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Regioselective Hydrogenation of *trans*-1-Phenyl-1,3-butadiene on Modified Pd/MOF Catalysts

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Regioselective hydrogenation of *trans*-1-phenyl-1,3-butadiene was studied using modified Pd/MOF catalysts in the liquid phase at 65 °C and P_{H_2} 5.0 MPa-G. Metal-organic framework compound, MOF-Cr with MIL-101 structure, was prepared with Cr^{3+} as the corner cation and terephthalic acid as the linker. NO_2 -MOF-Cr of the same fundamental structure as MOF-Cr was prepared with nitroterephthalic acid as the linker. Core-shell type MOF was prepared using NO_2 -MOF-Cr as the core MOF and this was covered with shell MOF-Cr. Amino group obtained by reduction of the nitro group of nitroterephthalic acid in the core MOF was essential to accommodate Pd. Pd was supported only on the core MOF by ion-exchange. Of the two aliphatic C=C double bonds of the substrate, the inner C=C double bond was preferentially hydrogenated on Pd catalyst supported on MOF-Cr and core-shell MOF-Cr. However, the end C=C double bond was preferentially hydrogenated on Pd supported on *t*-butoxycarbonyl (*t*-Boc) modified core-shell type MOF due to the steric effect.

KeywordsRegioselective hydrogenation, Palladium catalyst, MOF, Core-shell structure, *t*-Boc modification**1. Introduction**

Regioselective hydrogenation^{1),2)} and chemoselective hydrogenation^{3)~5)} are both important for the synthesis of intermediates for pharmaceuticals. Homogeneous and heterogeneous catalyst systems have been widely studied^{1)~5)}. The heterogeneous system is preferable for the *e*-factor. Recently, bimetal catalysts were reported to achieve chemoselective hydrogenation^{3),6)}. In addition, the support significantly influences the catalytic performance of metal catalysts. Various studies using zeolites and metal-organic frameworks (MOFs) as supports have been reported. Regioselective hydrogenation of dienes was studied such as 1,5-undecadiene using Pt/Zeolite-4A⁷⁾. Pt/Na- β was used for regioselective hydrogenation of alkenes such as 1-decene and 5-decene⁸⁾. Chemo- and regio-selective hydrogenation of various olefins was reported using Pd-MCM-48⁹⁾. Chemoselective cinnamaldehyde hydrogenation was investigated using Pt nanoclusters confined within MOF, UiO-66-NH₂¹⁰⁾ and using Pt nanoparticles sandwiched between an inner core and outer shell of a MOF, MIL-101¹¹⁾. Ag nanoparticles confined in MOF, Ag@HLUST-1, were prepared to study selective hydrogenation

of olefins with one double bond¹²⁾. An influence of a small amount of Ag on the surface of HKUST-1 on chemoselectivity is mentioned. Therefore, metal particles in a confined space exhibit chemo- and regioselective hydrogenation. However, regioselective hydrogenation with a noble metal in the micropores of MOF has not been well studied.

Here, we report the regioselective hydrogenation of diene, *trans*-1-phenyl-1,3-butadiene, with Pd/MOF (Scheme 1). The effects of the core-shell structure and *t*-butoxycarbonyl (*t*-Boc) modification of MOF were studied in detail.

Scheme 1 Hydrogenation of *trans*-1-Phenyl-1,3-butadiene

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2. Experimental

2.1. Preparation of Pd/MOF–Cr Catalysts

MIL-101 type MOF, consisting of Cr^{3+} and nitroterephthalic acid, was prepared as follows^{13)–15)}. $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ 8.35 mmol and nitroterephthalic acid 12.6 mmol were added to 30 mL of distilled water, and this mixture was stirred under supersonic agitation for 10 min. The mixture was transferred into a 50 mL autoclave with a Teflon inner tube. The autoclave was flushed with nitrogen to remove air and then treated at 180 °C for 12 h under stirring with a magnetic stirrer bar. The green-black suspension was filtered and the remaining product was washed with 50 mL of *N,N*-dimethylformamide (DMF) under supersonic agitation to remove unreacted nitroterephthalic acid. The product was further washed with acetone, and finally dried at 150 °C for 2 h under reduced pressure of 20 hPa to obtain light yellow $\text{NO}_2\text{-MOF-Cr}$.

The core-shell type MOF was prepared by adding $\text{NO}_2\text{-MOF-Cr}$ 0.70 g, $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ 3.34 mmol and terephthalic acid 5.02 mmol to 30 mL of distilled water. This suspension was transferred into the 50 mL autoclave and the above procedure was repeated to obtain $\text{NO}_2\text{-MOF-Cr@MOF-Cr}$.

To reduce the nitro group, $\text{NO}_2\text{-MOF-Cr@MOF-Cr}$ 0.30 g, $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ 1.21 g and ethanol 20 mL were mixed in a 50 mL flask under supersonic agitation (28 kHz) for 10 min. The green mixture was transferred into the 50 mL autoclave equipped with a Teflon inner tube. The air was removed with nitrogen and the mixture was heat-treated at 70 °C for 6 h under stirring with a magnetic stirrer bar. After filtration, the product was washed with conc. HCl to remove remaining Sn species. The product was washed with water and then with ethanol. The obtained product was dried at 120 °C for 2 h under reduced pressure of 20 hPa to obtain light green $\text{NH}_2\text{-MOF-Cr@MOF-Cr}$.

Finally, $\text{NH}_2\text{-MOF-Cr@MOF-Cr}$ was used as the support for Pd catalyst. $\text{NH}_2\text{-MOF-Cr@MOF-Cr}$ 0.20 g, PdCl_2 5.8 mg, 0.05 M HCl 2.5 mL were mixed in distilled water 50 mL in a 100 mL flask. The mixture was stirred at room temperature for 1 h to ligate the Pd species. After filtration, the product was washed with distilled water and then with acetone, and dried at 120 °C for 2 h under reduced pressure of 20 hPa. Finally, the obtained catalyst precursor material was reduced at 200 °C for 1 h under hydrogen flow 150 mL min^{-1} to obtain 1 wt% $\text{Pd/NH}_2\text{-MOF-Cr@MOF-Cr}$.

To narrow the micropores of the core $\text{NH}_2\text{-MOF-Cr}$, the amino group of core $\text{NH}_2\text{-MOF-Cr}$ was modified with *t*-butoxycarbonyl (*t*-Boc) modification. 1 wt% $\text{Pd/NH}_2\text{-MOF-Cr@MOF-Cr}$ 0.10 g and di-*t*-butyl dicarbonate 0.16 g (0.74 mmol) were added to DMF 20 mL in a 50 mL flask. This mixture was stirred at room temperature for 10 min under supersonic agitation and

then was stirred further at room temperature for 2 h with a magnetic stirrer. After centrifugation, the product was washed with acetone, and finally dried at 120 °C for 2 h under reduced pressure of 20 hPa to obtain 1 wt% $\text{Pd}/(\text{CH}_3)_3\text{COCO-NH-MOF-Cr@MOF-Cr}$.

2.2. Characterization

The crystalline structure of the catalysts was analyzed by X-ray diffraction (XRD; RINT2000, Rigaku Corp.) using Cu $K\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$) at 40 kV and 20 mA. The BET specific surface areas of MOF–Cr and MOF–Cr catalysts were calculated from the N_2 adsorption-desorption isotherms measured with a BELSORP BEL-mini (MicrotracBEL Corp., Japan). Pre-treatment for the measurement was performed at 140 °C for 1 h in N_2 stream. Fourier transform infrared spectra were measured with a FTIR-6200 (JASCO Corp., Japan) from 4000 to 400 cm^{-1} in the transmission mode. The sample powder was mixed with KBr to a concentration of about 10 % and the mixture was pelletized. Accumulation was 16 times. X-ray photoelectron spectra (XPS) of N 1s were measured with a JPS-9000 MX (JEOL Ltd., Japan) using Mg $K\alpha$ radiation at 10 kV and 10 mA. Peak position was calibrated for C 1s at 284.2 eV and scan accumulation was eight times.

2.3. Hydrogenation of *trans*-1-Phenyl-1,3-butadiene

The hydrogenation reaction was carried out with a 50 mL stainless steel autoclave. Catalyst 10 mg, *trans*-1-phenyl-1,3-butadiene 1.54 mmol and triglyme (solvent) were placed in the autoclave. The autoclave was purged with nitrogen and then hydrogen was supplied to 5.0 MPa-G. Reaction temperature and time were 65 °C and 3 h, respectively. The products were analyzed with a gas chromatograph equipped with a flame-ionization detector, GC-FID (GC-2014, Shimadzu Corp., Japan) and a BP-21 column (length 25 m, internal diameter 0.22 mm, film thickness 0.25 μm). The quantity of each product was calculated based on the peak area.

3. Results and Discussion

3.1. Properties of MOF–Cr and Pd/MOF–Cr

XRD patterns of $\text{NO}_2\text{-MOF-Cr}$, $\text{NO}_2\text{-MOF-Cr@MOF-Cr}$, 1 wt% $\text{Pd/NH}_2\text{-MOF-Cr@MOF-Cr}$ and 1 wt% $\text{Pd}/(\text{CH}_3)_3\text{COCO-NH-MOF-Cr@MOF-Cr}$ are shown in Fig. 1. The same pattern was generally observed for all four samples, in accordance with the reported pattern of MOF–Cr, MIL-101¹⁵⁾. Loading of 1 wt% Pd seems to reduce the heights for peaks between $2\theta = 9$ and 10. No peaks ascribed to Pd were observed for Pd-loaded catalysts, which suggests that Pd was highly dispersed in the micropores of MOF.

Nitrogen adsorption/desorption isotherms for $\text{NO}_2\text{-MOF-Cr}$, $\text{NO}_2\text{-MOF-Cr@MOF-Cr}$, 1 wt% $\text{Pd/NH}_2\text{-MOF-Cr@MOF-Cr}$ and 1 wt% $\text{Pd}/(\text{CH}_3)_3\text{COCO-NH-MOF-Cr@MOF-Cr}$

Fig. 1 XRD Patterns of NO₂-MOF-Cr, NO₂-MOF-Cr@MOF-Cr, 1 wt% Pd/NH₂-MOF-Cr@MOF-Cr and 1 wt% Pd/(CH₃)₃COCO-NH-MOF-Cr@MOF-Cr (CuKα, 40 kV, 20 mA)

Fig. 2 N₂ Adsorption/Desorption Isotherms of NO₂-MOF-Cr, NO₂-MOF-Cr@MOF-Cr, 1 wt% Pd/NH₂-MOF-Cr@MOF-Cr and 1 wt% Pd/(CH₃)₃COCO-NH-MOF-Cr@MOF-Cr

MOF-Cr@MOF-Cr are shown in **Fig. 2**. Very similar BET surface areas were obtained for NO₂-MOF-Cr and NO₂-MOF-Cr@MOF-Cr, suggesting that the nitro group in nitroterephthalic acid did not affect nitrogen adsorption/desorption. Furthermore, the BET values obtained were similar to that reported for MOF-Cr¹⁵. Slightly smaller BET surface areas, 1490 m² g⁻¹ and 1290 m² g⁻¹ were found for 1 wt% Pd/NH₂-MOF-Cr@MOF-Cr and 1 wt% Pd/(CH₃)₃COCO-NH-MOF-Cr@MOF-Cr, respectively, possibly because Pd and the *t*-butoxycarbonyl group blocked the micropores of MOF-Cr. The pore size distributions calculated by the MP method are given in **Fig. 3**. The pore size of about 0.9 nm is considered tentative because of the assumptions for the MP method calculation and the limitations of the instrument. The same peak top positions for NO₂-MOF-Cr and NO₂-MOF-Cr@MOF-Cr

Fig. 3 Pore Size Distributions of NO₂-MOF-Cr, NO₂-MOF-Cr@MOF-Cr, 1 wt% Pd/NH₂-MOF-Cr@MOF-Cr and 1 wt% Pd/(CH₃)₃COCO-NH-MOF-Cr@MOF-Cr by the MP Method

Fig. 4 FT-IR Spectra of 1 wt% Pd/NH₂-MOF-Cr@MOF-Cr and 1 wt% Pd/(CH₃)₃COCO-NH-MOF-Cr@MOF-Cr

were observed, showing that the nitro group had no effect on the pore size. With Pd loading, a bimodal pore size distribution was observed. In case of the catalyst modified with *t*-Boc, 1 wt% Pd/(CH₃)₃COCO-NH-MOF-Cr@MOF-Cr, the bimodal pore size distribution shifted to the smaller range, suggesting that the pores were narrowed by the presence of bulky *t*-Boc. The presence of wider pores of about 1 nm for 1 wt% Pd/NH₂-MOF-Cr@MOF-Cr has not been established because the bulk structure did not change (**Fig. 1**).

Figure 4 shows FT-IR spectra for catalysts with and without *t*-Boc modification. Peaks ascribed to CH₃, C=O and C-N vibrations appeared with *t*-Boc modification, suggesting that the amino group of NH₂-MOF-Cr was modified as expected. **Figure 5** shows XPS spectra for N 1s for NH₂-MOF-Cr@MOF-Cr. The peak ascribed to nitrogen was not observed without etching, but was observed after argon etching for 5 s, which suggests that core NH₂-MOF-Cr was covered by shell MOF-Cr. Based on these characterizations, we conclude that phase pure MOF, core-shell type MOF, and *t*-Boc modified core-shell type MOF were prepared as intended.

MOFs were used as the support for Pd in this study. The effect of the amino group on Pd loading was confirmed (**Table 1**). Comparing two MOFs with and without the amino group, Pd was not supported on

MOF-Cr, whereas Pd species interacted with the amino group and was loaded in a short time for $\text{NH}_2\text{-MOF-Cr@MOF-Cr}$. This finding suggests that Pd was located near the amino group with high dispersion not detected by XRD. In the case of $\text{NH}_2\text{-MOF-Cr@MOF-Cr}$, Pd was present only in the micropores of core $\text{NH}_2\text{-MOF-Cr}$ and we can anticipate the confined effect of the microporous structure of MOF.

3.2. Regioselective Hydrogenation of *trans*-1-Phenyl-1,3-butadiene

The results on regioselective hydrogenation of *trans*-1-phenyl-1,3-butadiene are given in **Table 2**. Under the conditions adopted, conversion of *trans*-1-phenyl-1,3-butadiene was 100 % in every case, suggesting that the substrate quickly diffused in the micropores of MOF-Cr. Without the MOF shell (Entry 1), 1-phenyl-3-butene ((b) in **Scheme 1**) was obtained,

Fig. 5 N 1s XPS Profiles of $\text{NH}_2\text{-MOF-Cr@MOF-Cr}$

Table 1 Effect of Amino Group on Pd Loading^{a)}

Support	Stirring ^{b)} [h]	Amount of Pd in filtrate [mg]	Pd loading [wt%]
$\text{NH}_2\text{-MOF-Cr}$	0.17	2.9×10^{-3}	1.0
	1.0	0.0	1.1
	3.0	0.0	1.1
MOF-Cr	1.0	2.2	0.0

a) Temp.: room temperature.

b) Stirring: time for ion-exchange.

meaning that the inner C = C double bond was hydrogenated. Without *t*-Boc modification (Entry 2), the selectivity for (b) was 97.2 %, possibly because the structural strain was not sufficient to select which C = C double bond was hydrogenated. When the amount of the shell was small (Entry 3), the result was similar to that without the shell (Entry 1) even with *t*-Boc modification, probably because of insufficient steric restriction. With an adequate amount of shell and *t*-Boc modification (Entry 5), hydrogenation of the double bond proceeded differently and *trans*-1-phenyl-1-butene ((c) in **Scheme 1**) was obtained with 70.7 % selectivity (**Fig. 6**). With the same amount of shell but with repeated shell formation (Entry 4), 60.7 % selectivity for (c) was obtained. With shell formation carried out with larger amounts of $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and terephthalic acid (Entry 6), low selectivity of (c) was obtained with higher selectivity for (b), possibly because MOF-Cr was formed independent of the seed $\text{NO}_2\text{-MOF-Cr}$ with larger amounts of metal and linker sources.

These results indicate that without the structural

Fig. 6 Scheme of Regioselective Hydrogenation of *trans*-1-Phenyl-1,3-butadiene

Table 2 Hydrogenation of *trans*-1-Phenyl-1,3-butadiene on Pd-based Catalysts^{a)}

Entry	Support	Shell preparation $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ [g]/ Terephthalic acid [g]	Conv. [%]	Selectivity ^{b)} [%]		
				(b)	(c)	(d)
1	$(\text{CH}_3)_3\text{COCO-NH-MOF-Cr}$	-	100	82.5	15.2	2.3
2	$\text{NH}_2\text{-MOF-Cr@MOF-Cr}$	1.34/0.88	100	97.2	1.1	1.7
3	$(\text{CH}_3)_3\text{COCO-NH-MOF-Cr@MOF-Cr}$	0.67/0.44	100	71.4	26.6	2.0
4	$(\text{CH}_3)_3\text{COCO-NH-MOF-Cr@MOF-Cr}$	0.67/0.44 + 0.67/0.44	100	35.3	60.7	4.0
5	$(\text{CH}_3)_3\text{COCO-NH-MOF-Cr@MOF-Cr}$	1.34/0.88	100	26.0	70.7	3.2
6	$(\text{CH}_3)_3\text{COCO-NH-MOF-Cr@MOF-Cr}$	3.35/2.20	100	97.9	0.0	2.1

a) Catalyst 10.0 mg (Pd loading 1 wt%), *trans*-1-phenyl-1,3-butadiene 1.54 mmol, Triglyme 10.0 g, Temp. 65 °C, H_2 5.0 MPa-G, Time 3 h.

b) (b) 1-Phenyl-3-butene, (c) *trans*-1-Phenyl-1-butene, (d) 1-Phenylbutane.

strain induced by *t*-Boc modification, the inner C=C double bond was easily hydrogenated. With Pd catalyst supported on MOF without shell, hydrogenation proceeded on Pd at the outer surface or near the outer surface and no preference to hydrogenation of the end C=C double bond was observed. Even though Pd/NH₂-MOF-Cr was covered with MOF-Cr shell, the inner double bond was still hydrogenated without *t*-Boc modification. Finally, with core-shell type MOF and with *t*-Boc modification, selective hydrogenation of the end double bond was attained for the first time probably due to the steric effect, suggested by the narrower pore size as indicated in **Fig. 3**. However, the electronic properties of Pd might have changed and influenced the selectivity. Pd was supposed to exist near the amino group and *t*-Boc was bonded with the amino group. Therefore, both steric and electronic effects of *t*-Boc modification can be proposed. As the regioselectivity differed by the amount of shell MOF, the steric influence seems to predominate. Further XPS study may give information on the electronic effect. The catalyst may be used repeatedly because the material balance was 100 % $\pm$ 5 %, which suggests that no substances remained in the micropores to block the active Pd sites.

4. Conclusions

Regioselective hydrogenation of *trans*-1-phenyl-1,3-butadiene was studied with Pd/MOF. MOF-Cr with the MIL-101 structure was solvothermally prepared with Cr³⁺ as the corner cation and terephthalic or nitroterephthalic acid as the linker. Pd/MOF-Cr without the shell MOF-Cr or Pd supported on core-shell type MOF-Cr without *t*-Boc modification catalyzed hydrogenation at the inner C=C double bond. In contrast,

Pd on Pd/MOF with core-shell structure and *t*-Boc modification, Pd/(CH₃)₃COCO-NH-MOF-Cr@MOF-Cr, catalyzed hydrogenation of the end C=C double bond to give *trans*-1-phenyl-1-butene. Therefore, a support confining the environment of Pd allowed control of the regioselectivity.

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要 旨

修飾 Pd/MOF 触媒によるトランス-1-フェニル-1,3-ブタジエンの位置選択的水素化

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修飾 Pd/MOF を触媒としてトランス-1-フェニル-1,3-ブタジエンの位置選択的な水素化を 65 °C, 5.0 MPa の水素圧力（ゲージ圧）下の液相で検討した。MIL-101 構造の金属-有機構造体 MOF-Cr は Cr^{3+} をコーナーのカチオンとし、カチオンをつなぐリンカーにテレフタル酸を用いて調製した。MOF-Cr と基本的に同じ構造を有する NO_2 -MOF-Cr にはリンカーとしてニトロテレフタル酸を用いた。コア-シェル構造の MOF は、 NO_2 -MOF-Cr をコアの MOF とし、これをシェルの MOF-Cr で覆った。コアの MOF 中のニトロテレフタル酸のニトロ基を還元し

て得られたアミノ基は、Pd を担持するために不可欠であった。Pd はコアの MOF にのみイオン交換で担持された。MOF-Cr, あるいはコア-シェル型 MOF-Cr に担持された Pd 触媒では、基質の二つの脂肪族 $\text{C}=\text{C}$ 二重結合のうち、内部の二重結合が選択的に水素化された。一方、コア-シェル構造、かつ *t*-ブトキシカルボニル (*t*-Boc) で修飾した MOF に担持された Pd 触媒では、立体的効果のため末端の $\text{C}=\text{C}$ 二重結合が選択的に水素化された。

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