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Article

Highly selective hydrogenation of furfural to tetrahydrofurfuryl alcohol over MIL-101(Cr)-NH₂ supported Pd catalyst at low temperature

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ABSTRACT

An efficient heterogeneous catalyst, Pd@MIL-101(Cr)-NH₂, is prepared through a direct pathway of anionic exchange followed by hydrogen reduction with amino-containing MIL-101 as the host matrix. The composite is thermally stable up to 350 °C and the Pd nanoparticles uniformly disperse on the metal organic framework (MOF) support, which are attributed to the presence of the amino groups in the frameworks of MIL-101(Cr)-NH₂. The selective hydrogenation of biomass-based furfural to tetrahydrofurfuryl alcohol is investigated by using this multifunctional catalyst Pd@MIL-101(Cr)-NH₂ in water media. A complete hydrogenation of furfural is achieved at a low temperature of 40 °C with the selectivity of tetrahydrofurfuryl alcohol close to 100%. The amine-functionalized MOF improves the hydrogen bonding interactions between the intermediate furfuryl alcohol and the support, which is conducive for the further hydrogenation of furfuryl alcohol to tetrahydrofurfuryl alcohol in good coordination with the metal sites.

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1. Introduction

Recently, research efforts have been devoted to the production of biofuels and biomass-derived chemicals from nonedible lignocellulosic biomass owing to the increasing awareness of energy exhaustion and environmental concerns [1,2]. Furfural (FUR), which is mainly produced from the acidic hydrolysis of hemicellulose and accounts for 25%–35% of the lignocellulosic biomass, has been selected as one of the top 30 biomass-derived platform chemicals and employed as the feed-

stock for the sustainable production of biofuels and value-added chemicals [3–6]. The catalytic hydrogenation of furfural has been extensively investigated, which can be transformed to furfural alcohol (FA) and tetrahydrofurfuryl alcohol (THFA) [7–10]. Hydrogenolysis may also occur during the hydrogenation process which can produce 2-methylfuran, 2-methyltetrahydrofuran, cyclopentanone, cyclopentanol and polyols, such as 1,5-pentanediol and 1,2-pentanediol [11–14].

THFA is widely used as green solvent, for the synthesis of special chemicals, such as dihydropyran, and has also been

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proposed for use as a biofuel or as a fuel additive because of its similar properties to kerosene [4,15]. THFA is usually produced by the hydrogenation of FA derived from FUR, and it can be obtained by the direct hydrogenation of furfural in the presence of noble or non-noble metals [16–19]. The production of THFA from furfural has been investigated extensively. Biradar et al. [9] reported an effective complete hydrogenation of furfural using a 3% Pd/MFI catalyst and achieved the highest conversion and THFA selectivity in the range of 93%–100% and 67%–95%, respectively, under optimized conditions of 220 °C and 3.5 MPa. Nakagawa et al. [18] prepared a Ni/SiO₂ catalyst with Ni particle size <4 nm and achieved a maximum THFA yield of 94% for the gas-phase hydrogenation of furfural. They found that the conversion of FA intermediate to THFA was strongly structure sensitive and the turnover frequency (TOF) decreased with increasing metal particle size. The same group also obtained a 94% yield of THFA catalyzed by a large amount of Pd–Ir/SiO₂ (Pd/Ir = 1) bimetallic catalysts in the liquid-phase process and suggested that a high hydrogen pressure (8 MPa) and low reaction temperature (2 °C) were useful to suppress side reactions [20]. However, harsh conditions, such as high hydrogen pressure and high reaction temperature, are usually required for the conversion of FUR to THFA. The design of novel and environmentally-friendly catalysts that can achieve a high THFA selectivity under mild conditions in a green process is of great importance.

Metal organic frameworks (MOFs), which have emerged as a new class of porous materials with diverse properties such as high surface area, permanent porosity and easy functionalization by post-synthetic modification or direct synthesis, have been widely studied and applied in catalysis, in particular, biomass catalysis [21–24]. For example, Zeolitic imidazolate frameworks (ZIFs) were used for the transformation of sugars to lactic acid derivatives with a high conversion and yield [25]. A MOF-based polyoxometalate [Cu-BTC][HPM] showed good catalytic activity in the conversion of 5-hydroxymethylfurfural (5-HMF) [26]. The metal nanoparticles supported on Zr-MOFs were proven to be highly efficient catalysts for biomass refining [27,28]. MIL-101, one of the most stable MOF structures, possesses a high surface area, large porosity, numerous coordinatively unsaturated metal sites and can be subjected to diverse functionalization or guest species encapsulation, and it has been widely used for biomass catalysis [29–32]. The sulfonic-acid-functionalized MIL-101(Cr) [MIL-101(Cr)-SO₃H] was investigated as a solid acid for the catalytic conversion of glucose to 5-HMF [33]. Noble metal nanoparticles, such as those containing Pd or Ru, incorporated within MIL-101 or organic-functionalized (–SO₃H, –NH₂) MIL-101 exhibited a high activity and selectivity in the hydrodeoxygenation or selective hydrogenation of biomass compounds [31,34,35]. It has been demonstrated that the presence of free amine groups in the MOF plays a key role on the formation of uniform, well-dispersed and leaching resistant metal nanoparticles within the MOF host. In addition, the nitrogen-containing support may have an effect on the selectivity towards the target products in hydrogenation reactions [36,37].

Herein, we reported the direct synthesis of

amine-functionalized MIL-101(Cr) [MIL-101(Cr)-NH₂], which exhibits excellent stability to moisture and acid compared with Fe-, Al- and V-MIL-101. The palladium nanoparticles were loaded into the MOF matrix through a direct anionic exchange approach followed by hydrogen reduction [38,39]. The resulting Pd@MIL-101(Cr)-NH₂ was found to be an efficient multifunctional catalyst for the aqueous selective hydrogenation of FUR to THFA with a selectivity of nearly 100% under mild conditions.

2. Experimental

2.1. Catalyst preparation

2.1.1. Preparation of MIL-101(Cr)-NH₂

Amine-functionalized MIL-101(Cr) was hydrothermally synthesized by the direct reaction of Cr(III) and 2-aminoterephthalic acid with assistance from hydroxide based on the previous literature with a slight modification [38]. To be specific, 2-aminoterephthalic acid (0.18 g, 1 mmol) and sodium hydroxide (0.1 g, 2.5 mmol) were dissolved in de-ionized water (7.5 mL) by ultrasonication, where the OH[–] ions could promote the dissolution of organic acid. Then, chromic nitrate hydrate (0.4 g, 1 mmol) was dispersed into the former clear aqueous solution. After ultrasonication for 5 min, the suspension was transferred to a Teflon-lined autoclave and heated at 150 °C for 18 h in a convection oven. After cooling to room temperature naturally, the resulting green precipitate was collected by centrifugation and washed sequentially with de-ionized water, DMF and ethanol several times to remove the excess reagents. The sample was then soaked in hot ethanol with continued heating and stirring at 100 °C for 24 h for further purification, after which the product was dried at 100 °C under vacuum for 12 h.

2.1.2. Preparation of Pd@MIL-101(Cr)-NH₂

Pd nanoparticles were successfully immobilized to MIL-101(Cr)-NH₂ by a direct anionic exchange and subsequent H₂ reduction. Taking the synthesis of 3.0 wt% Pd@MIL-101(Cr)-NH₂ as an example, activated MIL-101(Cr)-NH₂ (0.5 g) was first dispersed in deionized water (30 mL) by ultrasonication and treated with a suitable amount of diluted HCl to adjust the pH to approximately 4. Then a solution of H₂PdCl₄ (containing ca. 3.0 wt% of Pd) was added dropwise to the above slurry under vigorous stirring, and the mixture was further stirred for another 24 h. The solid was separated by centrifugation, repeatedly washed with deionized water, followed by drying at 100 °C under vacuum for 12 h. The resulting [MIL-101(Cr)-NH₃⁺]₂[PdCl₄]₂[–] sample was reduced in a H₂/Ar (H₂/Ar = 20/40 mL min^{–1}) flow at 200 °C for 4 h to yield Pd@MIL-101(Cr)-NH₂. The synthetic procedure is shown in Fig. S1.

2.1.3. Preparation of Pd@MIL-101(Cr)

MIL-101(Cr) was synthesized according to our previous report [40], then an impregnation procedure similar to the above-described was adopted for the incorporation of Pd

within MIL-101(Cr) except with an adjusting of the pH.

2.2. Catalyst characterization

The powder X-ray diffraction (XRD) patterns of the samples were recorded on a D/MAX-2400 diffractometer with Cu K_{α} radiation ($\lambda = 1.5418 \text{ \AA}$) at 40 kV and 100 mA. The Pd contents in MIL-101(Cr)-NH₂ were quantitatively determined by inductively coupled plasma-atomic emission spectroscopy (ICP-AES) using a Perkin-Elmer Optima 2000 DV. Thermogravimetric (TG) experiments were performed on a Mettler Toledo TGA/SDTA851e thermogravimetric analyzer with a heating procedure from 25 to 800 °C at a rate of 10 °C min⁻¹ under a nitrogen atmosphere. The nitrogen adsorption-desorption isotherms were performed at -196 °C on a Quantachrome Autosorb-IQ apparatus. The samples were degassed under vacuum at 150 °C for 10 h before the adsorption measurements. Fourier-transform infrared spectroscopy (FT-IR) characterization was performed on a Thermo fisher Nicolet 6700 spectrometer with a resolution of 0.09 cm⁻¹ at room temperature. The particle size distributions of the catalysts were analyzed by transmission electron microscopy (TEM) measurement using a JEM-2000EX instrument at 120 kV. Powder samples were ultrasonicated in ethanol and dispersed on TEM copper grids.

2.3. Catalytic performance

The selective hydrogenation of FUR was carried out in a 50 mL stainless steel autoclave equipped with a magnetic stirrer and an electrical heating jacket. The catalysts were reduced once again by H₂/Ar (H₂/Ar = 20/40 mL min⁻¹) at 200 °C for 2 h, and passivated under Ar overnight before use. In a typical run, catalyst (0.05 g), FUR (2.1 mmol), and water (20 mL) as a green solvent were added into the autoclave and purged with H₂ three times at room temperature. The autoclave was heated to 40 °C and then pressurized with H₂ to 2 MPa. After the reaction, the autoclave was cooled naturally, and the liquid products were separated by centrifugation, analyzed by gas chromatography (GC-7890F, FID, FFAP column 30 m × 0.32 mm × 0.5 μm) and identified by gas chromatography-mass spectrometry (Agilent 7890B-5977A GC/MSD). The quantitative analysis was performed by an internal standard method with propylene glycol added to the solution after the reaction as the internal standard.

3. Results and discussion

3.1. Characterization of MIL-101(Cr)-NH₂ and Pd@MIL-101(Cr)-NH₂

The XRD patterns of MIL-101(Cr)-NH₂ and Pd@MIL-101(Cr)-NH₂ with various Pd loadings are shown in Fig. S2. The as-synthesized MIL-101(Cr)-NH₂ exhibited a typical diffraction pattern of MIL-101(Cr), which indicated a successful formation of the MIL-101(Cr)-NH₂ crystalline structure. After Pd loading, no obvious structural changes were observed, which suggested a robust MIL-101(Cr)-NH₂ structure as a host

for the Pd nanoparticles [38]. It should be noted that the diffraction peaks derived from Pd NPs were barely observed in the wide-angle XRD patterns (Fig. S3) until the Pd content reached 5.4 wt%, which arose from the low Pd loading [41].

The thermal stability of MIL-101(Cr)-NH₂ and Pd@MIL-101(Cr)-NH₂ were examined and are shown in Fig. S4. TG analysis showed that both MIL-101(Cr)-NH₂ and Pd@MIL-101(Cr)-NH₂ were stable up to 350 °C. The weight losses under 140 °C were ascribed to desorption of the adsorptive and coordinated water molecules and other residuals remained in the MOF cavities [29].

Fig. 1 presents the N₂ adsorption-desorption property of the synthesized MIL-101(Cr)-NH₂ materials. The bare MIL-101(Cr)-NH₂ exhibited a BET surface area of 1669 m² g⁻¹ and a total pore volume of 1.35 cm³ g⁻¹, which was in agreement with the data reported previously [42]. The sharp uptake under low pressure ($P/P_0 = 10^{-6}$ to 0.1) and the pore size distribution centered at 1.4 and 1.8 nm demonstrated the microporous feature of the materials. The increased N₂ uptake near $P/P_0 = 1.0$ arose from the textural pores created by nanoparticle aggregation [43]. After Pd loading, an obvious decrease of the micropore area and pore volume were observed (Table S1), which was attributed to the occupation or blocking of cavities by the deposited Pd nanoparticles or the partial collapse of the framework.

The MIL-101 samples were further characterized by TEM as shown in Fig. 2. Pd NPs were uniformly dispersed on MIL-101(Cr)-NH₂ for the 3.0 wt% Pd@MIL-101(Cr)-NH₂ sample with an average particle size of 3.5 nm (Fig. 2(a)). However, an excessive Pd loading (5.4 wt%) resulted in the formation of much larger nanoparticles with an average size of 4.4 nm (Fig. 2(b)). For the purpose of comparison, MIL-101(Cr) was used to load Pd NPs (2.7 wt%) as shown in Fig. 2(d). A wide range of particle size distribution and larger particles were observed owing to the agglomeration of Pd NPs, which inferred that the presence of amine groups within the frameworks arose from the strengthened adsorption force between NH₂ groups and Pd precursors, which led to the formation of uniform and well-dispersed Pd nanoparticles within the frameworks [44,45].

Fig. 1. N₂ adsorption-desorption isotherms with pore distributions of the MIL-101(Cr)-NH₂ samples.

Fig. 2. TEM images and particle size distribution of 3.0 wt% Pd@MIL-101(Cr)-NH₂ (a), 5.4 wt% Pd@MIL-101(Cr)-NH₂ (b), 3.0 wt% Pd@MIL-101(Cr)-NH₂ after reaction (c) and 2.7 wt% Pd@MIL-101(Cr) (d).

The characterization of MIL-101(Cr) samples with IR spectroscopy are presented in Fig. S5. Compared with the unmodified MIL-101 (Cr), the two bands that appeared at 3490 and 3380 cm⁻¹ for MIL-101(Cr)-NH₂ were ascribed to the N-H bond stretching vibration of the aromatic primary amine in the crystal skeleton. The observed band at 1624 cm⁻¹ was associated with the bending vibration of N-H groups, and the bands at 1340 and 1256 cm⁻¹ were assigned to the stretching vibration of C-N bonds within aromatic amines [46].

3.2. Catalytic performance

The catalytic performance of the as-prepared Pd@MOF materials was evaluated for the catalytic selective hydrogenation of biomass-based FUR in aqueous media. The C=O group of FUR was more easily hydrogenated to form FA, owing to the lower bond energy than the C=C in the furan ring. Further hydrogenation of FA would facilitate the production of THFA. Fig. 3(a) shows the evolution of the reactants conversion and the products selectivity for the hydrogenation of FUR as a function of reaction time over the 3.0 wt% Pd@MIL-101(Cr)-NH₂ catalyst.

Nearly 100% conversion of FUR was achieved in the first 2 h, and the selectivity of THFA was up to 53%, which was accompanied by FA as an intermediate product. A full transformation of FA to THFA could be realized by prolonging the reaction time to 6 h. In addition, the FA could be fully converted to THFA within 2 h when the same amount of FA as the reactants was added into the reaction system. No further hydrogenolysis formed were produced with an extended reaction time (Fig. 3(b)). The above results suggested that THFA could be generated with high selectivity from FUR or FA under the current catalytic system. Comparing the Pd catalysts with other supports in the literature, such as Pd/MFI [9], Pd/Al₂O₃ [47] and

Fig. 3. Variations of substrate conversion and product selectivity for FUR/FA hydrogenation over Pd@MIL-101(Cr)-NH₂ (Pd 3.0 wt%). Reaction conditions: FUR/FA 2.1 mmol, water 20 mL, catalyst 0.05 g, 40 °C, 2 MPa H₂.

Pd/SiO₂ [20], our Pd@MIL-101(Cr)-NH₂ catalyst could obtain highly monodispersed Pd nanoparticles owing to the existence of amine groups on the framework and the abundant pore-structure of MIL-101(Cr)-NH₂. The smaller Pd nanoparticles could promote the production of THFA with high yield under mild conditions and prevent the side reactions, which require harsh reaction conditions.

Fig. 4. Influence of H₂ pressure on the selective hydrogenation of FUR; Reaction conditions: FUR 2.1 mmol, water 20 mL, catalyst (Pd 3.0 wt%) 0.05 g, 40 °C, 4 h.

The effect of H₂ pressure on the hydrogenation of furfural is shown in Fig. 4. It can be clearly seen that with the increase of H₂ pressure from 0.5 to 1 MPa, the hydrogenation rate for FUR to FA was significantly increased. FUR was fully converted at 1.0 MPa and the selectivity to THFA reached 67.8% simultaneously under the investigated conditions. The intermediate FA reached a maximum selectivity at 0.5 MPa and was hydrogenated to THFA when the pressure was gradually raised to 3 MPa. However, the generation rate of THFA showed a slow improvement with the increased H₂ pressure, which indicated that the pressure had no dramatic effect on THFA generation under the current catalytic reaction system.

The temperature dependence of the product distribution was investigated from 30 to 100 °C (Fig. 5(a)) with 100% conversion of FUR. A complete hydrogenation saturation of FUR to THFA could be achieved when the temperature was increased to 40 °C. The selectivity of THFA decreased when the reaction temperature was increased gradually. Cyclopentanone (CPONE), which originated from the hydrogenation rearrangement of FUR and FA in water media, was generated and became the main product at 100 °C. At the same time, a small amount of 2-methyltetrahydrofuran and 5-hydroxy-2-pentanone as well as other unidentified substances were found in the products. The results suggested that temperature had a significant effect on the product distribution for the hy-

drogenation of FUR. A high reaction temperature would promote the rearrangement reaction to form CPONE, which hindered the transformation of FA to THFA (Fig. 5(b)) [14,48]. However, we were unable to obtain more CPONE by further increasing the temperature owing to the aggravated polymerization of FUR and FA under the corresponding catalytic conditions [49]. The target product THFA could be obtained with high selectivity under a mild temperature of 40 °C over the Pd@MIL-101(Cr)-NH₂.

The higher activity and selectivity of Pd@MIL-101(Cr)-NH₂ compared with the other catalysts in the literatures [8,17,19] were mainly attributed to the existence of highly dispersed small Pd nanoparticles on MIL-101(Cr)-NH₂, which was more beneficial for the excitation of reactants. Meanwhile, there were strong host-guest interactions between the framework and metal nanoparticles through coordination and π - π forces, which could also enhance the catalytic activity [50,51].

Table 1 lists the reaction results over Pd@MIL-101(Cr)-NH₂ with different Pd contents and Pd@MIL-101(Cr) at 40 °C and H₂ pressure of 2 MPa. No products were detected at the corresponding reaction time when MIL-101(Cr)-NH₂ was used as catalyst. However, THFA could be obtained as a final product with a selectivity >99.9% through the direct hydrogenation of FUR when using Pd@MIL-101(Cr)-NH₂ with a Pd content of 3.0 wt%. A higher Pd content of 5.4 wt% had no effect on FUR hydrogenation but only slightly reduced the completion time of the reaction, which could be attributed to the greater number of active Pd sites. For comparison, the Pd@MIL-101(Cr) catalyst, which was prepared through a similar impregnation method, could only yield THFA with a selectivity of 53.2% under the same conditions. The higher catalytic performance for the hydrogenation saturation of FUR to THFA over Pd@MIL-101(Cr)-NH₂ compared with that over Pd@MIL-101(Cr) arose from the existence of free amine moieties within the frameworks, which could enhance the hydrophilic nature of the support and the formation of highly dispersed Pd NPs. Furthermore, the amine groups could improve the hydrogen bonding interactions between FA and the MOF matrix, which thus promoted a further hydrogenation of FA to THFA in cooperation with the metallic sites [36]. Therefore, the multifunctional Pd@MIL-101(Cr)-NH₂ resulted in a higher selectivity of THFA for FUR hydrogenation.

The recyclability test was performed with Pd@MIL-101(Cr)-NH₂ under the same reaction conditions to evaluate the catalyst stability. After each cycle of the reaction, the catalyst was separated and washed thoroughly with water and

Fig. 5. (a) Influence of reaction temperature on the products selectivity of FUR hydrogenation over Pd@MIL-101(Cr)-NH₂ (Pd 3.0 wt%) catalyst. Reaction conditions: FUR 2.1 mmol, water 20 mL, amount of catalyst 0.05 g, 2 MPa H₂, 6 h, others include MTHF, 5-hydroxy-2-pentanone and some unknown intermediate products. (b) Reaction pathways of the aqueous phase selectivity hydrogenation of furfural over Pd@MIL-101(Cr)-NH₂ catalysts.

Table 1
Hydrogenation of FUR under different catalysts.

Catalyst	Time (h)	Conversion (%)	Selectivity (%)	
			FA	THFA
MIL-101(Cr)-NH ₂	6	–	–	–
1.3 wt% Pd@MIL-101(Cr)-NH ₂	6	98.9	43.3	56.7
3.0 wt% Pd@MIL-101(Cr)-NH ₂	6	>99.9	0.0	>99.9
5.4 wt% Pd@MIL-101(Cr)-NH ₂	4	>99.9	0.4	99.6
2.7 wt% Pd@MIL-101(Cr)	6	97.7	46.8	53.2

Reaction conditions: FUR, 2.1 mmol, water, 20 mL, catalyst, 0.05 g, hydrogen pressure, 2 MPa, 40 °C, stirring speed, 700 r·min⁻¹.

Fig. 6. Recyclability of Pd@MIL-101(Cr)-NH₂ (Pd 3.0 wt%) for FUR hydrogenation. Reaction conditions: FUR 2.1 mmol, water 20 mL, catalyst 0.05 g, 40 °C, 2 MPa H₂, 6 h.

ethanol, and reduced again at 200 °C for 2 h under an atmosphere of Ar:H₂ = 2:1. In Fig. 6, the conversion rate of FUR exhibited a decrease after the first cycle, which indicated a slight decay of the catalytic activity. However, the FUR could be fully consumed with prolongation of the reaction time, and the THFA could still achieve a high selectivity above 90%. It should be noted that the activity of the catalyst became steady during the next three-cycle experiments. The XRD pattern of the Pd@MIL-101(Cr)-NH₂ catalyst after the reaction showed some decrease in crystallinity compared with the fresh catalyst (Fig. S2), which indicated partial destruction of the crystal framework of the MOF support after several cycles of reaction. The N₂ adsorption experiment showed a slight decrease of the BET surface area for the used Pd@MIL-101(Cr)-NH₂, while the significantly reduced micropore area and volume suggested the collapse of the partial microporous structure (Fig. 1). Meanwhile, the insoluble polymer derived from the polymerization of FA also affected the adsorption of N₂ [11]. Undesirably, the TEM image (Fig. 2) displayed a growth of the particle size from an average diameter size of 3.5 nm for the fresh Pd@MIL-101(Cr)-NH₂ to 5.2 nm for the used Pd@MIL-101(Cr)-NH₂, which suggested that the Pd nanoparticles could not be well stabilized by the MIL-101(Cr)-NH₂ support, which might be the main reason for the slight decrease in the activity of the as-prepared catalyst. To confirm that the decrease of catalytic activity mainly arose from the growth of the Pd rather than the

Pd leaching, ICP experiments with the used Pd@MIL-101(Cr)-NH₂ and reaction liquid were performed. The results showed that the Pd content in Pd@MIL-101(Cr)-NH₂ was higher than 2.9 wt% and no Pd in the reaction liquid was detected.

4. Conclusions

Palladium nanoparticles were successfully incorporated into MIL-101(Cr)-NH₂ by a direct anionic exchange approach followed by hydrogen reduction. The presence of amino groups within the frameworks plays a key role in the formation of uniform and highly dispersed Pd nanoparticles on the support. Pd@MIL-101(Cr)-NH₂ has been demonstrated to be an efficient and reusable heterogeneous catalyst in the aqueous phase selective hydrogenation of the biomass platform compound FUR to THFA under the mild conditions of 40 °C and 2 MPa of H₂. The high activity and selectivity toward THFA benefit from the cooperation between the highly dispersed Pd nanoparticles and amino groups in the framework of MIL-101(Cr)-NH₂. The present results provide the possibility to further extend the applications of Metal@MOF composites to biomass usage.

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Graphical Abstract

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Highly selective hydrogenation of furfural to tetrahydrofurfuryl alcohol over MIL-101(Cr)-NH₂ supported Pd catalyst at low temperature

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Palladium nanoparticles are highly dispersed into MIL-101(Cr)-NH₂ by a direct anionic exchange approach and provide a high yield of tetrahydrofurfuryl alcohol in the hydrogenation of furfural.

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MIL-101(Cr)-NH₂负载Pd低温催化糠醛高选择性加氢生成四氢糠醇

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摘要: 随着资源枯竭和环境污染严重问题的凸显, 生物质转化的研究越来越多, 特别是生物质催化裂解制备生物燃料及高附加值的化学品。糠醛是一种半纤维素酸解的产物, 也是生产糠醇、四氢糠醇、2-甲基呋喃、环戊酮等的重要原料。其中四氢糠醇既可以用于生产其他高附加值化学品, 也可以用作生物燃料或者燃料添加剂。虽然Pd/MFI, Ni/SiO₂, Pd-Ir/SiO₂等催化剂均可用于糠醛选择加氢制备四氢糠醇, 但是反应通常在高温高压条件下进行。为此我们希望找到一种在温和条件下使用的高效催化剂。MOF多孔材料具有丰富的孔道结构、极高的比表面积、表面可修饰的特点, 还可与其他客体发生相互作用, 进而影响催化性能。因此本课题组合成了一种含有氨基的MOF材料MIL-101(Cr)-NH₂, 进一步利用表面氨基吸附Pd的氯酸盐前体, 经还原直接制得负载型催化剂Pd@MIL-101(Cr)-NH₂, 并用于糠醛选择加氢反应。

本文采用X射线粉末衍射(PXRD)、热重分析(TG)、N₂物理吸附-脱附、透射电镜(TEM)等手段表征了所制的MOFs和催化剂。通过将MIL-101(Cr)-NH₂和不同Pd@MIL-101(Cr)-NH₂的XRD谱与标准谱图对比, 发现MIL-101(Cr)-NH₂已成功合成, 并在催化剂制备过程中和反应之后仍然保持稳定。TG结果表明, 所制备MIL-101(Cr)-NH₂在低于350 °C时结构不会被破坏。MIL-101(Cr)-NH₂的比表面积可达1669 m² g⁻¹, 孔容达1.35 cm³ g⁻¹, 从而为Pd纳米粒子均匀分散在载体上提供了可能性。各Pd@MIL-101(Cr)-NH₂样品的TEM照片我们看出, Pd纳米粒子可均匀分散在MIL-101(Cr)-NH₂上, 粒径为3–4 nm。对比实验表明, 氨基与金属的相互作用有利于Pd纳米粒子分散均匀。

将Pd@MIL-101(Cr)-NH₂用于糠醛选择加氢反应时, 在40 °C, 2 MPa H₂的温和条件下, 反应6 h后糠醛完全转化为四氢糠醇其选择性接近100%。表现出比文献报导的更加优异的催化性能。这得益于高度均匀分散的Pd纳米粒子, 以及催化剂载体与Pd纳米粒子的配位作用和 π - π 相互作用。结果还表明当高于80°C反应时, 即有副产物生成, 进一步提高反应温度会促进环戊酮的生成。可见, Pd@MIL-101(Cr)-NH₂所表现的低温高加氢活性对提高四氢糠醇选择性至关重要。

关键词: 金属有机框架材料; 氨基功能化; 钯纳米粒子; 生物质; 选择加氢

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