

Efficient Hydrogenation of Benzaldehydes Over Mesopolymer-Entrapped Pt Nanoparticles in Water

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Abstract: Pt nanoparticles entrapped in the matrices of FDU-14 periodic mesoporous organic polymer (abbreviated as mesopolymer), prepared by a simple and facile method, serve as an efficient catalyst for the liquid-phase hydrogenation of benzaldehydes under mild conditions. Water was confirmed to be a better choice of solvent for the hydrogenation of benzaldehydes on the

Pt/FDU-14 catalyst. The highest activity (turnover frequency) was about 5700 mol mol⁻¹ h⁻¹ for 3-fluorobenzaldehyde hydrogenation in water and no distinct loss of activity or selectivity

was observed after the catalyst was recycled nine times. For the *para*-substituted benzaldehydes, the catalytic performance of Pt/FDU-14 was superior to the commercial Pt/alumina catalyst owing to the more hydrophobic nature of the FDU-based catalyst.

Keywords: catalysis · hydrogenation · nanoparticles · platinum · polymers

Introduction

The reduction of aldehydes to corresponding alcohols is an important step in the preparation of fine chemicals and pharmaceuticals. The transformation can be achieved either through hydrogen-transfer reduction,^[1–9] including a Meerwein–Ponndorf–Verley reaction with alcohol as a hydrogen donor,^[4–6] or by direct hydrogenation using atmospheric or pressured H₂ as a hydrogen source.^[10–35] There are many heterogeneous catalytic systems reported for aldehyde hydrogenation in the gas^[10–14] or liquid phase.^[15–35]

Recently, the liquid-phase hydrogenation of aldehydes has undergone fast evolution. Attention is now focused on exploring new catalysts by using different catalytic active centers or new materials as catalyst supports. In particular, noble and transition metals, such as Pt,^[15–23] Ru,^[17,24–26]

Au,^[27–29] Pd,^[17,30] Ir,^[31,32] Co,^[33] and Cu-based^[34,35] catalysts have been employed in the liquid-phase hydrogenation. Among these catalysts, the Pt-based catalysts have been extensively studied in the past decade and new materials have been explored as Pt-catalyst supports for the aforementioned liquid-phase reactions. For example, the molecular interactions and pressure effects on the hydrogenation of benzaldehyde and cinnamaldehyde over a 5 wt. % Pt/C catalyst in supercritical medium was studied.^[18] The influence of the inner^[16] and outer^[20] diameters of the carbon nanotubes on the selective hydrogenation of cinnamaldehyde over carbon nanotube supported Pt catalysts were recently reported. The support pretreatment and phase behavior were also investigated by using rice-husk based porous carbon (RHCs)-supported Pt catalysts in the hydrogenation of aldehydes.^[21] More recently, a zeolitized pumice supported Pt catalyst was shown to display better performance in the selective reduction of carbonyl groups in comparison with a silica-supported Pt catalyst.^[23] Furthermore, a nanostructured Pt catalyst, derived from the platinum carbonyl cluster supported on a polymer, proved to be more active in water than a commercial Pt/alumina catalyst.^[19]

However, the organic polymer supported Pt catalysts have rarely been used for the liquid-phase hydrogenation of aldehydes.^[19,22] Organic polymers have attracted much more attentions in recent years owing to their special physico-chemical properties, which enable easy product separation and catalyst recycling.^[36,37] Of particular interest are the

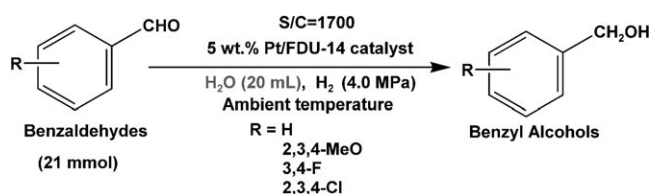
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FDU-type mesoporous organic polymers (abbreviated as mesopolymers), such as FDU-14 with *Ia3d* symmetry and FDU-15 with *p6mm* symmetry, both of which are derived from organic–organic self-assembly of resols (phenol/formaldehyde) with triblock copolymers.^[38] The FDU-type mesopolymers possess a three-dimensionally connected benzene ring framework and are highly hydrophobic. Since the discovery of FDU-type mesopolymers, extensive interest has been focused on their unique structural and physico-chemical properties as well as potential applications. The functionalization through the introduction of functional groups or by loading metal nanoparticles into the mesopores of FDU-type mesopolymers proved to be efficient routes for expanding their utilization in the catalytic research field.^[39–41]

In addition to the catalysts, solvents usually play an important role in the whole reaction. With regard to the aldehyde hydrogenation reactions, most studies were carried out in organic media such as alkanes and alcohols.^[16,26,27,33,34] Although supercritical fluids can be used as eco-friendly reaction media, they require special equipment to operate.^[17,18,21] Therefore, the use of environmentally benign solvents like water for organic syntheses has emerged as one of the most interesting subjects both in academia and in industry for substantial economical and ecological gains.^[1,19,25,32,41]

We have preliminarily reported the preparation and catalytic application of Pt nanoparticles supported on a hexagonally structured mesopolymer, the Pt/FDU-15 catalyst. It proved to be an effective, robust, and remarkably reusable catalyst after it was chirally modified with cinchonidine for the asymmetric hydrogenation of ethyl pyruvate, affording up to 62% *ee* value.^[41] Encouraged by these achievements, we have expected to generalize the application of this class of novel catalysts in the clean hydrogenation. In this study, the FDU-14 mesopolymer-supported Pt nanoparticles are prepared and applied to the hydrogenation of benzaldehydes under mild conditions, namely at ambient temperature and in water (Scheme 1). A commercial 5 wt.% Pt/alumina catalyst and a common organic solvent, ethanol, were also employed for comparison. The Pt/FDU-14 catalyst was more efficient in water compared with ethanol as the sol-



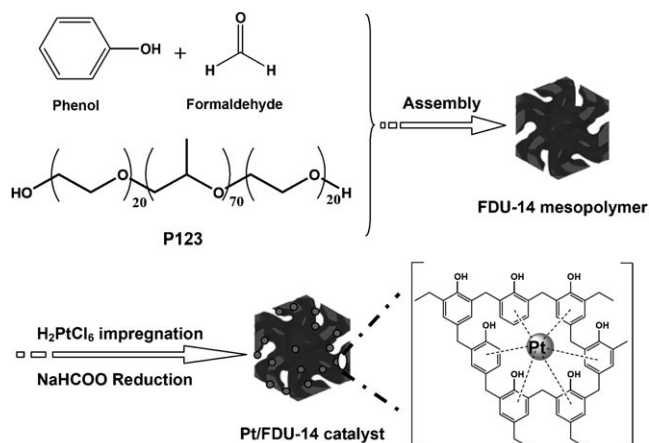
Scheme 1. Hydrogenation of benzaldehyde derivatives on a FDU-14-supported Pt catalyst.

vent, and showed a higher performance, particularly for *para*-substituted benzaldehydes, than the commercial Pt/alumina catalyst.

Results and Discussion

Preparation and Characterization of the Pt/FDU-14 Catalyst

The 5 wt.% Pt/FDU-14 catalyst was prepared by incorporation of Pt nanoparticles into the matrices of the FDU-14 mesopolymer through a facile and simple impregnation method (Scheme 2) according to references [41,42]. As we



Scheme 2. Synthesis of the FDU-14 mesopolymer and preparation of Pt/FDU-14 catalysts.

Abstract in Chinese:

FDU-14 是一种新型的有机酚醛树脂介孔材料, 由于其具有三维有序孔道以及纯有机骨架和丰富的表面羟基等特点而引起人们的关注。通过浸渍法将 Pt 纳米粒子负载于 FDU-14 孔道后可以在温和条件下于液相体系中高效催化苯甲醛及其衍生物的氢化反应。和常规有机溶剂乙醇比较, Pt/FDU-14 催化的苯甲醛氢化反应在水溶剂中表现出较高的催化活性。Pt/FDU-14 催化剂对 3-氟苯甲醛的氢化反应活性最高, 转换频率可以达到约 $5700 \text{ mol mol}^{-1} \text{ h}^{-1}$ 。Pt/FDU-14 在水溶剂中重复使用 9 次后, 催化剂的活性和选择性都没有明显降低。对于对位取代苯甲醛的氢化反应 Pt/FDU-14 催化剂的性能要明显优于商品化 Pt/Al₂O₃ 催化剂。

already know from the case of the Pt/FDU-15 catalyst, the aggregation of Pt to large particles takes place easily during the high-temperature calcination of the Pt catalyst precursor in a nitrogen atmosphere.^[41] We therefore reduced the Pt/FDU-14 catalyst precursor in an aqueous solution of sodium formate directly after impregnation and drying at 353 K in an oven without high temperature calcination.

The physico-chemical properties of the FDU-14 mesopolymer and the corresponding Pt/FDU-14 catalyst are summarized in Table 1. The well-ordered mesoporous structure of the FDU-14 mesopolymer was still maintained after loading the Pt nanoparticles, which was confirmed by the low-angle XRD patterns and N₂ adsorption–desorption isotherms of the FDU-14 mesopolymer before and after Pt

Table 1. Physico-chemical properties of the FDU-14 mesopolymer and the corresponding Pt/FDU-14 catalyst.

Sample	S_{BET} [m^2g^{-1}]	V_p [cm^3g^{-1}] ^[a]	D_p [nm] ^[b]	Pt dispersion [%] ^[c]	Pt size [nm] ^[c]
FDU-14	508	0.40	3.4	–	–
Pt/FDU-14	472	0.39	3.1	22.7	5.0

[a] N_2 adsorption volume at $P/P_0=0.998$. [b] D_p is the mesopore diameter determined from the adsorption branch of N_2 sorption isotherms by using the BJH method. [c] Estimated from the measured CO uptake. S_{BET} = BET specific area.

loading (Figure 1 and Figure 2). The decreased diffraction intensity in the low-angle XRD pattern of the Pt/FDU-14 catalyst compared with the parent FDU-14 mesopolymer

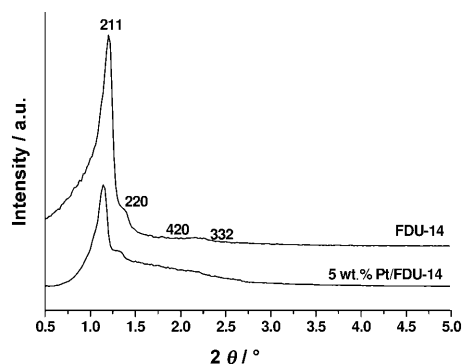
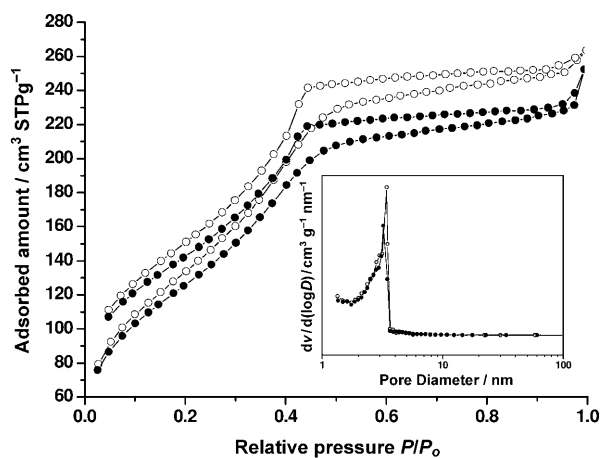


Figure 1. Low-angle XRD patterns of the FDU-14 mesopolymer before and after Pt loading.

Figure 2. N_2 adsorption-desorption isotherms and pore-size distribution curves (inset) of the FDU-14 mesopolymer before (—○—) and after (—●—) they were loaded with Pt nanoparticles.

can be explained by the decreased contrast between the pore walls and channels after loading of the Pt particles. The specific surface area of FDU-14 decreased reasonably from 508 to 472 m^2g^{-1} after Pt-nanoparticle loading. As a consequence, the pore size decreased from 3.4 to 3.1 nm. The average Pt nanoparticle size of Pt/FDU-14 was around 5 nm with a dispersion of 22.7% according to CO chemisorption, which is in agreement with the TEM image (Figure 3) and

the wide-angle XRD pattern (Figure S1 in the Supporting Information). This infers that the mesopores of FDU-14 were partially broken.

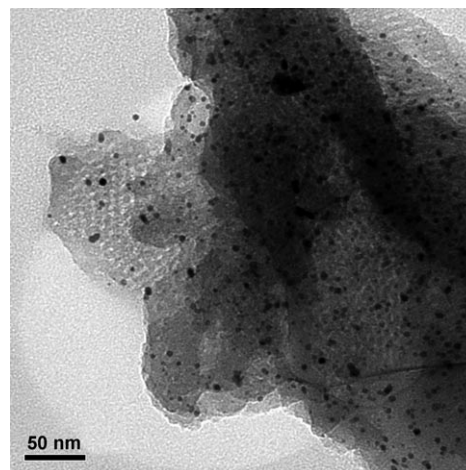
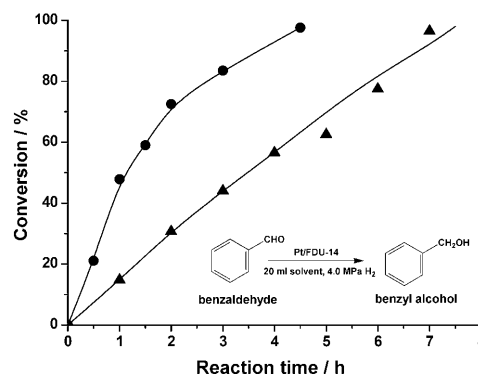


Figure 3. TEM image of Pt/FDU-14 catalyst with the incidence direction parallel to the pore axis.

Optimization of Reaction Conditions for Benzaldehyde Hydrogenation

To identify the optimum reaction conditions for the hydrogenation of various aldehydes, the simplest aromatic aldehyde, benzaldehyde, was chosen as a model substrate. The benzaldehyde hydrogenation was first carried out at ambient temperature under 4.0 MPa pressure of hydrogen in different solvents. Figure 4 shows the kinetic profiles of benzaldehyde conversion versus reaction time in ethanol and in

Figure 4. Kinetic profiles for hydrogenation of benzaldehyde on the Pt/FDU-14 catalyst in water (—●—) and in ethanol (—▲—). Reaction conditions: benzaldehyde (21 mmol), catalyst/substrate = 5.85×10^{-4} , solvent (20 mL), H_2 (4.0 MPa), 1200 rpm, ambient temperature.

water. There is a roughly linear correlation between benzaldehyde conversion and the reaction time without any induction period when the hydrogenation was carried out in ethanol, which is indicative of a zero-order dependence on the aldehyde concentration. This phenomenon is in agreement with what has been reported in reference [30], in which the same zero-order plots for benzaldehyde hydrogenation over Pd catalysts supported on various materials, such as silica, alumina, and carbon, were also observed. Finally, the reaction took more than 7 h to complete. For the same reaction carried out in water, however, the trend is different from that observed in ethanol. The conversion rate increased sharply at the initial stage and then slowed down till the reaction was completed. It took only about 4 h to finish the reaction. Notably, the reaction ran much faster in water than in ethanol, as the initial activity based on the conversions within 1 h were 3462 and 730 mol mol⁻¹ h⁻¹, respectively. Nevertheless, the selectivities to benzyl alcohol were higher than 99% in both solvents, as by-products detected after the reaction were negligible.

The striking water effect that we observed upon the hydrogenation of benzaldehyde catalyzed by Pt/FDU-14 is similar to our previous observation in the chiral hydrogenation of ethyl pyruvate on Pt/FDU-15.^[41] This can be interpreted firstly in terms of the limited solubility of the reactant benzaldehyde, but also the relatively good solubility of the product benzyl alcohol in water. Thus, the product would diffuse quickly from the catalyst surface into water

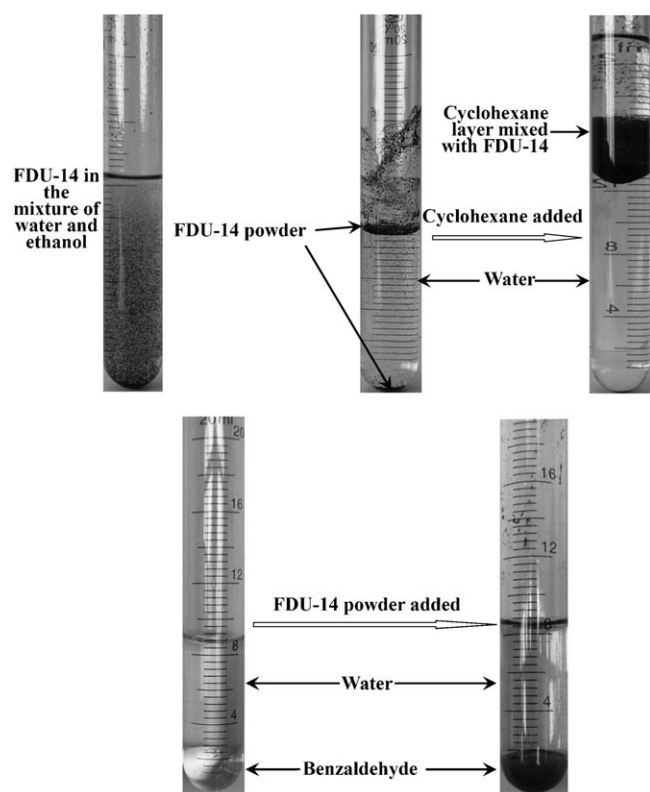


Figure 5. Soakage properties of the FDU-14 mesopolymer in different media.

once it is formed. The quick transfer of product from the catalyst surface to the solvent is expected to accelerate the reaction. Secondly, the high hydrophobicity of the FDU-14 mesopolymer with a pure organic framework could result in the aggregation of benzaldehyde around the Pt/FDU-14 nanoparticles when the reaction is carried out in water. As benzaldehyde is soluble in ethanol and the Pt/FDU-14 catalyst can also soak well in this solvent, the substrate and the catalyst are uniformly dispersed in ethanol (Figure 5 shows the soakage properties of FDU-14 in different media). The distribution of the Pt/FDU-14 catalyst in the reaction mixtures is similar to those described in reference [43]. As a result, the quicker transfer of product and the higher substrate concentration on the Pt/FDU-14 surface can lead to faster benzaldehyde hydrogenation in water.

In addition to studying the influence of solvents, we investigated the temperature effects on the hydrogenation of benzaldehyde. As shown in Figure 6, the conversion of benzaldehyde increased, whereas the selectivity to benzyl alcohol decreased with increasing the reaction temperature for the benzaldehyde hydrogenation in ethanol. This can be interpreted by different reaction pathways at different temperatures as benzyl alcohol is predominantly formed at low temperatures in polar solvents.^[44]

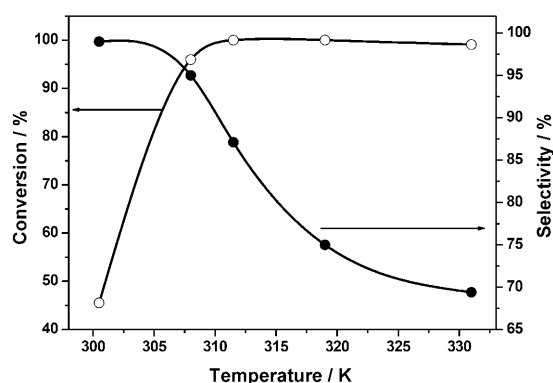
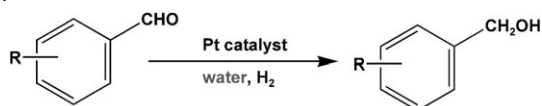


Figure 6. Reaction temperature effects on the benzaldehyde hydrogenation on Pt/FDU-14 in ethanol. Reaction conditions: benzaldehyde (21 mmol), catalyst/substrate = 5.85×10^{-4} , ethanol (20 mL), H₂ (4.0 MPa), 1200 rpm, 2 h.

Hydrogenation of Benzaldehydes with Different Substituents at the Phenyl Ring

To broaden the scope of Pt/FDU-14 catalysis, we extended the hydrogenation to a range of benzaldehydes with different substituents at the phenyl ring. Based on the findings presented above, we chose water as the solvent and performed the reaction at ambient temperature. A commercial 5 wt. % Pt/alumina catalyst was also employed for comparison. It had an average Pt particle size of about 3.4 nm and a dispersion of 33.3% according to the measured CO uptake. As shown in Table 2, the Pt/FDU-14 catalyst delivered higher conversions for *para*-substituted benzaldehydes in a short reaction time compared with the Pt/alumina catalyst.

Table 2. Hydrogenation of benzaldehydes with different substituents at the phenyl ring on Pt/FDU-14 and commercial Pt/Al₂O₃ catalysts in water.^[a]



Entry	R group	Catalyst	Conversion [%] ^[b]	Selectivity [%] ^[b]
1		Pt/FDU-14	99	97
2	4-MeO	Pt/Al ₂ O ₃	66	99
3		Pt/FDU-14	47	97
4	3-MeO	Pt/Al ₂ O ₃	97	94
5		Pt/FDU-14	96	99
6	2-MeO	Pt/Al ₂ O ₃	99	98
7		Pt/FDU-14	91 ^[c]	95
8	4-F	Pt/Al ₂ O ₃	73 ^[d]	98
9		Pt/FDU-14	39 ^[e]	92
10	3-F	Pt/Al ₂ O ₃	60 ^[e]	91
11		Pt/FDU-14	41	94
12	4-Cl	Pt/Al ₂ O ₃	21	73
13		Pt/FDU-14	84	89
14	3-Cl	Pt/Al ₂ O ₃	92	81
15		Pt/FDU-14	91	87
16	2-Cl	Pt/Al ₂ O ₃	93	64

[a] Reaction conditions: the molar ratio of catalyst/substrate is about 5.85×10^{-4} , benzaldehyde (21 mmol), water (20 mL), H₂ (4.0 MPa), 1200 rpm, ambient temperature, 2 h. [b] Detected by GC. [c] 3 h. [d] 5 h. [e] 0.5 h.

This is evident that the activities furnished by Pt/FDU-14 were much higher than those obtained by Pt/alumina for 4-methoxy-, 4-fluoro-, and 4-chlorobenzaldehydes (Table 2, entries 1, 2, 7, 8, 11, and 12). However, for *meta*-substituted benzaldehydes (3-methoxy-, 3-fluoro-, and 3-chlorobenzaldehydes), Pt/FDU-14 was less active than Pt/alumina (Table 2, entries 3, 4, 9, 10, 13, and 14). For example, Pt/FDU-14 gave only 47% conversion of 3-methoxybenzaldehyde, whereas Pt/alumina furnished 97% conversion under the same conditions (Table 2, entries 3 and 4). For *ortho*-substituted benzaldehydes (2-methoxy- and 2-chlorobenzaldehydes), the two catalysts showed a comparable performance (Table 2, entries 5, 6, 15, and 16). The results displayed here for benzaldehyde hydrogenation on the Pt nanoparticles entrapped in FDU-14 are also much higher than those obtained in the same reactions when operated under the similar conditions on a water-soluble, poly(diallyldimethylammonium chloride)-supported, $\{[\text{Pt}_{30}(\text{CO})_{60}]^{2-}\}$ -derived Pt catalyst.^[19]

As also shown in Table 2, the selectivities to the corresponding benzyl alcohols of methoxybenzaldehydes in water by the two catalysts are excellent. However, with respect to the hydrogenation of halogen-substituted benzaldehydes, side reactions were observed and the main by-products were dehalogenation and oligomerization products as confirmed by GC-MS analysis. It should be pointed out that no obvious product from the hydrogenation of the phenyl ring was detected for all substrates. This essentially means that the two Pt catalysts preferentially hydrogenate the carbonyl group under the reaction conditions employed.

The higher performance of the Pt/FDU-14 catalyst than the Pt/Al₂O₃ catalyst for the *para*-substituted benzaldehydes in water may be attributable to the high hydrophobicity of the Pt/FDU-14 catalyst, which has a pure organic framework. The hydrophobic features of the Pt/FDU-14 and Pt/Al₂O₃ catalysts were measured by thermogravimetric analyses. As shown in Figure 7, in the temperature range from

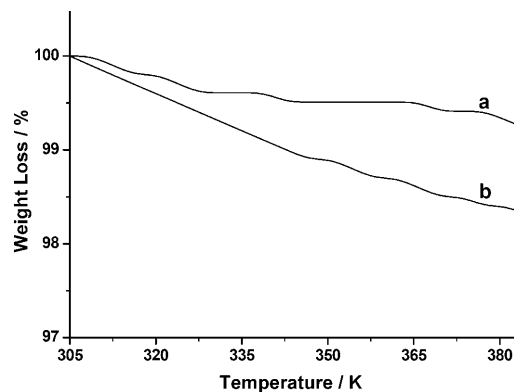


Figure 7. Thermogravimetric profiles of Pt/FDU-14 (a) and Pt/Al₂O₃ catalysts (b).

ambient temperature to 380 K to remove the physisorbed water, only 0.6% of the weight was lost for Pt/FDU-14, whereas nearly twice as much weight loss was measured for Pt/Al₂O₃ in a nitrogen atmosphere. This indicates that Pt/FDU-14 contained less water, and thus showed a higher hydrophobicity than Pt/Al₂O₃. It was therefore deduced that the hydrophobic Pt/FDU-14 catalyst is not surrounded by water molecules, but by the organic substrate benzaldehydes during the reaction in water. Consequently, it is more likely that the substrate molecules could be adsorbed and activated by the Pt particles entrapped in FDU-14. On the contrary, the hydrophilic Pt/Al₂O₃ catalyst preferentially adsorbs water molecules rather than aldehyde molecules. As a result, the more aldehyde molecules adsorbed and activated by Pt/FDU-14, the faster the hydrogenation rate under the same reaction conditions.

The reason that the *meta*- or *ortho*-substituted benzaldehyde hydrogenation on Pt/FDU-14 gave lower or comparable conversions compared with the commercial Pt/Al₂O₃ catalyst can be elucidated by the different extents of steric hindrance of benzaldehydes substituted at the different positions and the subsequent mass transfer in the mesopores of FDU-14. In comparison with *para*-substituted benzaldehydes, *meta*- or *ortho*-substituted isomers normally have comparatively large dynamic molecular diameters. This means that the mass transfer of the substrates and the corresponding products in the mesopores of FDU-14 plays a significant role in the whole reaction process. Although the FDU-14 mesopolymers have an average mesopore diameter of 3.4 nm determined from the adsorption branch of N₂ sorption isotherms by using the Barrett–Joyner–Halenda (BJH) method, the Pt nanoparticles located inside the meso-

pores occupy quite a substantial amount of room, leading to restricted diffusion for more bulky substrates and products with substituents at the *meta* or *ortho* position of the carbonyl group on the phenyl ring. On the other hand, the Pt/Al₂O₃ catalyst is an open and broad system with the Pt particles dispersed on the exterior surface of alumina crystals. As a result, mass transfer is not significant regardless of the molecular size of the substrates.

The initial activities (represented as turnover frequency (TOF) based on the conversions within 30 min) for benzaldehyde hydrogenation on Pt/FDU-14 and Pt/Al₂O₃ catalysts in water have also been measured (Figure 8). It can be seen

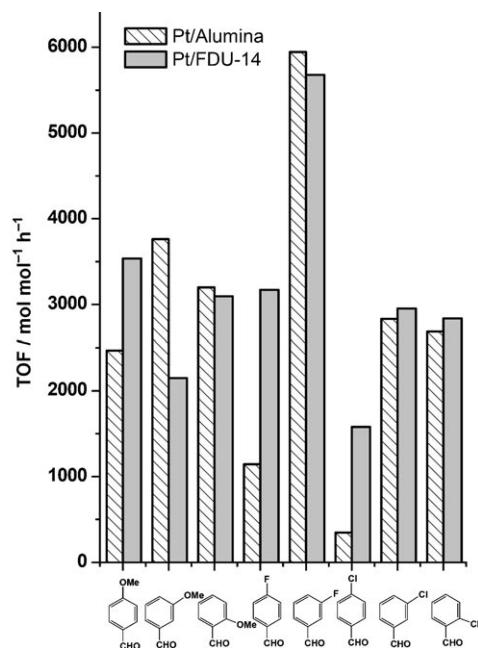


Figure 8. Initial activity (TOF, mol mol⁻¹ h⁻¹) based on the conversions within 30 min for different benzaldehydes hydrogenation on Pt/FDU-14 and Pt/Al₂O₃ catalysts in water and at ambient temperature. Reaction conditions: 0.5 h, other conditions are identical to those listed in Table 2.

that, for electron-donating groups, such as methoxy, the benzaldehydes substituted at the *ortho* and *para* positions were more active than their *meta*-substituted isomer in the hydrogenation on Pt/FDU-14. Hence, the TOF for 3-methoxybenzaldehyde was the lowest, only affording about 2150 mol mol⁻¹ h⁻¹, whereas the TOF values for 2- and 4-methoxybenzaldehydes reached above 3000 mol mol⁻¹ h⁻¹ and the *para*-substituted compound was the most active. However, for the hydrogenation of benzaldehydes substituted with comparatively electron-withdrawing groups like fluorine or chlorine at the phenyl ring, the aldehydes substituted at the *meta* position gave higher activities than the *ortho*- or *para*-substituted isomers. In particular, the Pt/FDU-14 catalyst afforded the highest TOF of approximately 5700 mol mol⁻¹ h⁻¹ for 3-fluorobenzaldehyde hydrogenation in water at ambient temperature. Despite the increased steric hindrance of 2-chloro- compared with 4-chlorobenzaldehyde, the chlorine

atom at the *ortho* position to the carbonyl group probably participates in the interaction with the Pt particles, which is beneficial to its activation. As a result, a higher activity for 2-chlorobenzaldehyde hydrogenation on the Pt/FDU-14 catalyst of about 2700 mol mol⁻¹ h⁻¹ was afforded. This indicates that the electron-efficient benzaldehydes are easily activated by Pt/FDU-14 catalyst through conjugation with the substituents at the phenyl ring. The electrons at the oxygen atom of the carbonyl group of benzaldehydes could be transferred to Pt atoms and then to the support as the FDU-14 mesopolymer could interact with Pt particles through the π donation of their organic framework and consequently accept the electrons from the carbonyl group.^[45]

Similar phenomena were observed for the Pt/Al₂O₃ catalyst as well, except for the methoxy-substituted benzaldehydes as the lowest TOF was obtained for 4-methoxybenzaldehyde hydrogenation.

Reusability of Pt/FDU-14 Catalyst

The reusability of Pt/FDU-14 is also an important matter to consider. Hence, we investigated its reusability in water for the hydrogenation of 4-methoxybenzaldehyde at ambient temperature within 1.5 h. Figure 9 shows the conversions and selectivities to the corresponding benzyl alcohol against the run numbers. The catalyst showed no distinct loss of activity and selectivity after reusing the catalyst nine times. The activity decreased gradually when the catalyst was subjected to further use. This is partially owing to the catalyst powder gradually washing out from the reaction system, trace amount of Pt leaching, and agglomeration of a few Pt particles during the recycling processes. The reusability of the Pt/FDU-14 catalyst for the hydrogenation of benzalde-

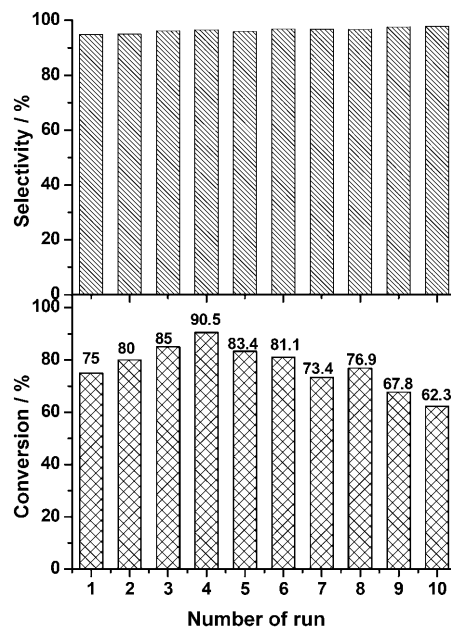


Figure 9. Reusability of the Pt/FDU-14 catalyst in the hydrogenation of 4-methoxybenzaldehyde in water. Reaction conditions: 1.5 h, other conditions are identical to those listed in Table 2, entry 1.

hydrides in water complemented our previous findings that were observed on the Pt/FDU-15 catalyst for the chiral hydrogenation of ethyl pyruvate in acetic acid. In this case, it afforded constant activity and enantioselectivity after the 25th cycle.^[41] The entrapment of the Pt nanoparticles in the porous resin matrices and the π -donating interaction with benzene rings would prevent effectively the agglomeration and leaching of Pt nanoparticles during reactions^[45] so that the Pt particles can be stabilized and recycled smoothly. In addition, as discussed above, the high hydrophobicity of FDU-14 mesopolymers with a pure organic framework may also contribute to the high performance in water.

Conclusions

In conclusion, the Pt nanoparticles entrapped in the mesopores of FDU-14 mesopolymer were confirmed to work well as an efficient catalyst for the liquid-phase hydrogenation of various benzaldehydes under mild conditions. With regard to the benzaldehyde hydrogenation on the Pt/FDU-14 catalyst, water is a better choice of solvent in contrast to conventional solvents like ethanol. The Pt/FDU-14 catalyst gave the highest activity of about $5700 \text{ mol mol}^{-1} \text{ h}^{-1}$ for the 3-fluorobenzaldehyde hydrogenation in water at ambient temperature and showed a good reusability. Compared with the commercial Pt/Al₂O₃ catalyst, the Pt/FDU-14 catalyst showed superior performance, particularly for the *para*-substituted benzaldehydes, which is mainly owing to its hydrophobic character. The results obtained in the hydrogenation of benzaldehydes with various groups substituted at different positions of the phenyl ring indicate that the electron-rich benzaldehydes are easily activated by the Pt/FDU-14 catalyst.

The catalyst preparation procedure has now been further improved to prepare the Pt catalyst with a smaller and more-uniform particle size. Those Pt particles confined in the mesopores of the FDU-14 mesopolymer are expected to be more efficient in relevant hydrogenation reactions. The results obtained in this study also imply that the FDU-type mesopolymer can be applicable for supporting other noble metal particles such as Pd, Ru, and Au, resulting in useful catalysts for the Heck coupling reaction or redox reactions of unsaturated compounds containing C=C bonds.

Experimental Section

Materials

Benzaldehyde, hydrogen hexachloroplatinate (IV) hexahydrate (H₂PtCl₆·6H₂O), sodium formate, and other chemicals were of analytical grade and used as received. 2-Methoxybenzaldehyde (98%), 3-methoxybenzaldehyde (98%), 4-methoxybenzaldehyde (98%), 3-fluorobenzaldehyde (97%), 4-fluorobenzaldehyde (98%), 2-chlorobenzaldehyde (98%), 3-chlorobenzaldehyde (97%), and 4-chlorobenzaldehyde (98%) were purchased from Alfa Aesar and used as received. A commercial Pt/alumina (5 wt.%) was also purchased from Alfa Aesar. The FDU-14 mesopolymers were synthesized according to the literature.^[58]

Catalyst Preparation and Characterization

Pt/FDU-14 (5 wt.%) was prepared according to literature.^[41,42] FDU-14 was impregnated with an aqueous solution of platinum precursor and stirred for 4–6 h. Then the mixture was evaporated to remove the excess water, followed by drying at 353 K overnight, and finally reduced in an aqueous solution of sodium formate.

X-ray diffraction patterns were recorded on a Bruker D8 ADVANCE instrument with Cu_{K α} radiation. The nitrogen sorption isotherms were measured at 77 K on a Belsorp-max system. The Brunauer–Emmett–Teller (BET) specific area was calculated by using adsorption data in the relative pressure range from 0.05 to 0.35. The pore-size distribution curves were calculated from the analysis of the adsorption branch of the isotherm by using the BJH algorithm. Transmission electron microscopy images were taken on an FEI Tecnai G2 Spirit at an acceleration voltage of 120 kV. Thermogravimetric analysis (TGA) to investigate the hydrophobic property of the catalyst was performed in a N₂ atmosphere from 303 K to 423 K with a heating rate of 2 K min⁻¹ by using a METTLER TOLEDO TGA/SDTA851^e apparatus. CO chemisorption of samples was measured at 313 K on a CHEMBET-3000 pulse chemisorption analyzer after the sample was pretreated in a hydrogen flow at 573 K (673 K for Pt/alumina) for 2 h. The degree of dispersion and the mean particle size (cubic model) were estimated from the measured CO uptake, assuming a cross-sectional area for a surface platinum atom of $8.0 \times 10^{-20} \text{ m}^2$ and a stoichiometric factor of one by using nominal platinum concentrations.

General Procedures for Liquid-phase Hydrogenation of Benzaldehydes

For a standard hydrogenation, the molar ratio of catalyst/substrate is about 5.85×10^{-4} . Pt/FDU-14 or Pt/alumina (5 wt.%) was pretreated in a hydrogen flow (40 mL min⁻¹) at 573 or 673 K, respectively, for 2 h before use. The catalyst was then mixed with the benzaldehyde (21 mmol) and solvent (20 mL) and then transferred to an autoclave with magnetic stirring (1200 rpm). The hydrogenation reaction started at ambient temperature after hydrogen (4.0 MPa) was introduced. The reaction was stopped after a period of time and then the products were analyzed by GC (GC-2014, Shimadzu Co.) equipped with an FID and a capillary column (DM-WAX, 30 m \times 0.25 mm \times 0.25 μm).

Recycling

The recycle experiment was also carried out in water. The detailed procedures are as follows. After the each run, the catalyst (50 mg) was centrifuged, washed with ethanol several times, and finally naturally dried in air overnight. Fresh reactant (21 mmol), water (20 mL), and hydrogen (4.0 MPa) were then charged to the autoclave together with the recovered catalyst to carry out the next run reaction.

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