[Regular Paper]

Preparation of Pd/MOF and Ru/MOF Catalysts and Catalytic Performance for Hydrogenation and Cross-coupling Reactions

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(Received July 22, 2013)

Metal-organic framework compound consisting of terephthalic acid and chromium cation (TPA-Cr) was prepared by the hydrothermal method and characterized by XRD, N2 adsorption-desorption isotherm, TGA-DTA and TEM. The prepared TPA-Cr was crystalline and phase-pure. Noble metal was supported on TPA-Cr by the conventional impregnation method. The specific Pd salt and solvent for impregnation significantly influenced the location of Pd. With [Pd(NH3)4][NO3]2 dissolved in water, Pd was located in the micropores of TPA-Cr, whereas with PdCl2 dissolved in water or methanol, Pd was located on the external surface of TPA-Cr. Hydrogenation of cinnamaldehyde and crotonaldehyde, and cross-coupling between aryl bromides and phenylboronic acid were studied using Pd/TPA-Cr and Ru/TPA-Cr prepared as above. Hydrogenation of the two model aldehydes occurred in the micro- and meso-pores of TPA-Cr whereas cross-coupling reaction of bulkier compounds occurred mostly on the external surface of TPA-Cr.

Keywords
Metal-organic framework, Hydrogenation, \(\alpha,\beta\)-Unsaturated aldehyde, Palladium catalyst, Ruthenium catalyst, Cross-coupling

1. Introduction

Inorganic porous materials such as SiO2, Al2O3, active carbon and zeolites have been widely used as adsorbents, supports or catalysts for many years.\(^1\) Active carbon is a typical inorganic porous material, but the pore structure is not uniform because the active carbon is not crystalline. Zeolite is a typical crystalline inorganic material consisting of AlO4 and SiO4 tetrahedrons as the building units.\(^9\) Zeolites have unique properties such as high surface area, thermal stability, and ion-exchange properties, and their micropores have similar size to many low molecular weight molecules.\(^10\)–\(^13\) However, the inorganic structure is rigid, so the pore size is difficult to modify to specific requirements.

Porous materials made of organic compounds have not been widely investigated until recently, probably because of the low thermal stability. Crystalline organic-inorganic materials called metal-organic frameworks (MOFs), or porous coordination polymer (PCP) were synthesized in the 1990s. The thermal stability of MOFs depends on their components, but MOFs are generally stable up to 350 °C or in some cases 500 °C, which stimulated studies on MOFs in the 2000s.

The pore size of MOFs can be tuned by changing agents used as so-called linkers such as dicarboxylic acids or diamines. The molecular weight of the constituent elements is light, so the specific surface area becomes as high as or even higher than 3000 m² g⁻¹. Furthermore, the molecules that can be used as linkers are unlimited, so linkers with other functional groups can also be used. For example, using bipyridyl dicarboxylic acid as the linker incorporates the bipyridyl site which can ligate metals, and the resultant MOF-ligated metals can function as organometallic catalysts. Based on these unique properties, MOFs have been studied intensively as adsorbents for gases like hydrogen.\(^19\)–\(^23\) Many interesting features have been reported for the gases trapped in the micropores,\(^22\)–\(^27\). Therefore, MOFs are considered as promising materials for separation,\(^28\) storage,\(^29,30\) and catalysts\(^31\)–\(^35\) based on these favorable physical and chemical properties.

In this study, we prepared a MOF compound consisting of terephthalic acid and chromium cation (TPA-Cr) and evaluated the MOF compound as a catalyst support. Noble metals supported on the MOF were examined as catalysts for chemoselective hydrogenation of \(\alpha,\beta\)-unsaturated aldehydes and for cross-coupling reactions.
2. Experimental

2.1. Preparation of TPA–Cr

Typically, 8.0 mmol of Cr(NO_3)_3 \cdot 9H_2O, 24 mmol of terephthalic acid (TPA) and 120 mL of distilled water were placed in an autoclave of 200 mL. After stirring at 150 rpm for 30 min, the temperature was increased to 180 °C at 2.5 °C min⁻¹ and held at this temperature for 12 h. After cooling to room temperature, the product was filtered, washed with distilled water and dried at 70 °C. To remove un-reacted TPA, the product was washed with N,N-dimethyl formamide (DMF) followed by distilled water. Then, the product was heat-treated at 250 °C for 1 h under N₂ flow. Finally, 1.91 g of deep green solid, TPA_Cr, was obtained.

2.2. Preparation of Pd/TPA–Cr and Ru/TPA–Cr Catalysts

As will be discussed later, the location of the noble metals on the exterior surface or in the micropores of the MOF is crucial. To control the location of noble metals, various noble metal precursors and solvents for impregnation were examined.

Typically, a 0.50 g portion of TPA–Cr was impregnated with an aqueous solution containing PdCl₂ or [Pd(NH₃)₄]([NO₃]₂) to give 3.0 wt% Pd/TPA–Cr. After impregnation, the catalyst precursor was dried at 80 °C at 350 hPa and then reduced at 70 °C for 2 h under H₂ flow of 150 mL min⁻¹. In addition, Pd/TPA–Cr was prepared from PdCl₂ using methanol as the solvent for impregnation. For Ru/TPA–Cr catalysts, RuCl₃·xH₂O and water were used as the Ru source and solvent for impregnation, respectively.

For comparison, α-Al₂O₃ (Wako Pure Chemical Ind., Ltd., Japan; <1 m² g⁻¹) and γ-Al₂O₃ (Sumitomo Chemical Co., Ltd., Japan; 167 m² g⁻¹) were also used as catalyst supports.

2.3. Characterization

Crystal structure was analyzed by X-ray diffraction (Rigaku Corp., RINT 2000) using Cu Kα radiation at 40 kV and 20 mA. The surface area and pore-size distribution were measured by the conventional N₂ adsorption-desorption method (Bel Japan Inc., BELSORP BEL-mini II). The surface area was calculated by the BET method. The pore-size distributions were calculated by the BJH method and MP method for the mesopore and micropore regions, respectively. Before measurement, the materials were dried at 250 °C for 1 h under N₂ flow. Infrared absorption spectra were obtained with FTIR-8300 (Shimadzu Corp.). Fifty interferograms were collected by the KBr method. Thermogravimetric and differential thermal analyses (TGA-DTA) were carried out with a DTG-60H (Shimadzu Corp.) under air flow of 100 mL min⁻¹ and ramp rate of 10 °C min⁻¹ from room temperature up to 800 °C. Morphology of the TPA–Cr particles was observed with a field-emission scanning electron microscope (FE-SEM; JEOL JSM-6700) at 10 kV and 10 μA. Metal particle size was studied with a transmission electron microscope (TEM; JEOL JSM-2010K) at 200 kV and 100 μA.

2.4. Hydrogenation, Cross-coupling Reaction and Product Analysis

For the hydrogenation reaction, 31.7 mg of catalyst, 3.00 mmol (0.390 g) of cinnamaldehyde and 5.0 g of toluene (solvent) were introduced into a 50 mL autoclave. Pd/TPA–Cr catalysts used for the reactions were all prepared with [Pd(NH₃)₄]([NO₃]₂) using water as the impregnation solvent except for a Pd/TPA–Cr catalyst prepared with PdCl₂ and water, indicated in Table 1 as Pd⁺. After flushing with N₂, the autoclave was pressurized with H₂ to 5.0 MPa (gauge pressure). The hydrogenation reaction was performed at 65 °C for 3 h. To study the hydrogenation at Pd on the exterior of TPA–Cr or at Pd inside the micropores of TPA–Cr, the catalyst was poisoned with 1,10-phenanthroline or 4,7-diphenyl-1,10-phenanthroline.

For the cross-coupling reaction, 35.5 mg of catalyst, 0.75 mmol of dihydroxyphenylborane and 0.50 mmol of bromobenzene, 1-bromonaphthalene or 9-bromanthracene, 1.5 mmol (0.21 g) of K₂CO₃ and 10.6 g of α-xylene (solvent) were introduced into the 50 mL autoclave. After flushing with N₂, the autoclave was pressurized with N₂ to 0.4 MPa. The reaction was performed at 150 °C for 5 h.

For the analysis of liquid products, the catalyst was removed by centrifugation. A 2.0 g portion of the solution was mixed with 0.10 g of benzyl alcohol as an internal standard, and the products were analyzed with a gas chromatograph (Shimadzu Corp., GC-18A) equipped with a flame ionization detector. A capillary column (BP21 (polar), SGE Corp., length 25 m, I.D. 0.22 mm and film thickness 0.25 μm) was used. The material balance was 100 ± 7 %. Products were identified by comparing retention times with those of authentic reagents. To analyze the products of cross-coupling reaction, another capillary column, Inert Cap 1 (GL Sciences Inc.), was used instead of BP21.

3. Results and Discussion

3.1. Characterization of TPA–Cr, Pd/TPA–Cr and Ru/TPA–Cr

The X-ray diffraction (XRD) pattern, N₂ adsorption-desorption isotherm, and thermogravimetric profile of TPA–Cr are shown in Figs. 1, 2 and 3, respectively. The XRD pattern (Fig. 1 a) coincided with that of reported TPA–Cr⁶⁰. Figure 2 clearly shows the presence of both micro- and meso-pores. Analyses of the isotherm revealed that the pore sizes of the micropores and mesopores were ca. 0.9 nm and 20 nm, respectively and the BET surface area was 1500 m² g⁻¹. Figure 3 indicates that TPA–Cr was stable up to 300 °C in air and...
the decomposition curve was very sharp. If TPA-Cr decomposes to Cr2O3, the theoretical weight decrease is ca. 67%. As the observed weight decrease was 66%, the purity of TPA-Cr was high. The Fourier transform infrared spectroscopy (FT-IR) spectra (data not shown) detected no substantial peaks characteristic of free carboxylic acid group, but the observed peaks were ascribed to carboxylate for TPA-Cr.

Figure 4 shows TEM images of TPA-Cr and 3 wt% Pd/TPA-Cr catalysts prepared with different impregnation methods. Figure 4a) of TPA-Cr indicates high homogeneity throughout the particles. Figures 4b) and 4c) show Pd/TPA-Cr prepared by impregnation with PdCl2 in methanol solvent and PdCl2 in H2O solvent, respectively. Pd particles of a few to ca. 100 nm size could be seen, suggesting that Pd was present not only in the micro- and meso-pores but also on the exterior of MOF particles. Figures 4d) and 4e) show Pd/TPA-Cr prepared with [Pd(NH3)4](NO3)2 in H2O solvent. These images are similar to that in Figure 4a), indicating that Pd is present inside the micro- and meso-pores as very fine particles. Figure 4b) and c) show the XRD patterns of Pd/TPA-Cr ([Pd(NH3)4](NO3)2 in H2O solvent) before and after H2 reduction, respectively. These patterns are similar to the original TPA-Cr, suggesting that the MOF structure was mostly retained during impregnation and H2 reduction. The XRD pattern of reduced Pd/TPA-Cr catalyst prepared using PdCl2 and H2O solvent showed no distinct peaks for metallic Pd (figure not shown). The TEM image in Figure 4c) confirmed the presence of large Pd particles in this catalyst, suggesting detection by XRD. This discrepancy may be because the relative amount of Pd with large particle sizes was small.

Large Pd particles in the catalysts prepared with PdCl2 may have been formed because PdCl2 can form clusters in the impregnation solution through the action of Cl as a bridging ligand, and the clusters were too large to penetrate into the micro- and meso-pores of TPA-Cr. In contrast, such a cluster formation was less likely using [Pd(NH3)4](NO3)2, so the Pd species could enter the pores to form fine Pd particles difficult to observe by TEM.

3.2. Hydrogenation of α,β-Unsaturated Aldehydes; Cinnamaldehyde and Crotonaldehyde

Hydrogenation of cinnamaldehyde (CMA) was studied to assess the effect of micropores on the selectivity for C·C and C·O hydrogenation. Hydrogenation at C·O gives cinnamyl alcohol (CMO) and hydrogenation at C·C gives dihydrocinnamaldehyde (HCMA). Table 1 compares the effect of the supports, TPA-Cr, α-Al2O3 and γ-Al2O3. Firstly, using TPA-Cr as the support, very high activities were obtained irrespective of the Pd source. Pd/α-Al2O3 showed the lowest activity. The selectivities for HCMA and dihydrocinnamaldehyde (HCMA) are similar for all catalysts. These results suggest that CMA could diffuse rapidly in the micro- and meso-pores of TPA-Cr and the first hydrogenation occurred at the C·C double bond and not at the C·O double bond even at the early stage of the reaction. Comparison of selectivities on supported
Pd and Ru catalysts showed that the specific noble metal governed the selectivity, as Pd preferentially hydrogenated the C=C double bond and Ru preferentially hydrogenated the C=O double bond. Tables 2 and 3 indicated the effects of additives on the catalytic activity and selectivity. Addition of less bulky 1,10-phenanthroline to 3 wt% Pd/TPA-Cr drastically decreased the conversion (Table 2). On the other hand, addition of bulkier 4,7-diphenyl-1,10-phenanthroline caused a relatively small activity loss (Table 3). These diamine compounds are strongly adsorbed on Pd and retard the activity, so that bulky 4,7-diphenyl-1,10-phenanthroline was adsorbed mostly on Pd on the exterior of TPA-Cr because of its limited rate of diffusion into the micro- and meso-pores. This also suggests that hydrogenation mainly occurred in the micro- and meso-pores of TPA-Cr. On the other hand, 1,10-phenanthroline is smaller than 4,7-diphenyl-1,10-phenanthroline, so that 1,10-phenanthroline affected the activities of Pd located both in the micro- and meso-pores and on the external surface. To discuss this point further, the molecular sizes of 1,10-phenanthroline and 4,7-diphenyl-1,10-phenanthroline were estimated by MOPAC 6.0[58].

**Table 1. Effects of Supports and Noble Metals on Hydrogenation of Cinnamaldehyde**

| Support | Loaded metal | Conv. [%] | Selectivity [%] |
|---------|--------------|-----------|-----------------|
|         | Pd*          | 22.2      | 0.0             |
|         |               | 100.0     | 0.0             |
|         | Pd            | 26.9      | 0.0             | 100.0           |
|         |               | 75.9      | 0.0             | 100.0           |
|         | Ru            | 57.3      | 70.7             |
|         |               |           | 16.1             |
|         |               |           | 13.2             |
| γ-Al2O3 | Pd            | 89.9      | 0.0             | 90.5             |
|         | Ru            | 25.2      | 45.2             |
|         |               |           | 40.9             |
|         |               |           | 13.9             |
| α-Al2O3 | Pd            | 64.0      | 0.0             | 83.9             |
|         |               |           | 16.1             |

a) Metal loading: 3.0 wt%, Catalyst: 62.5 mg, Cinnamaldehyde: 0.790 g (5.98 mmol), Solvent: triglyme 11.6 g, 65 °C, 6 h, P_{H2}: 5.0 MPa.
b) [Pd(NH3)4](NO3)2, PdCl2 and RuCl3·nH2O were used as noble metal sources.
c) CMO: cinnamyl alcohol, HCMA: dihydrocinnamaldehyde, HCMO: dihydrocinnamyl alcohol.
d) P_{H2}: 1.0 MPa.
e) Metal loading: 0.50 wt%, Catalyst: 125 mg, Cinnamaldehyde: 1.58 g (12.0 mmol), Solvent: triglyme 22.5 g, 100 °C, 6 h, P_{H2}: 1.0 MPa.
4,7-diphenyl-1,10-phenanthroline were calculated to be 11.6 and 14.9, respectively. These values suggest that 1,10-phenanthroline may diffuse into the micropores of TPA-Cr and retard the reaction whereas 4,7-diphenyl-1,10-phenanthroline cannot easily diffuse into the micropores resulting in less effect on the activity, which agreed well with the results in Tables 2 and 3.

Hydrogenation of crotonaldehyde was also studied, as shown in Table 4. Pd/TPA-Cr and Ru/TPA-Cr had superior activity compared to Pd and Ru on α-Al₂O₃ because the molecular size of crotonaldehyde is small enough to diffuse through the micro- and meso-pores of TPA-Cr. The C=CH₂ double bond was preferentially hydrogenated on Ru/TPA-Cr catalyst whereas C=C and C=O hydrogenation occurred at a similar reaction rates on Pd/TPA-Cr catalyst. We have no rationale to explain this phenomenon at present.

### Table 2  Effect of 1,10-Phenanthroline (P) on Hydrogenation of Cinnamaldehyde with 3 wt% Pd/TPA-Cr

| Pd : P [mol : mol] | Conv. [%] | Selectivity [%] |
|-------------------|-----------|-----------------|
|                   |           | CMO | HCMA | HCMO |
| 100.0             | 3.4       | 81.0 | 15.6 |
| 1 : 3             | 21.5      | 0.0  | 100.0 | 0.0 |
| 1 : 10            | 23.3      | 0.0  | 100.0 | 0.0 |
| 1 : 15            | 25.0      | 0.0  | 100.0 | 0.0 |

a) Catalyst: 31.7 mg, Cinnamaldehyde: 0.39 g (3.0 mmol), Solvent: toluene 5.0 g, 65 °C, 3 h, P H₂: 5.0 MPa.

**Table 3** Effect of 4,7-Diphenyl-1,10-phenanthroline (DP) on Hydrogenation of Cinnamaldehyde with 3 wt% Pd/TPA-Cr

| Pd : DP [mol : mol] | Conv. [%] | Selectivity [%] |
|---------------------|-----------|-----------------|
|                     |           | CMO | HCMA | HCMO |
| 100.0               | 3.4       | 81.0 | 15.6 |
| 1 : 3               | 73.1      | 0.0  | 76.7 | 22.3 |
| 1 : 10              | 71.4      | 0.0  | 89.3 | 10.7 |
| 1 : 15              | 65.0      | 0.0  | 91.5 | 8.5 |

Conditions: see Table 2.

### Table 4  Hydrogenation of Crotonaldehyde on Various Catalysts

| Support | Loaded metal | Conv. [%] | Selectivity [%] |
|---------|--------------|-----------|-----------------|
|         |              | Crotyl alcohol | Butylaldehyde | Butyl alcohol |
| TPA-Cr  | Pd           | 26.6       | 37.7           | 48.3      | 13.9 |
|         | Ru           | 100.0      | 0.0            | 98.1      | 1.9  |
| α-Al₂O₃ | Pd           | 5.3        | 0.0            | 100.0     | 0.0  |
|         | Ru           | 20.4       | 0.0            | 83.5      | 16.5 |

a) Metal loading: 3 wt%, Catalyst: 125 mg, Crotonaldehyde: 0.841 g (12.0 mmol), Solvent: triglyme 22.75 g, 65 °C, 6 h, P H₂: 5.0 MPa.

3.3. Cross-coupling of Aryl Bromides and Phenylboronic Acid

To generalize the effect of the location of Pd on Pd/TPA-Cr on selectivity, the cross-coupling reaction between bromine compounds and phenylboronic acid was studied on 3 wt% Pd/TPA-Cr and 3 wt% Pd/α-Al₂O₃ (Table 5). Dissolution of Pd was not observed at least at the ppm level, possibly because we adopted less-polar ortho-xylene as the solvent.

The yields on Pd/TPA-Cr were always higher than those on Pd/α-Al₂O₃. Addition of 4,7-diphenyl-1,10-phenanthroline significantly decreased the yield of the target compound, especially 9-phenylanthracene, which suggests that for bulkier compounds like 9-phenylanthracene the coupling reaction mainly occurred on Pd on the external surface of TPA-Cr.
4. Conclusions

Metal-organic framework compound consisting of terephthalic acid and chromium cation (TPA-Cr) was prepared by the hydrothermal method. Various characterizations showed that the prepared TPA-Cr was crystalline and phase-pure.

For preparation of Pd/TPA-Cr by the impregnation method, the specific Pd salt and solvent significantly influenced the position of Pd. Using [Pd(NH₃)₄][NO₃]₂ dissolved in water, fine Pd particles were formed in the micro- and meso-pores of TPA-Cr. In contrast, using PdCl₂ dissolved in water or methanol, Pd particles of a few to ca. 100 nm size were mainly located on the external surface of TPA-Cr.

Hydrogenation of cinnamaldehyde and crotonaldehyde occurred in the micro- and meso-pores of TPA-Cr. The cross-coupling reaction between 9-bromoanthracene and phenylboronic acid on Pd/TPA-Cr formed bulky 9-phenylanthracene. Poisoning with 4,7-diphenyl-1,10-phenanthroline drastically retarded the cross-coupling reaction, indicating that the cross-coupling reaction proceeded mainly on Pd on the external surface of TPA-Cr.

The effect of micro-pores of MOF compounds requires the use of MOF compounds with sufficiently smaller pore size or much bulkier substances.

References
1) Batista, M. S., Santos, R. K. S., Assaf, E. M., Assaf, J. M., Ticianelli, E. A., *J. Power Sources*, 134, 27 (2004).
2) Karimi, A., Pour, A. N., Torabi, F., Hatami, B., Tavasoli, A., Alaei, M. R., Irani, M., *J. Natural Gas Chem.*, 19, 503 (2010).
3) Kulkarni, S. J., Rohitha, C. N., Narender, N., Koeckritz, A., *J. Porous Mater.*, 17, 321 (2010).
4) Samoila, P., Boutzeloit, M., Especel, C., Epron, F., Marecot, P., *Appl. Catal. A: General*, 369, 104 (2009).
5) Lambert, S. D., Graham, N. J. D., *Water Res.*, 29, 2421 (1995).
6) Olson, E. S., Miller, S. J., Sharma, R. K., Dunham, G. E., Benson, S. A., *J. Hazard. Mater.*, 74, 61 (2000).
7) Kheirkar, M. V., Tamhade, P. J., Qureshi, Z. S., Bhanage, B. M., *Eur. J. Org. Chem.*, 2010, 6981 (2010).
8) Álvarez-Montero, M. A., Gómez-Sainero, L. M., Juan-Juan, J., Linares-Solano, A., Rodriguez, J. J., *Chem. Eng. J.*, 162, 599 (2010).
9) Olson, D., Baerlocher, C., Meier, W. M., Olson, D. H., "Atlas of Zeolite Framework Types," 5th Edition, Butterworth-Heinemann, (2001).
10) Imi, T., *Stud. Surf. Sci. Catal.*, 105B, 1441 (1997).
11) Barrer, R. M., *Stud. Surf. Sci. Catal.*, 36, 537 (1988).
12) Barrer, R. M., *Stud. Surf. Sci. Catal.*, 24, 1 (1985).
13) Meyer, U., Hoelderich, W. F., *J. Mol. Catal. A: Chemical*, 142, 213 (1999).
14) Eddaoudi, M., Moler, D. B., Li, H., Chen, B., Reineke, T. M., O’Keefe, M., Yaghi, O. M., *Acc. Chem. Res.*, 34, 319 (2001).
15) Kitagawa, S., Kitaura, R., Noro, S., *Angew. Chem., Int. Ed.*, 43, 2334 (2004).
16) Chae, H. K., Silberio-Perez, D. Y., Kim, J., Go, Y., Eddaoudi, M., Matzger, A. J., O’Keefe, M., Yaghi, O. M., *Nature*, 427, 523 (2004).
17) Férey, G., Mellot-Draznieks, C., Serre, C., Millange, F., Dutour, J., Surble, S., Margiokaki, I., *Science*, 309, 2040 (2005).
18) Kyougoku, K., Yamada, C., Suzuki, Y., Nishiyama, S., Fukumoto, K., Yamamoto, H., Indo, S., Sano, M., Miyake, T., *J. Jpn. Petrol. Inst.*, 53 (5), 308 (2010).
19) Leslie, J. M., Mircea, D., Jeffrey, R. L., *Chem. Soc. Rev.*, 38, 1294 (2009).
20) Wang, X., Ma, S., Forster, P. M., Yuan, D., Eckert, J., Lpez, J. J., Murphy, B. J., Parise, J. B., Zhou, H., *Angew. Chem., Int. Ed.*, 47, 7263 (2008).
21) Panella, B., Hirscher, M., Puettner, H., Mueller, U., *Adv. Funct. Mater.*
テトラフルタル酸とクロムカチオンからなる金属-有機構造体（TPA-Cr）を水熱法により調製し、XRD、窒素吸着脱着等温線、TGA-DTA および TEM でキャラクタリゼーションを行った。調製した TPA-Cr は結晶性で純粋なものであったことが分かった。金属を通常の含浸法で TPA-Cr に担持した。Pd 塩または含浸溶液の選択が Pd の存在位置に大きな影響を及ぼした。Pd と溶液にそれぞれ[Pd(NH₃)₄(NO₃)₂] と水を用いると、Pd は TPA-Cr のミクロ細孔内に担持されたが、Pd は TPA-Cr の外表面に担持された。α,β-不飽和アリドヒドであるシナナールアルドヒドとクロトンアルドヒドの水素化反応と脱硫化アリルとフェニルポロン酸のクロスカップリング反応を Pd/TPA-Cr や Ru/TPA-Cr を触媒として検討した。その結果、二つのモデルアリドヒド化合物においては水素化が TPA-Cr のメチルあるいはメタノール溶液特ににおいても Pd は TPA-Cr の外表面に担持された。α,β-不飽和アルデヒドであるシンナアールアルデヒドとクロトンアルデヒドの水素化反応と脱硫化アリルとフェニルポロン酸のクロスカップリング反応を Pd/TPA-Cr や Ru/TPA-Cr を触媒として検討した。その結果、二つのモデルアリドヒド化合物においては水素化が TPA-Cr のメチルあるいはメタノール溶液特ににおいても Pd は TPA-Cr の外表面に担持された。α,β-不飽和アルデヒドであるシンナアールアルデヒドとクロトンアルデヒドの水素化反応と脱硫化アリルとフェニルポロン酸のクロスカップリング反応を Pd/TPA-Cr や Ru/TPA-Cr を触媒として検討した。その結果、二つのモデルアリドヒド化合物においては水素化が TPA-Cr のメチルあるいはメタノール溶液特ににおいても Pd は