Catalysis Science & Technology

COMMUNICATION



View Article Online View Journal | View Issue

Cite this: Catal. Sci. Technol., 2014, 4, 329

Received 1st November 2013, Accepted 22nd November 2013

PVP-Pd@ZIF-8 as highly efficient and stable catalysts for selective hydrogenation of 1,4-butynediol[†]

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DOI: 10.1039/c3cy00873h

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Cubic Pd nanoparticles were rapidly encapsulated in ZIF-8 through a PVP-assisted synthetic method at room temperature. The obtained PVP-Pd@ZIF-8 exhibited high activity and stability for hydrogenation of 1,4-butynediol, with excellent selectivity to 1,4-butenediol.

Selective hydrogenation of carbon-carbon triple bonds to double bonds is a challenge relevant to commodity chemical production as well as for synthesis of fine and special chemicals.^{1,2} The partial hydrogenation of 2-butyne-1,4-diol (BYD) is especially interesting because the product 2-butene-1,4-diol (BED) is an important intermediate in the production of endosulfan³ and vitamins A and B.⁴ It is also used as an additive in resin manufacturing.⁵ Lindlar catalysts⁶ (Pd on CaCO₃ poisoned with lead) are the prototypical examples of a highly selective supported metal catalyst for liquid phase hydrogenation of BYD created by addition of an appropriate surface modifier. For this catalyst, the lead is used as an irreversible dopant to promote the selective reduction of BYD to cis-BED, while a basic compound such as quinoline is often added during the reaction to slow the subsequent hydrogenation of the desired product to 1,4-butanediol (BDO).¹ The outstanding selectivity is thus associated with the use of undesirable, toxic lead compounds and other soluble additives. Therefore, it is necessary to develop alternative, green and stable catalysts for this transformation.

In recent years, metal-organic frameworks (MOFs) have been extensively explored as metal supports for heterogeneous catalysts.⁷⁻¹¹ In particular, using MOFs as the support allows stabilization of catalytically active metal nanoparticles that are too labile under other conditions.¹² The high surface area and narrow pore distribution of MOFs may lead to uniform distribution of highly dispersed NPs, which is of great interest for controlling catalytic activity and selectivity.¹³ Our investigation aims at the elucidation of the main characteristics of ZIF-8 as a support for polyvinyl-pyrrolidone (PVP) protected Pd catalysts for selective hydrogenation of BYD. The PVP-Pd@ZIF-8 catalysts were synthesized through a PVP-assisted process described by Lu *et al.*,¹⁴ except for using water as the solvent instead of methanol and a much shorter time. The strong adsorption between the PVP and ZIF-8 frameworks resulted in the insertion of PVP-Pd into the lattice of ZIF-8. The loading of Pd can be tuned by adding different amounts of PVP-Pd colloid during the formation of ZIF-8.

XRD patterns (Fig. S1[†]) showed that the rapidly produced ZIF-8 and PVP-Pd@ZIF-8 materials have very high crystallinity. The diffraction peak of metallic palladium at 40° cannot be detected until the Pd loading is up to 5 wt%, indicating a high dispersion of Pd, which can be further confirmed from TEM images as shown in Fig. 1. The TEM images show that the original cubic Pd nano-sol has almost no change after being encapsulated in ZIF-8 crystals. The nanocubic Pd particles with the size of 4–6 nm are randomly dispersed without any aggregation.



Fig. 1 TEM images of PVP–Pd colloid (a) and PVP–Pd@ZIF-8 (0.3 wt% (b), 1 wt% (c), 5 wt% (d)) and N_2 adsorption results (e, f) for PVP–Pd@ZIF-8 catalysts.

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 $[\]dagger$ Electronic supplementary information (ESI) available. See DOI: 10.1039/ c3cy00873h

This agrees well with what has been reported in a study involving similar synthesis methodology but with much shorter synthetic time and lack of control over the time for adding PVP-Pd.¹⁴ The size of the ZIF-8 framework is about 100 nm, which can also be confirmed from SEM results (Fig. S3[†]). It can be seen that most of the Pd particles are embedded inside of the ZIF-8 crystal lattice and almost no particles on the edges of ZIF-8 can be seen when Pd loading is low. However, when Pd loading is up to 5 wt%, some Pd particles can be occasionally seen on the edges of the ZIF-8 lattice, but still with no aggregation. The N₂ adsorption isotherms (Fig. 1 (e, f)) of the ZIF-8 support and PVP-Pd@ZIF-8 catalysts show typical type I isotherms as classified by IUPAC, which match well with the microporous structure of ZIF-8. A narrow pore size distribution (1-1.7 nm) was observed. No obvious differences can be detected between the support and the catalysts, which indicate the intactness of ZIF-8 after even high Pd loading. The encapsulation of ZIF-8 to PVP-Pd can also be indirectly proven by the hydrogenation of n-hexylene and cyclooctene, in which PVP-Pd@ZIF-8 had extremely high selectivity to n-hexylene for its linear structure making it possible to pass through the narrow canal of ZIF-8 (Table S1[†]). As a consequence, a surface area and pore volume change happened. Though the BET surface area does not make so much sense for MOFs, for reference only, the results are listed in Table 1. The total surface areas of these three samples are almost the same. However, as the Pd loading increases, the micropore area decreases and the external surface area increases. In addition, the micropore volumes also decrease when Pd amount increases.

The catalytic performance of PVP–Pd@ZIF-8 catalysts was tested in a batch reactor with H₂O as solvent. The hydrogenation pathways of BYD are shown in Scheme S1. BYD can be easily fully hydrogenated to BDO by monometallic Pd or Pt

Table 1 N_2 physisorption results of PVP-Pd@ZIF-8 catalysts								
Sample	$\begin{array}{c} \mathbf{SA}^{a} \\ \left(\mathbf{m}^{2} \ \mathbf{g}^{-1}\right) \end{array}$	$\begin{array}{c} \mathbf{MA}^{b} \\ \left(\mathbf{m}^{2} \ \mathbf{g}^{-1}\right) \end{array}$	$\begin{array}{c} \mathbf{EA}^c \\ \left(\mathbf{m}^2 \ \mathbf{g}^{-1}\right) \end{array}$	$\frac{\text{MV}^d}{(\text{cm}^3 \text{ g}^{-1})}$				
0.3 wt% PVP-Pd@ZIF-8	1757	1717	39	0.64				
1 wt% PVP–Pd@ZIF-8	1754	1666	88	0.62				
5 wt% PVP-Pd@ZIF-8	1600	1488	112	0.57				
a a h		<u> </u>						

^{*a*} BET surface area. ^{*b*} Micropore area. ^{*c*} External surface area. ^{*d*} Micropore volume.

catalysts. The selectivity to monoene products can often be improved by poisoning step or terrace sites of catalysts with bismuth,¹⁵ sulfur adatoms,¹⁶ lead,¹⁷ Ag,¹⁸ etc. These catalytic systems usually provide high selectivity to partially hydrogenated products with the hazards of toxic heavy metals. A residual bacterial biomass poisoned Pt catalyst had been reported by Bennett et al.¹⁹ The bio-Pt catalyst had a better selectivity to butenediol than the 5 wt% Pt/graphite catalyst. However, the selectivity was still relatively low. Some other catalytic systems for hydrogenation of 2-butyne-1,4-diol are summarized in Table S2† in which most catalysts had good selectivity only when BYD was incompletely converted. Pd@MOFs catalysts have also been applied in the hydrogenation of BYD.²⁰ The Pd@MOF-5 had the highest selectivity to BED at the first hydrogenation stage (BYD conversion ~95%), and the butenediol products could be consecutively hydrogenated with longer reaction time. Unfortunately, the Pd@MOFs showed low stability during the reaction process. In contrast, the PVP-Pd@ZIF-8 catalysts here almost completely blocked the second hydrogenation stage, leading to excellent selectivity to cis-BED even with very long reaction time or high temperature.

The catalytic activities and selectivities under different conditions are shown in Table 2, in which the reaction time is 0.5 h. The activity increased with the rise of Pd loading. Full conversion accompanied with 97.5% selectivity to cis-BED was obtained at 50 °C and 2 MPa when the Pd loading was about 1 wt%. It can be seen that a few more products of the second hydrogenation stage (BDO) were obtained at 5 wt% Pd loading, where some Pd particles were embedded on the edge of ZIF-8. Higher temperatures often lead to deep hydrogenation of BED to BDO. However, very high selectivity to BED (94.5) was still obtained when the temperature was raised to 100 °C. The pressure also affects the activity, and the decrease in conversion at lower pressure was expected. The unexpected phenomenon was that excessive pressure also reduced the activity. This is attributed to the high internal surface area and metal cation sites of ZIF-8 that facilitate hydrogen adsorption.²¹ With higher hydrogen pressure (over 2 MPa), increased adsorption of H₂ molecules into the micropore of ZIF-8 limited the substrate to reach the Pd encapsulated in the ZIF-8 framework. Another possible reason for this behavior might be the competitive adsorption of the substrate with surface Pd hydride.

Table 2	Hydrogenation	of 1,4-butynedio	l on the PVP-Pd@ZIF-8	catalysts with differe	nt Pd loadings
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Catalyst	Т (°С)	Р (MPa)	Conversion (%)	Selectivity (%)			
				cis-BED	BDO	<i>n</i> -Butanol	Side products ^a
0.3 wt% PVP-Pd@ZIF-8	50	2	66.9	98.8	0.7	Trace	0.5
1 wt% PVP-Pd@ZIF-8	20	2	26.6	98.0	1.3	Trace	0.7
1 wt% PVP-Pd@ZIF-8	50	2	99.7	97.5	1.5	Trace	1.0
1 wt% PVP-Pd@ZIF-8	100	2	94.5	94.5	3.5	Trace	2.0
1 wt% PVP-Pd@ZIF-8	50	1	77.1	97.2	1.2	Trace	1.6
1 wt% PVP-Pd@ZIF-8	50	3	87.8	98.0	1.3	Trace	0.7
1 wt% PVP-Pd@ZIF-8	50	4	79.6	97.9	1.2	Trace	0.9
5 wt% PVP-Pd@ZIF-8	50	2	98.2	95.5	4.0	Trace	0.5

 a Isomerization products such as γ -oxybutyraldehyde, 2-hydroxytetrahydrofuran, etc.

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Fig. 2 Kinetic data for hydrogenation of 1,4-butynediol obtained for 1 wt% PVP-Pd@ZIF-8 (a) and PVP-Pd colloid (b).

The kinetic data for BYD hydrogenation for 1 wt% PVP-Pd@ZIF-8 are shown in Fig. 2a. BYD was almost completely converted in 30 min, and the extremely high selectivity kept constant during the whole reaction process. Even with another 3.5 h after the complete consumption of BYD, there was surprisingly still no hydrogenation of cis-BED or isomerization. The selectivity to BED was still high (97.7) after 4 h of reaction, indicating that the reaction stopped after the first hydrogenation stage. These facts suggest that the selectivity of our catalysts should be mainly derived from their structural properties rather than controlling their kinetics. In comparison, the original cubic PVP-Pd nano-sol was directly applied in the same reaction under the same conditions and the relevant kinetic data are shown in Fig. 2b. The PVP-Pd nano-sol had a lower activity, needing 2.5 h to fully convert BYD because of the aggregation of Pd nano-sol as observed during the reaction process. A relatively high selectivity to BED (93%) can also be gained at the point of 2.5 h and then the further hydrogenation and isomerization began to happen as the reaction continues. The results above clarified that the outstanding partial hydrogenation performance of PVP-Pd@ZIF-8 was not just because of the adsorption of PVP around Pd particles. The protection of long-chain PVP definitely reduces the activity of Pd, but obviously the PVP-Pd particles were still active enough for the hydrogenation of BED.

The most probable reason for this interesting performance is the encapsulation within ZIF-8. It is known that the step and edge atoms are less coordinated than those atoms on faces of metal particles.²² Thus, there must be more PVP molecules adsorbed on the vertex and edge sites on the present Pd particles, which would in turn have more tendency to adsorb on the ZIF-8 framework during the synthetic process. Based on the above reasons, the edge and vertex sites of Pd were much more blocked by ZIF-8 than the terrace sites (Scheme S2[†]). It has been proven that the C-C triple bonds are hydrogenated upon terrace sites of Pd catalysts, while the resulting double-bond products are further hydrogenated on the edge and vertex sites.^{15,20} Thus, the linear BYD could only be hydrogenated upon the terrace sites but couldn't be further hydrogenated due to the blockage of the edge sites, leading to a high selectivity to BED. At the same time, the narrow pore canal of ZIF-8 may limit the isomerization process. In addition, the 2-methylimidazole in ZIF-8 is



Fig. 3 Recyclability of 1 wt% PVP-Pd@ZIF-8 catalyst (a) and XRD (b)/TEM (c) characterization for the recycled catalyst.

an N containing compound that may play a role in adjusting the selectivity of the catalysts.²³ To confirm the effects of the encapsulation of ZIF-8, the same synthesis method was extended to another acetate protected Pt nano-sol. Once again, in this case the Pt@ZIF-8 also had a similar outstanding performance in this reaction (Fig. S4[†]).

The PVP-Pd@ZIF-8 catalysts can be reused without any reactivation treatments except for two-time washing with H₂O. The recyclability data for 1.0 wt% PVP-Pd@ZIF-8 are shown in Fig. 3a. It shows that the sample had reproducible performance over five runs, sustaining very good conversion of BYD (97%) and excellent selectivity of BED (98%) even after the fifth run. The XRD pattern of PVP-Pd@ZIF-8 after reaction is shown in Fig. 3b. No obvious differences can be detected compared with the fresh sample, indicating the intactness of the ZIF-8 crystal structure during the reaction. The N₂ adsorption data (Fig. S5[†]) also confirmed the unchanged pore structure of the recycled catalyst. The TEM image (Fig. 3c) clearly showed that the ZIF-8 framework and the cubic Pd particles are all preserved during the reaction runs. No aggregation/growth of Pd particles or collapse of the ZIF-8 structure occurred.

In summary, we have demonstrated the successful preparation of PVP-Pd catalysts encapsulated by ZIF-8 through a PVP-assisted rapid dynamic crystallization method at room temperature. The monometallic PVP-Pd@ZIF-8 catalysts showed prominently enhanced selectivity to *cis*-1,4-butenediol for hydrogenation of 1,4-butynediol, due to edge site blocking by ZIF-8 and assistance of the N containing organic ligand in ZIF-8. At the same time, high activity was obtained due to the high catalyst surface area and high dispersion of Pd particles. Notably, the PVP-Pd@ZIF-8 not only had an excellent performance but also had a great stability in the reaction. The method can be extended to other metal particles (*e.g.* Pt), which can find wide potential applications in catalytic reactions.

Acknowledgements

This work was supported by the National Natural Science Foundation of China (21073023 and 21373038) and the Fundamental Research Funds for the Central Universities (DUT12YQ03 and DUT13RC(3)41).

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