Shape Selective Hydrogenation of Alkynes by Palladium(II) Complexes Supported on Hectorite

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(Accepted March 18, 1993)

Summary

Clay-intercalated palladium(II) complexes were prepared and characterized by IR, XRD, and XPS measurements. Lithium hectorite (LHT) as a host compound and palladium(II) complexes, $[\text{Pd}(\text{NH}_3)_4]^{2+}$ and $[\text{Pd}(\text{PDT})_3]^{2+}$, as guest compounds were utilized. The basal spacings of $[\text{Pd}(\text{NH}_3)_4]^{2+}/\text{LHT}$ (PdAm/LHT) and $[\text{Pd}(\text{PDT})_3]^{2+}/\text{LHT}$ (PdPDT/LHT) were 1.30 nm and 2.21 nm, respectively. These intercalation complexes increased in basal spacing when swollen with solvents; i.e. 1.45 nm for PdAm/LHT and 2.94 nm for PdPDT/LHT in DMSO. These intercalation complexes were used as catalysts for the hydrogenation of different alkynes. The activities of the intercalation complexes remarkably depended on the basal spacing and the size of substrates. PdAm/LHT with smaller basal spacing did not hydrogenate phenyl and *t*-butylacetylene, while PdPDT/LHT bearing larger basal spacing hydrogenated phenylacetylene and aliphatic derivatives only except for *t*-butylacetylene. These intercalation complexes also exhibited high selectivity for the partial hydrogenation of alkynes.

1 Introduction

Clay compounds have become one of the important inorganic materials as a new type of host guest catalysts due to the layered structures¹¹⁻¹⁰. Hitherto, the surface modification for clays toward catalysis has been focused on the pillaring of clays by polynuclear hydroxy metal cations to form zeolite-like supports: several studies have been reported on the pillaring of clays with metal complexes^{11,12}. On the other hand, studies in the modification of clay by transition metal complexes which have been well characterized in their structures and used in heterogeneous catalytic systems have been reported in a

limited number. Choudary et al. have reported the studies of catalytic properties of palladium complexes anchored in montmorillonite¹³. Tsvetkov et al. have prepared pillared clays by organometallic complexes and estimated the interpillar distances¹⁴. Hikita et al. investigated the asymmetric catalysis with optically active tris (2,2'-bipyridyl)ruthenium(II)-montmorillonite¹⁵. Since the interlayer spacing of clay can be controlled by the intercalation of various molecular sizes of metal complexes¹⁶, the study for the size selectivity of these clay catalysts has great significance in the development of new clay catalysts.

In the present paper, preparations of clay-

intercalated palladium(II) complex catalysts, $[\text{Pd}(\text{NH}_3)_4]^{2+}/\text{LHT}$ (PdAm/LHT) and $[\text{Pd}(\text{PDT})_3]^{2+}/\text{LHT}$ (PdPDT/LHT), and their catalytic properties for alkyne hydrogenations are described.

2 Experimental

Materials

Solvents were purified by published methods before use¹⁷⁾. 3-(2-Pyridyl)-5, 6-diphenyl-1, 2, 4-triazine(PDT)¹⁸⁾ and $[\text{Pd}(\text{NH}_3)_4]\text{Cl}_2$ ¹⁹⁾ were prepared according to the published procedures. $[\text{Pd}(\text{PDT})_3](\text{OAc})_2$ was prepared by mixing $\text{Pd}(\text{OAc})_2$ (Kanto Chemical) and PDT in acetone for 4 h at room temperature. The addition of water gave rise to a brown precipitate in 71 % yield; mp 515 K (decomp.). UV (25 % EtOH): 452 nm $\epsilon = 4850$. IR (ν_{CN} , $\text{KBr}(\text{cm}^{-1})$): 1480(m), 1379(m), 1360(s), 1249(w), 790(vs), 764(s), 694(vs).

Preparation of PdAm/LHT and PdPDT/LHT

The intercalation of $[\text{Pd}(\text{PDT})_3]^{2+}$ into LHT (cation exchange capacity = $87.8 \text{ meq} \cdot (100\text{g-LHT})^{-1}$, Topy Kogyo) was carried out by the addition of 50 ml of a $[\text{Pd}(\text{PDT})_3]^{2+}$ (2.0 mmol) solution (33 % EtOH) to 50 ml of a dispersed solution (33 % EtOH) of LHT (3 g) and the mixture was stirred for 24 h at room temperature. IR (ν_{CN} , $\text{KBr}(\text{cm}^{-1})$): 1472(m), 1378(m), 1370(s), 1279(w), 799(s), 765(s), 700(vs). The loading amount of complexes into LHT was calculated from the estimation of the concentration differences between the initial complex solution and the final solution after the completion of intercalation by measuring UV-visible spectra. The amount of palladium complex in PdPDT/LHT was $54.8 \text{ meq} \cdot (100\text{-LHT})^{-1}$.

In the same manner, PdAm/LHT was prepared using H_2O as a solvent. The loading amount was $53.8 \text{ meq} \cdot (100\text{-LHT})^{-1}$.

Physical measurements

XRD lattice constants were obtained from measurements made on a Rigaku X-ray diffraction spectrometer RAD-B by means of a Cu target. XPS spectra were obtained with a Kratos 800 spec-

trometer. The binding energies (BE in eV) were corrected for by placing the Au $4f_{7/2}$ line of gold wire at 83.0 eV. In situ IR spectra were measured using a Pyrex glass cell equipped with KBr windows and a heater, in which a sample disk (20 mm diameter) containing KBr as a binder was placed and recorded by a JASCO A-202 spectrometer. Before the IR measurements, samples were treated at various temperatures from 300 K to 717 K in vacuo (1.33×10^{-2} Pa) for 1 h and then cooled down to room temperature. UV-visible spectra were measured by JASCO Ubest-30.

Hydrogenation reaction

A catalyst was placed in a reaction tube which was fitted with rubber spectra and connected with a closed circulation system and dried in vacuo at room temperature for 1 h. Solvent (5 ml) and hydrogen gas were introduced into the reaction system. Before the catalytic reactions, the mixture was stirred by a magnetic stirrer for 10 min and the reaction was initiated by the addition of reactants. Samples of the reaction mixtures in a liquid and a gas phase were collected and analyzed by GC using a Porapak Q column. The heterogeneous catalysts were dispersed in DMSO. The homogeneous counterparts, $\text{Pd}(\text{OAc})_2$ and $[\text{Pd}(\text{PDT})_3](\text{OAc})_2$, were completely dissolved in solvents.

3 Results and Discussion

Characterization

Results of XRD measurements are shown in Fig.1. The d_{001} spacings of PdAm/LHT and PdPDT/LHT were 1.30 nm and 2.21 nm, respectively, although the intercalation of Pd complexes caused the broadening of the d_{001} peak. Each clearance spacing is corresponding to the molecular size of each metal complex intercalated. These results indicate that monomolecular layer of metal complexes were formed between silicate sheets. When these intercalated hectorites were swollen with DMSO, values of d_{001} became 1.45 nm for PdAm/LHT and 2.94 nm for PdPDT/LHT . The above results indicate that these intercalated hectorites may retain their layer struc-

Fig.1 Basal spacings (d_{001}) of hectorites intercalated with various metal complexes under various conditions.

tures even in DMSO.

Figure 2 Shows the XPS spectra of PdAm/LHT and PdPDT/LHT compared with those of $[\text{Pd}(\text{NH}_3)_4]\text{Cl}_2$ and $[\text{Pd}(\text{PDT})_3](\text{OAc})_2$. PdAm/LHT and PdPDT/LHT had Pd $3d_{5/2}$ peaks at 338.4 and 338.3 eV, respectively. These Pd $3d_{5/2}$ peaks can be assigned to Pd[II] according to the published data^{20, 21}. Pd 3d peaks of both intercalation compounds were shifted to higher BE from each of the original Pd(II) complexes. These shifts were 0.5 eV for PdAm/LHT and 1.7 eV for PdPDT/LHT. This observation indicates that cationic palladium complexes were formed in the interlayer of LHT by cation exchange. As indicated by Choudary et al.²¹, the peak at 335.4 eV corresponds to Pd $3d_{5/2}$ for Pd(0) which was formed during the measurements²².

Hydrogenations of alkynes

These intercalated Pd(II) complexes were used for the catalytic reduction of various sizes of alkynes such as ethyne, propyne, butyne, phenyl and *t*-butyla-

cetylene in order to verify the effect of the clearance spacings on their catalytic activities and selectivities. Products were the corresponding alkenes and alkanes. **Fig.3 (a) and (b)** show the hydrogenation profiles of propyne by PdPDT/LHT and $[\text{Pd}(\text{OAc})_3]_3$, respectively²³. In the initial period, only propene was formed, while the formation of propane was observed until the consumption of propyne. This trend was observed for all the catalytic systems and substrates. We evaluate the formation rates of alkenes (r^-) and alkanes (r^+) from the hydrogenation profiles of alkynes. **Table 1** shows the formation rates of alkenes and alkanes²⁴. The hydrogenation rate (r^-) of PdAm/LHT dramatically decreased for phenyl and *t*-butylacetylene. On the other hand, PdPDT/LHT showed remarkably low activity only for *t*-butylacetylene. The above results suggest that phenylacetylene can intercalate into PdPDT/LHT but not into PdAm/LHT and *t*-butylacetylene can hardly intercalate into both intercalation complexes due to its bulkiness. The homogeneous catalysts did not

Fig. 2 XPS spectra (Pd 3d) of (a) $[\text{Pd}(\text{NH}_3)_4]\text{Cl}_2$, (b) PdAm/LHT, (c) $[\text{Pd}(\text{PDT})_3](\text{OAc})_2$, and (d) PdPDT/LHT.

show any of such trends.

Another important observation is the high selectivity for the partial reduction of alkynes (Table 2). PdAm/LHT formed only alkenes for propyne, phenyl, and *t*-butylacetylene and also show very high selectivity for butyne even after the complete consumption of alkynes. PdPDT/LHT also showed remarkably high selectivity compared to the homogeneous system except for phenylacetylene. This low selectivity for phenylacetylene can be explained by the relative strong coordination of styrene to the palladium atom due to its π -conjugated system. Terasawa et al. reported that the selectivity in alkyne semihydrogenation was much higher for isolated triple bonds than for those in a conjugated system²⁰. These results indicate that the heterogeneous catalysts have an advantage for partial hydrogenation compared to the corresponding homogeneous catalysts. This advantage of the heterogenized palladium complexes may be attributable to the formation of cationic palladium complexes which are more positively charged than the corresponding palladium complexes in the homogeneous systems. The increase of positive charge on the palladium complexes in the interlayer was observed by the XPS measurements as discussed in

Fig. 3 Hydrogenation of propyne by (a) PdPDT/LHT and (b) $[\text{Pd}(\text{OAc})_2]_3$ under 1.01×10^5 Pa of hydrogen at 323 K. $\square$ =propyne; $\bullet$ =propene; $\blacksquare$ =propane.

Table 1 Formation rates for alkyne hydrogenations by PdAm/LHT and PdPDT/LHT compared with homogeneous palladium(II) complexes^a

Substrate	Rate (mol · (mol-Pd · h) ⁻¹)							
	PdAm/LHT		PdPDT/LHT		[Pd(OAc) ₂] ₃		[Pd(PDT) ₃](OAc) ₂	
	r ⁺	r ⁻	r ⁺	r ⁻	r ⁺	r ⁻	r ⁺	r ⁻
HC≡CH	11.2	3.6	11.8	0.47	57.1	14.5	8.0	1.3
CH ₃ C≡CH	17.7	0	45.7	0.49	92.5	21.9	17.4	2.2
C ₂ H ₅ C≡CH	11.4	0.04	19.8	0.71	364.6	40.7	23.6	1.7
Ph C≡CH	0.41	0	29.4	8.7	8.2	6.1	29.6	8.2
+C≡CH	0.13	0	5.6	0.06	13.5	2.6	32.1	0.9

^aReaction conditions: substrate, 2mmol (P_{HCCH} = 2.0x10⁴ Pa); P_{H₂} = 1.01x10⁵ Pa (6.0x10⁴ Pa in the case of HCCH as a substrate); solvent, DMSO 5 ml; temp., 323 K.

Table 2 Selectivity for partial alkyne hydrogenation by PdAm/LHT and PdPDT/LHT compared with homogeneous palladium(II) complexes^a

Substrate	Selectivity ^b			
	PdAm/LHT	PdPDT/LHT	[Pd(OAc) ₂] ₃	[Pd(PDT) ₃](OAc) ₂
HC≡CH	3.1	25.1	3.9	6.1
CH ₃ C≡CH	. ^c	93.0	4.2	7.9
C ₂ H ₅ C≡CH	127	22.2	12.2	7.4
Ph C≡CH	. ^c	3.4	1.3	3.4
+C≡CH	. ^c	93.3	5.2	34.9

^aReaction conditions: substrate, 2 mmol (P_{HCCH} = 2.0x10⁴ Pa); P_{H₂} = 1.01x10⁵ Pa (6.0x10⁴ Pa in the case of HCCH as a substrate); solvent, DMSO 5 ml; temp., 323 K.

^bSelectivity = r⁺/r⁻. ^cAlkane was not observed.

an early section. The bonding in alkene-transition metal complexes can be described by the Dewar-Chatt-Duncanson model, that is, there are two components to the total bonding: (a) a weak π -donor bond from the C=C double bond to the metal and a

strong back-bond from filled metal orbitals to the π^* orbitals of the alkene²⁹. Therefore, the more positive charge on the metal complexes increases, the more weakly the alkene coordinates to the metal. It is possible that alkene coordination to palladium com-

plexes in the interlayer is weakened according to the above reason. This weak coordination of alkene to the metal may contribute the deactivation of alkene hydrogenation. The similar selectivity in the hydrogenation of alkynes has been reported for cationic complexes, $[ML_2]^+$ ($M = Rh(I), Ir(I), Pd(II), Pt(II); L = \text{ligand}$)²⁶⁾.

This work was supported by the National Research Institute for Metals of the Science and Technology Agency.

References

- 1) T. J. Pinnavaia and P. K. Welty, *J. Am. Chem. Soc.*, **97**, 3819 (1975).
- 2) T. J. Pinnavaia, R. Raythatha, J. G-S. Lee, L. J. Halloran and J. F. Hoffman, *J. Am. Chem. Soc.*, **101**, 6891 (1979).
- 3) Y. Morikawa, T. Goto, Y. Moro-oka and T. Ikawa, *Chem. Letters*, 1667 (1982).
- 4) T. Enomoto, M. Iemoto, T. Okuhara and M. Misono, *Nippon Kagaku Kaishi*, 1097 (1985).
- 5) A. Yamagishi and M. Soma, *J. Am. Chem. Soc.*, **103**, 4640 (1981).
- 6) A. Yamagishi, *J. Phys. Chem.*, **86**, 2472 (1982).
- 7) S. Shimazu, T. Hirano and T. Uematsu, *Appl. Catal.*, **34**, 255 (1987).
- 8) B. M. Choudary, K. R. Kumar, Z. Jarmil and G. Thyagarajan, *J. Chem. Soc., Chem. Commun.*, 931 (1985).
- 9) K. R. Kunmar, B. M. Choudary, Z. Jamil and G. Thyagarajan, *ibid.*, 130 (1986).
- 10) B. M. Choudary and P. Bharathi, *ibid.*, 1505 (1987).
- 11) T. J. Pinnavaia, *Science*, **220**, 365 (1983).
- 12) E. P. Giannelis, E. G. Rightor and T. J. Pinnavaia, *J. Am. Chem. Soc.*, **110**, 3880 (1988).
- 13) B. M. Choudary, K. Ravi Kumar and M. Lakshmi Kantam, *J. Catal.*, **130**, 41 (1991).
- 14) F. Tsvetkov and J. White, *J. Am. Chem. Soc.*, **110**, 3183 (1988).
- 15) T. Hikita, K. Tamaru, A. Yamagishi and T. Iwamoto, *Inorg. Chem.*, **28**, 2221 (1989).
- 16) S. Shimazu, W. Teramoto and T. Uematsu, *3rd Symposium for Jpn. Ass. of Ion Exchange*, Kyoto, Japan, Oct. 1-2, 1987, p.32.
- 17) D. D. Perrin and W. L. F. Armarego, "Purification of Laboratory Chemicals", 3rd ed., Pergamon Press, Oxford (1988).
- 18) F. J. Case, *J. Org. Chem.*, **30**, 931 (1965).
- 19) F. G. Mann, D. Crawfoot, D. C. Gattiker and H. Wooster, *J. Chem. Soc.*, 1642 (1935).
- 20) M. Terasawa, K. Kaneda, T. Imanaka, and S. Teranishi, *J. Catal.*, **51**, 406 (1978).
- 21) B. M. Choudary, K. R. Kumar, and M. L. Kantam, *J. Catal.*, **130**, 41 (1991).
- 22) The peak at 335.4 eV which did not appear in the initial period of the measurements increased in its intensity during the measurement.
- 23) Although $[Pd(NH_3)_4]X_2$ ($X = OAc, Cl$) should be used as a homogeneous catalyst for the comparison to PdAm/LHT, it was readily reduced to palladium metal in the hydrogenation and showed extremely low activity. $[Pd(OAc)_2]_3$ was utilized for the reference since it was not reduced to metal during the reaction.
- 24) The reaction rates of acetylene were relatively low compared to the other alkynes since its reaction condition was different from those of other alkynes due to its low solubility in DMSO.
- 25) E. P. Pruchnik, "Organometallic Chemistry of the Transition Elements", Plenum, New York (1990) p.327.
- 26) R. R. Schrock, J. A. Osborn, *J. Am. Chem. Soc.*, **93**, 3089 (1971).

リチウムヘクトライトに担持したパラジウム(II)錯体による アルキンの形状選択水素化

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(1993年3月18日受理)

要 旨

粘土層間担持パラジウム(II)錯体を合成し, IR, XRD, XPSにより構造分析を行った。ホスト化合物としてリチウムヘクトライト(LHT), ゲスト化合物として $[\text{Pd}(\text{NH}_3)_4]^{2+}$ と $[\text{Pd}(\text{PDT})_3]^{2+}$ を用いた。 $[\text{Pd}(\text{NH}_3)_4]^{2+}/\text{LHT}(\text{PdAm}/\text{LHT})$ と $[\text{Pd}(\text{PDT})_3]^{2+}/\text{LHT}(\text{PdPDT}/\text{LHT})$ の底面間隔(d_{001})はそれぞれ1.30nmと2.21nmに変化した。これらの錯体担持ヘクトライトをDMSO溶媒に膨潤させると底面間隔はさらに拡大し, PdAm/LHTとPdPDT/LHTはそれぞれ, 1.45と2.94nmに拡大したが層構造を保持していた。これらの層間担持錯体を用いて種々の形状を持つアルキンの水素化反応を行った。層間担持触媒の活性は, その層間隔と基質の分子サイズに大きく依存した。小さい層間隔を持つPdAm/LHTでは, 分子サイズの大きいフェニル, *t*-ブチルアセチレンの水素化にほとんど活性を示さなかった。しかし, 大きい層間隔を持つPdPDT/LHTではフェニルアセチレンを容易に水素化したが, *t*-ブチルアセチレンに対しては低活性であった。さらに, これら層間担持触媒は, アルキンからアルケンへの高い部分水素化選択性を示した。