate of the nitrobenzene derivatives was greatly affected by the nature of the substituent of the substrate. The rate increases in the following order: $-\text{NH}_2 < -\text{CHO} < -\text{CH}_3$. This phenomenon probably comes from the electronic effect on the nitro group through benzene ring.

Fig.3 and Fig.4 show the hydrogenation yield of benzaldehyde and p-nitroaniline as a function of reaction time with the catalyst of Sn-N-Pd and Sn-N-Pt respectively. It was found

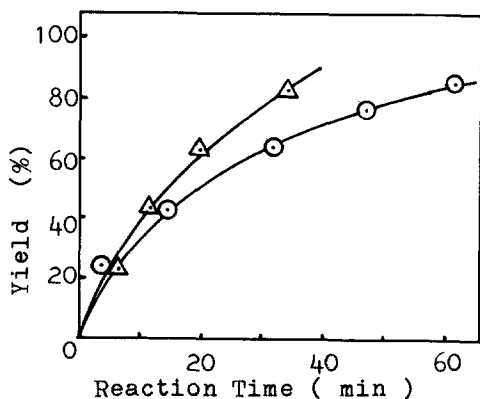


Fig.3, Hydrogenation yield of benzaldehyde catalyzed by Sn-N-Pd(Δ) and Sn-N-Pt(○) as a function of reaction time.

10 mmol of benzaldehyde.

0.04 mmol of Pd or Pt, N/Pd=32, N/Pt=16, 20 ml of methanol as solvent. 30°C, 1 atm of hydrogen.

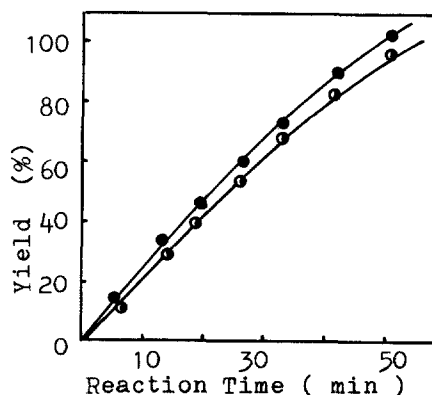


Fig.4, Hydrogenation yield of p-nitroaniline catalyzed by Sn-N-Pd(●) and Sn-N-Pt(•) as a function of reaction time.

10 mmol of p-nitroaniline.

that benzaldehyde can be converted more than 80% to benzyl alcohol within an hour using either Sn-N-Pd or Sn-N-Pt, while p-nitroaniline can be converted quantitatively to p-phenylenediamine within 50 minutes. The catalytic activity of Sn-N-Pd is higher than that of Sn-N-Pt for benzaldehyde, but the order is opposite for p-nitroaniline.

From the point of view of practical application, the stability of polymer catalyst is very important. Fig.5 shows the stability of Sn-N-Pd used in catalyzing the hydrogenation of p-nitroaniline. It can be seen that the turnover number of the catalyst has achieved more than 2500 without any noticeable loss in the reaction rate. The total turnover number can be reached to even 9000.

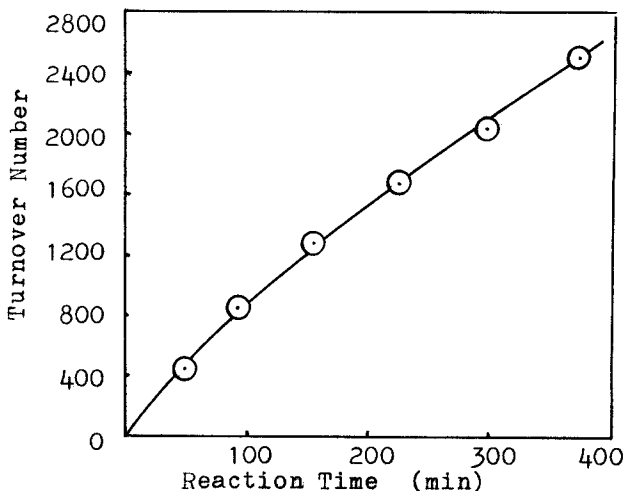


Fig.5, Relationship between turnover number and reaction time in the hydrogenation of p-nitroaniline catalyzed by Sn-N-Pd. 0.01 mmol Pd, N/Pd=32, 10 ml of methanol, 30 mmol of p-nitroaniline, 30°C, 1 atm H₂.

Table 4, Hydrogenations of Various Kinds of Nitro-compounds Catalyzed by Sn-N-Pd.

Substrates (10 mmol)	Initial Hydrogen Uptake (ml/min)	Products
nitrobenzene	20.0	aniline
p-nitroaniline	19.4	p-phenylenediamine
p-nitrobenzaldehyde ^a)	22.0	p-aminobenzylalcohol
p-nitrotoluene	28.6	p-methylaniline
nitromethane	10.0	methylamine

0.04 mmol Pd, N/Pd=32, 20 ml of methanol, 30°C, 1 atm of H₂.

a) The hydrogenation product of p-nitrobenzaldehyde is an insoluble solid in various organic solvents.

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