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Article

Catalytic activity of immobilized Ru nanoparticles in a porous metal-organic framework using supercritical fluid

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ABSTRACT

A Zr-based metal-organic framework (Zr-MOF) with both micropores and mesopores was prepared by the reaction of 1,4-benzenedicarboxylic acid (H_2BDC) and $ZrOCl_2 \cdot 8H_2O$ with the aid of a citric acid (CA) chelating agent and a cetyltrimethylammonium bromide (CTAB) surfactant. This was followed by formation of a $Ru@Zr-MOF$ catalyst from $RuCl_3 \cdot 3H_2O$ in a supercritical CO_2 -methanol solution. The catalyst was characterized by Fourier transform infrared spectroscopy, power X-ray diffraction, transmission electron microscopy, thermo-gravimetric analysis, N_2 adsorption-desorption, X-ray photoelectron spectroscopy, and inductively coupled plasma-atomic emission spectroscopy. Ru particles with an average diameter of 2.3 nm were uniformly supported in the Zr-MOF. The catalytic performance of $Ru@Zr-MOF$ for the hydrogenation of benzene and its derivatives was investigated and was found to be active and stable.

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1. Introduction

Metal-organic frameworks (MOFs) have attracted much attention because of their excellent properties including high surface areas, large pore volumes, and uniform microporous structures [1–4]. These materials have shown great potential for applications in gas storage, separation processes, chemical sensing, optics, and molecular electronics [5–9]. Some MOFs can be used to catalyze reactions owing to their high metal content, highly ordered pores, and internal micropores that can be used as channels for both reactant and product [10–12]. The micropores of most MOFs reported to date, however, are less than 2 nm [13], which results in slow diffusion and decreased reaction rates [14]. It is also sterically more difficult for large molecules to reach the active sites inside a MOF [15]. An effective method to increase the pore size is to use larger linkers that can control pore size and the shape of MOFs [16–19]. However, these extended ligands lead to framework instability

[17]. MOFs with both micropores and mesopores can be produced by the interaction between surfactant molecules and MOF precursors [20–22]. Although this helps increase pore size without sacrificing framework stability, the issue remains a problem with only some progress being made [23–25].

Immobilizing metal nanoparticles in MOFs to prepare Metal@MOF catalysts is usually accomplished by chemical vapor deposition (CVD) and solution-based impregnation methods, followed by reduction of the metallic precursors. They can catalyze various reactions such as oxidation, epoxidation, methoxylation, and hydrogenation [14,15,26,27]. The CVD method is limited by complicated procedures and expensive metal precursors. Solution-based impregnation method is much simpler. However, it creates problems for water-sensitive MOFs (e.g. MOF-5). Furthermore, it is difficult to produce uniformly immobilized metal nanoparticles in the MOFs.

Supercritical fluids (SCFs) have some unique physical properties, such as low viscosity, excellent diffusivity, zero interfa-

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cial tension, and tunable physicochemical properties. They have been applied in extraction and fractionation, chemical reactions, and materials processing [28–33]. Supported catalysts have also been prepared in SCFs, including MOFs and nano-catalysts supported on carbon nanotubes (CNTs) [34–36]. MOFs having both micropores and mesopores are an excellent support for catalysts, and can uniformly immobilize metal nanoparticles. In this work, Zr-MOF with both microporous and mesoporous was prepared as a precursor for Ru@Zr-MOF catalyst that was created in supercritical CO₂-methanol solution. Ru nanoparticles with small size were supported in the Zr-MOF uniformly and robustly catalyzed the hydrogenation of benzene and its derivatives.

2. Experimental

2.1. Catalyst preparation

The procedures to prepare the Zr-MOF were similar to that reported previously [21]. To 2.0 g (12 mmol) of 1,4-benzenedicarboxylic acid (H₂BDC, AR, Beijing Chemical Reagent company, China) dissolved in 50 ml of *N,N*-dimethylformamide (DMF, AR, Beijing Chemical Reagent company, China), 2.4 g of cetyltrimethylammonium bromide (CTAB, AR, Beijing Chemical Reagent company, China) and 0.6 g of citric acid (CA) dissolved in 50 ml of DMF were added. After adding 3.9 g (12 mmol) of zirconium chloride oxide octahydrate (ZrOCl₂·8H₂O, AR, Beijing Chemical Reagent company, China) dissolved in 100 ml of DMF, the mixture was heated at 120 °C for 24 h. The resulting solid was centrifuged and washed with DMF to remove unreacted materials. After washing it twice with ethanol, the powder was dried under vacuum at 60 °C for 24 h. The template was removed by ethanol extraction using a Soxhlet apparatus for 48 h. The final Zr-MOF was obtained by drying the powder at 60 °C for 24 h under vacuum.

The method to prepare Ru@Zr-MOF is similar to that for fabricating CNT-supported noble metal nanoparticles [35]. Zr-MOF powder (0.5 g) dispersed in 5 ml of 0.025 mol/L ruthenium chloride hydrate (RuCl₃·3H₂O, AR, Shenyang Jinke Reagent Factory) methanol solution was placed into a Teflon-lined stainless-steel reactor. After the air in reactor was replaced by CO₂, the reactor was held at 35 °C for 1 h, followed by CO₂ pressure increase to 5.0 MPa. The reactor was then heated at 200 °C for 5 h. After cooling to room temperature, the CO₂ in the reactor was slowly released. The resulting grey solid was washed twice with 20 ml of ethanol and dried under vacuum at 60 °C for 24 h, and dried grey powder was denoted as Ru@Zr-MOF. The loading of Ru in Ru@Zr-MOF determined by inductively coupled plasma-atomic emission spectroscopy (ICP-AES) was 2.42%. During the preparation of Ru@Zr-MOF, methanol served as the co-solvent for enhancing the solubility of RuCl₃ in the solution, as well as being the reductant for the conversion of Ru³⁺ into metallic Ru [35].

Ru/Zr-MOF catalyst was prepared by a impregnation method. Zr-MOF powder (0.5 g) and 5 ml of 0.025 mol/L RuCl₃·3H₂O aqueous solution were added into a Teflon-lined stainless-steel reactor. The mixture was stirred at 30 °C for 5 h

and centrifuged, and then washed twice with water. After washing it with ethanol, the powder was dried under vacuum at 60 °C for 24 h. The dried powder was reduced by H₂ at 220 °C for 4 h, resulting in grey powder denoted as Ru/Zr-MOF. The 2.22% loading of Ru was determined by ICP-AES.

2.2. Hydrogenation of benzene and its derivatives

Hydrogenation of benzene and its derivatives was carried out using the apparatus and procedures similar to that for phenol hydrogenation to cyclohexanone [37]. Here, 0.5 ml of benzene (or its derivatives) and 10 mg of either Ru@Zr-MOF or Ru/Zr-MOF were placed in a 6 ml Teflon-lined stainless-steel reactor. After being purged by low-pressure hydrogen several times to remove the air, the reactor was heated to the desired temperature. Hydrogen was charged to a suitable pressure that was maintained while the reaction mixture was stirred. The pressure was monitored by a transducer (Foxboro/ICT model 930). After a specified reaction time, the mixture was analyzed by Agilent 6820 gas chromatography equipped with a flame ionization detector and a PEG-20M capillary column. In the recycling experiment, the catalyst was separated from the liquid by centrifugation after reaction. After washing it three times with 5 ml of ethanol, it was dried at 60 °C under vacuum for 24 h for the next reaction.

2.3. Catalyst characterization

Fourier transform infrared (FT-IR, Bruker Tensor 27) spectra of the catalysts through compressing with KBr powder were obtained in the region of 4000–400 cm⁻¹. Thermo-gravimetric analyses (TGA) were performed using a NETZSCH STA 409 PC/PG Series Thermal Analysis System with a heating rate of 5 °C/min and air flow of 20 ml/min. The N₂ adsorption-desorption isotherms were measured at –196 °C on a Micromeritics ASAP 2020M. The sample was degassed at 150 °C for 4 h under vacuum before the measurement. Powder X-ray diffraction (XRD) patterns were recorded on a Model D/MAX2500 diffractometer using Cu K_α radiation in the region of 2θ = 1°–80° and a rate of 4°/min. X-ray photoelectron spectroscopy (XPS) data were obtained with an ESCALab 220i-XL (VG Scientific) electron spectrometer using 300 W Al K_α radiation (*hν* = 1486.6 eV). The morphology of the catalysts was characterized by transmission electron microscopy (TEM, JEOL-2011). The content of Ru in the catalysts was determined by ICP-AES (Vista-MPX). The elemental analysis of C, H, and N was performed on a Flash EA 1112 instrument.

3. Results and discussion

3.1. Catalyst characterization results

Figure 1 shows FT-IR spectra of H₂BDC, Zr-MOF, and Ru@Zr-MOF. For H₂BDC, the peaks at 1681 and 1285 cm⁻¹ are attributed to the antisymmetric and symmetric stretching vibrations of the –COO⁻ group, respectively [22,36]. After the reaction of H₂BDC and ZrOCl₂·8H₂O, the FT-IR spectrum of

Fig. 1. FT-IR spectra of H₂BDC (1), Zr-MOF (2), and fresh (3) and used (4) Ru@Zr-MOF samples.

Zr-MOF differs considerably from that of H₂BDC. In the Zr-MOF spectrum, the peaks at 1586 and 1404 cm⁻¹ are also attributed to the antisymmetric and symmetric stretching vibration of the -COO⁻ group, respectively. The wavenumber difference between these two modes in the Zr-MOF (182 cm⁻¹) is smaller than that of H₂BDC (396 cm⁻¹), mainly due to the coordination of the carboxylate group of H₂BDC with the Zr⁴⁺ ion. Similarly, after Ru nanoparticles were supported on Zr-MOF in supercritical CO₂-methanol solution, the antisymmetric and symmetric stretching vibration of the -COO⁻ groups in Ru@Zr-MOF catalyst appear at 1559 and 1409 cm⁻¹, respectively. The wavenumber difference between the modes in Ru@Zr-MOF (150 cm⁻¹) is even smaller than that of the Zr-MOF (182 cm⁻¹). This is mainly due to the coordination of the carboxylate group with Ru, which enhances the stability of the Ru@Zr-MOF. Therefore, Ru nanoparticles can be stably supported in the Zr-MOF, which is beneficial to the recycling of the catalyst.

Figure 2 shows the TGA curves of Zr-MOF and Ru@Zr-MOF. The weight loss below 300 °C is mainly due to desorption of water or residual solvent adsorbed at the surface. The structural decomposition of the Zr-MOF occurs at 555.8 °C and the TGA curve rapidly declines, suggesting the decomposition of organic linker. However, the decomposition temperature of the Ru@Zr-MOF (511 °C) is lower than that of the Zr-MOF (555.8 °C), which may result from the coordination of the carboxylate

Fig. 2. TGA curves of Zr-MOF (1) and Ru@Zr-MOF (2) samples.

Fig. 3. XRD patterns of Zr-MOF (1) and Ru@Zr-MOF (2) samples.

groups of H₂BDC with Ru, as evidenced by the wavenumber shifts of the FT-IR spectra. The interaction of -COO⁻ and Zr⁴⁺ is weakened due to the existence of Ru, leading to the decreased decomposition temperature of Ru@Zr-MOF. It is noteworthy that the decomposition temperatures of both Zr-MOF and Ru@Zr-MOF are higher than 500 °C, indicating that they have excellent thermal stability. The decomposition temperature of Zr-MOF (555.8 °C) prepared from ZrOCl₂·8H₂O in this work is higher than that prepared from ZrCl₄ reported in the literature (Uio-66, 500 °C) [24].

Figure 3 shows the XRD patterns of the Zr-MOF and the Ru@Zr-MOF. It can be seen that the patterns are almost identical, indicating that the Ru nanoparticles have no significant affect on Zr-MOF crystallinity. The diffraction peak for Ru is not observed for Ru@Zr-MOF, because of the small size and high dispersion of the Ru particles. The contents of C, H, and N in Zr-MOF determined by elemental analysis were 27.53%, 2.71%, and 1.11%, respectively. The N may result from DMF and CTAB residues.

Figure 4 shows TEM images of Ru@Zr-MOF (prepared in

Fig. 4. TEM images of Ru@Zr-MOF (a) and Ru/Zr-MOF (b) samples.

Fig. 5. N_2 adsorption-desorption isotherms of Zr-MOF (1) and Ru@Zr-MOF (2) samples.

supercritical CO_2 -methanol) and Ru/Zr-MOF (prepared in aqueous solution). In the Ru@Zr-MOF, Ru nanoparticles (black arrows) with the size of 2.3 nm are supported uniformly. In contrast, Ru particles (white arrows) are inhomogeneously dispersed with appreciable aggregation in the Ru/Zr-MOF. The uniform dispersion in the Ru@Zr-MOF results from the physical properties of the supercritical CO_2 -methanol solution. Furthermore, the methanol reduces the Ru^{3+} to Ru nanoparticles at higher temperatures [35].

Figure 5 shows the N_2 adsorption-desorption isotherms of the Zr-MOF and the Ru@Zr-MOF. Their similar adsorption-desorption isotherms indicate that the Ru nanoparticles have no significant effect on the porous structure. Their isotherms are between type I and type IV, revealing the existence of both micropores and mesopores due to the addition of CA chelating agent and the CTAB surfactant. This is similar with Zhou et al. [21] who reported that microporous and mesoporous Cu-MOF can be obtained only when both CTAB and CA were present, since the chelating agent enables interactions between framework building blocks and surfactants.

The pore size distribution of the Zr-MOF is given in Fig. 6, where the micropore and mesopore distribution curves were obtained by Horvath-Kawazoe and Barrett-Joyner-Halenda

Fig. 6. Pore size distribution (a) and micropore size distribution (b) curves of Zr-MOF.

Fig. 7. Full XPS spectrum of the Ru@Zr-MOF sample.

methods, respectively. The data clearly shows that the Zr-MOFs have both micropores and mesopores. In addition, the BET surface area and total specific pore volume are $235 \text{ m}^2/\text{g}$ and $0.13 \text{ cm}^3/\text{g}$ before, and $273 \text{ m}^2/\text{g}$ and $0.37 \text{ cm}^3/\text{g}$ after, respectively, Ru was supported on the Zr-MOF. The larger BET surface area of Ru@Zr-MOF relative to the Zr-MOF could be due to two factors. One is the efficient elimination of residual DMF, H_2BDC , and CTAB in the pores during supercritical CO_2 -methanol processing. The other is that Ru nanoparticles with small size have high surface areas.

The full XPS spectrum of the Ru@Zr-MOF is showed in Fig. 7. It can be seen that no peak for Cl is detected, indicating that Ru^{3+} is completely converted into Ru in supercritical CO_2 -methanol solution at 200°C .

The Ru 3d spectrum of Ru@Zr-MOF is showed in Fig. 8, where the Ru 3d signal is obscured by the 284.6 eV C 1s signal from a contaminant. The deconvoluted spectrum reveals a doublet for two chemically different Ru entities with peak binding energies of 279.3 eV (Ru $3d_{5/2}$) and 284.8 eV (Ru $3d_{3/2}$). There is no Ru-O peak at 281.1 eV , which confirms the presence of Ru^0 in Ru@Zr-MOF.

3.2. Hydrogenation of benzene and its derivatives

The hydrogenation of aromatics is critical to the petrochemical industry [38], such as reducing the aromatic content of diesel fuel. Moreover, cyclohexane obtained by benzene hydrogenation is one of the key raw materials in the synthesis of

Fig. 8. Ru 3d XPS spectrum of Ru@Zr-MOF sample.

Scheme 1. Schematic illustration for the hydrogenation of benzene and its derivatives.

Nylon-6 and Nylon-66. Here, we carried out the hydrogenation of benzene and its derivatives (Scheme 1) using the Ru@Zr-MOF and the Ru/Zr-MOF catalysts, and the results are listed in Table 1. From Table 1, it can be seen that Ru@Zr-MOF exhibits high catalytic activity at lower temperature (40 °C) and H₂ pressure (2 MPa) in the hydrogenation of benzene (entry 1). By comparison between entries 2 and 3, the catalytic activity of Ru@Zr-MOF is obviously better than that of Ru/Zr-MOF. The main reason is that the Ru nanoparticles in Ru@Zr-MOF are uniformly dispersed in the Zr-MOF and their size is small (Fig. 4(a)), while in Ru/Zr-MOF the Ru particles are inhomogeneously dispersed and their size is larger (Fig. 4(b)). The reaction pressure and temperature are two important factors for the hydrogenations. It is found from entries 1, 2 and entries 2, 8, 9 for benzene that an increase in reaction pressure and temperature can accelerate the reaction rate. Entries 4–7 show that activity of the Ru@Zr-MOF is not reduced notably after it has been used and recycled four times, suggesting that it has very high activity and excellent stability. The FT-IR spectra in Fig. 1 also illustrate the high stability. The spectrum of the recycled Ru@Zr-MOF is nearly the same as that of the virgin catalyst.

Table 1 (entries 10–16) also shows that both Ru@Zr-MOF and Ru/Zr-MOF have high activity for the hydrogenation of toluene, ethylbenzene and *tert*-butylbenzene at 110 °C and 6 MPa of H₂ pressure. For the same benzene derivatives under the same conditions, however, the catalytic activity of the Ru@Zr-MOF is higher than that of the Ru/Zr-MOF. The data also show that the reaction rate decreases with the increasing

length of the reactant carbon chains, primarily due to steric effects.

In our previous work [36], Ru nanoparticles were dispersed (by a supercritical CO₂-methanol solution) on the surface of a La-MOF with only microporous structure. The turnover frequency (TOF) for the hydrogenation of benzene to cyclohexane was 2475 h^{−1} at 60 °C and H₂ pressure of 6 MPa. Under the same reaction conditions, the TOF in the present work reached 5260 h^{−1} (entry 8 in Table 1). The higher activity of the Ru@Zr-MOF originates from the presence of both micropores and mesopores, which enhance the diffusivity of the reactants and products.

4. Conclusions

Zr-MOF materials having both micropores and mesopores were synthesized by the reaction of H₂BDC and ZrOCl₂·8H₂O with the aid of a CA chelating agent and a CTAB surfactant. The Ru@Zr-MOF catalyst was then prepared in supercritical CO₂-methanol solution. This resulted in Ru nanoparticles with small size that were uniformly supported in the Zr-MOF. Whereas in the Ru/Zr-MOF catalyst prepared by immobilizing Ru on the support in aqueous solution, the Ru particles were larger and the dispersion in the Zr-MOF was inhomogeneous. The catalytic activity for hydrogenation of benzene and its derivatives was significantly higher for the Ru@Zr-MOF, relative to that of the Ru/Zr-MOF. Therefore, MOFs having both micropores and mesopores resulting from the supercritical CO₂-methanol method have better diffusivity, which can be quite advantageous in catalysis.

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Table 1

The hydrogenation of benzene and its derivatives under different conditions.

Entry	Catalyst	Substrate	Substrate/Ru (mol/mol)	Temperature (°C)	<i>p</i> (H ₂)/MPa	Time (min)	Conversion (%)	TOF ^b (h ^{−1})
1	Ru@Zr-MOF	benzene	2370	40	2	42	>99.5	>3380
2	Ru@Zr-MOF	benzene	2370	40	6	35	>99.5	>4060
3	Ru/Zr-MOF	benzene	2580	40	6	83	98	1830
4 ^a	Ru@Zr-MOF	benzene	2370	40	6	35	>99.5	>4060
5 ^a	Ru@Zr-MOF	benzene	2370	40	6	35	>99.5	>4060
6 ^a	Ru@Zr-MOF	benzene	2370	40	6	35	>99.5	>4060
7 ^a	Ru@Zr-MOF	benzene	2370	40	6	35	>99.5	>4060
8	Ru@Zr-MOF	benzene	2370	60	6	27	>99.5	>5260
9	Ru@Zr-MOF	benzene	2370	110	6	5	>99.5	>28430
10	Ru@Zr-MOF	toluene	1960	110	6	9	>99.5	>13080
11	Ru@Zr-MOF	ethylbenzene	1705	110	6	22	>99.5	>4650
12	Ru@Zr-MOF	<i>tert</i> -butylbenzene	1350	110	6	39	>99.5	>2070
13	Ru/Zr-MOF	benzene	2580	110	6	11	>99.5	>14090
14	Ru/Zr-MOF	toluene	2140	110	6	20	>99.5	>6420
15	Ru/Zr-MOF	ethylbenzene	1860	110	6	45	>99.5	>2480
16	Ru/Zr-MOF	<i>tert</i> -butylbenzene	1470	110	6	70	>99.5	>1260

Reaction conditions: substrate 0.5 ml, catalyst 10 mg. The product is corresponding to saturation hydrocarbon.

^aRecycling experiments of the catalyst.

^bMoles of substrate consumed per mole of ruthenium per hour.

Graphical Abstract

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超临界流体中制备微孔和介孔结构金属有机框架负载 Ru 及其催化性能

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摘要: 以柠檬酸为螯合剂, 十六烷基三甲基溴化胺为表面活性剂, 通过 $ZrOCl_2 \cdot 8H_2O$ 与对苯二甲酸 (H_2BDC) 反应制备了同时具有微孔和介孔结构的 Zr 基金属有机骨架材料 (Zr-MOF), 并在超临界 CO_2 -甲醇流体中将 Ru 负载于 Zr-MOF 上, 制备了 Ru@Zr-MOF 催化剂. 采用傅里叶变换红外光谱、X 射线粉末衍射、透射电子显微镜、热重分析、 N_2 吸附-脱附、X 射线光电子能谱和电感耦合等离子体发射光谱对催化剂进行了表征, 研究了该催化剂在苯及其同系物加氢反应中的催化性能. 结果表明, Ru 纳米金属颗粒均匀地分散在 Zr-MOF 载体上, 平均粒径约为 2.3 nm, 在苯及其同系物的加氢反应中表现出很高的催化活性和稳定性.

关键词: 金属有机骨架材料; 钌; 超临界流体; 苯同系物; 加氢

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1. 前言

近年来,金属有机骨架(MOFs)材料引起了人们的普遍关注^[1-4],它具有比表面积和孔体积大、材料中有规整的微孔结构等特点,广泛应用于气体储存、物质分离、气体传感、光学和分子电子学等领域^[5-9]. 由于MOFs中金属含量较高,孔型结构规整,内部的微孔为反应物和产物扩散提供了通道,因而可用作许多反应的催化剂^[10-12]. 但是,由于大部分MOFs的孔为微孔,小于2 nm^[13],导致传质受限,因而降低了催化反应速率^[14];而且,尺寸较大的反应物难于进入孔道发生催化反应^[15]. 通过改变有机配体的长度可有效调控MOFs孔径尺寸和形状^[16-19],但有机配体长度的增加容易造成有机骨架稳定性变差^[17]. 研究表明^[20-22],通过表面活性剂和金属前驱体的相互作用能够增加MOFs的孔径,且使材料同时具有微孔和介孔. 因而,制备高稳定性的MOFs备受人们的关注^[23-25].

随着研究的深入,MOFs应用范围不断扩大,其中它可用作负载纳米金属粒子(如Pd, Au, Cu和Ru等)的载体,它主要通过化学气相沉积法和浸渍法将金属前驱物置入MOFs的孔道中,经还原得到Metal@MOF催化剂,可用于氧化、环氧化、甲氧基化和加氢等催化反应^[14,15,26,27]. 化学气相沉积法制备过程比较复杂,所用的金属前驱物比较昂贵,因而其应用受到限制;浸渍法操作简单,广泛用于金属催化材料的负载,可在水介质中进行,因而不适用于水敏感性的MOFs材料(如MOF-5). 另外,如何将金属粒子均匀负载到MOFs上一直是制备的难点.

超临界流体具有粘度低,扩散系数大,表面张力为零,物理化学性质连续可调等特性,可用于萃取分离、化学反应和材料制备等领域,表现出广阔的应用前景^[28-33]. 利用超临界流体制备负载型催化材料已见诸多报道,其中包括碳纳米管和MOF等载体负载的纳米金属催化材料^[34-36]. 因此,用超临界流体制备同时具有微孔和介孔结构MOFs负载金属纳米粒子可以发挥超临界流体的许多特点,但目前尚未见报道. 本文制备了具有微孔和介孔结构的Zr-MOF,然后用超临界CO₂-甲醇流体制备了Ru@Zr-MOF催化剂,并用于苯及苯同系物的加氢反应研究.

2. 实验部分

2.1. 催化剂的制备

Zr-MOF的制备方法与文献[21]相似. 在50 ml溶有2.0 g (12 mmol) 对苯二甲酸(H₂BDC, AR, 北京化学试剂公司)的*N,N*-二甲基甲酰胺(DMF, AR, 北京化学试剂公司)溶液中,加入50 ml含有2.4 g十六烷基三甲基溴化胺(CTAB, AR, 北京化学试剂公司)和0.6 g柠檬酸(CA, AR, 北京化学试剂公司)的DMF溶液,搅拌均匀后,加入100 ml溶有3.9 g ZrOCl₂·8H₂O (AR, 北京化学试剂公司)(12 mmol)的DMF溶液,将混合溶液搅拌均匀后加热至120 °C静置反应24 h再离心分离除去剩余的反应物和溶剂,并用DMF洗两次,乙醇洗两次. 在60 °C真空干燥沉淀产物. 然后,以乙醇作为提取液将得到的固体粉末在索氏提取器中洗涤48 h,最后在60 °C真空烘干得到Zr-MOF粉末.

Ru@Zr-MOF的制备见文献[35]. 将0.5 g Zr-MOF粉末和5 ml RuCl₃·3H₂O 甲醇溶液(0.025 mol/L)加入带有聚四氟乙烯内衬的不锈钢反应釜中,用CO₂置换釜中的空气,然后在35 °C通入5 MPa CO₂并保持1 h,然后加热至200 °C. 反应5 h,再冷却至室温,缓慢放出釜中的CO₂,将所得灰色沉淀用20 ml乙醇洗两次后,在60 °C真空烘干,所得灰色固体粉末记为Ru@Zr-MOF. ICP-AES测定表明,样品中Ru负载量为2.42%. 在此过程中,甲醇既作为共溶剂增加CO₂对Ru前驱体的溶解能力,又作为还原剂将Ru离子还原为金属^[35].

采用浸渍法制备Ru/Zr-MOF. 将0.5 g Zr-MOF粉末和5 ml RuCl₃·3H₂O 水溶液(0.025 mol/L)加入带有聚四氟乙烯内衬的不锈钢反应釜中,在30 °C搅拌5 h后离心分离,沉淀物用水洗两次,乙醇洗一次,再在60 °C的真空烘箱中烘干,然后在220 °C用H₂还原4 h,得到的灰色固体粉末记为Ru/Zr-MOF. ICP-AES测得Ru/Zr-MOF中Ru负载量为2.22%.

2.2. 苯及其同系物的加氢反应^[37]

将0.5 ml苯或苯的同系物和10 mg Ru@Zr-MOF(或Ru/Zr-MOF)催化剂加入到6 ml带有聚四氟乙烯内衬的不锈钢反应釜中,用H₂置换釜中的空气,再加热至所需温度,充入H₂到适当压力,启动磁力搅拌器,反应过程中

维持压力不变,可通过压力传感器(Foxboro/ICT model 930)进行测定.反应结束后,通过Agilent 6820型气相色谱仪(配有PEG-20M毛细管柱和FID检测器)分析反应产物的组成.将离心分离出的催化剂用5 ml乙醇洗三次,然后在60 °C真空干燥24 h后直接用于下次反应.

2.3. 催化剂的表征

用Bruker Tensor 27型红外光谱仪测定催化剂的红外光谱(FT-IR),KBr压片制样,扫描范围4000~400 cm^{-1} ,仪器分辨率1 cm^{-1} .催化剂的热重分析(TGA)使用NETZSCH STA 409 PC/PG型热重分析仪,加热速率5 °C/min,空气流速20 ml/min.样品 N_2 吸附-脱附等温线采用Micromeritics ASAP2020M型物理吸附仪在-196 °C下测定,样品在150 °C预处理4 h. X射线粉末衍射分析(XRD)在D/MAX 2500型X射线衍射仪上测定,扫描范围 $2\theta=1^\circ\sim 80^\circ$,扫描速率4°/min. X射线光电子能谱(XPS)在ESCALab220i-XL型能谱仪上采集,使用 $\text{Al K}\alpha$ 线为激发源($h\nu=1486.6\text{ eV}$).催化剂的形貌用日本JEOL-2011型透射电子显微镜(TEM)进行观测.催化剂中Ru负载量采用电感耦合等离子体发射光谱(ICP-AES, Vista-MPX)仪测定. C, H和N元素分析在Flash EA 1112型元素分析仪上进行.

3. 结果与讨论

3.1. 催化剂的表征结果

图1为 H_2BDC , Zr-MOF和 Ru@Zr-MOF 样品的FT-IR谱. 1681和1285 cm^{-1} 处吸收峰分别归属于 $-\text{COO}^-$ 的对称和不对称伸缩振动^[22,36],当它与 $\text{ZrOCl}_2\cdot 8\text{H}_2\text{O}$ 反应形成Zr-MOF后,这对吸收峰分别移至1586和1404 cm^{-1} ,波数差(182 cm^{-1})明显小于 H_2BDC (396 cm^{-1}).这主要是由于 H_2BDC 的两个羧基与 Zr^{4+} 发生了配位作用.当Zr-MOF在超临界 CO_2 中负载纳米Ru后, Ru@Zr-MOF 催化剂中的 $-\text{COO}^-$ 对称和不对称伸缩振动峰分别出现在1559和1409 cm^{-1} 处,其波数差值(150 cm^{-1})进一步减小.这主要是由于 $-\text{COO}^-$ 不仅和 Zr^{4+} 发生了配位作用,还与Ru发生作用,从而增加了 Ru@Zr-MOF 的稳定性.可见,Ru纳米颗粒能稳定地负载在Zr-MOF载体上,因而有利于 Ru@Zr-MOF 催化剂的重复利用.

图2为Zr-MOF和 Ru@Zr-MOF 样品的TGA曲线.可以看出,两个样品在300 °C前均有失重,这主要是由于样品表面有吸附的水或者少量残余溶剂,其中Zr-MOF样品在555.8 °C后失重显著,表明有机配体发生分解;而 Ru@Zr-MOF 在511 °C开始分解.这主要是由于

Ru@Zr-MOF 中 $-\text{COO}^-$ 不仅和 Zr^{4+} 发生了配位作用,还与Ru发生作用,在一定程度上减弱了有机配体 $-\text{COO}^-$ 与 Zr^{4+} 的作用,导致样品分解温度略有下降.总体而言,Zr-MOF和 Ru@Zr-MOF 分解温度都高于500 °C,表明均具有良好的热稳定性.当采用 ZrCl_4 制备Zr-MOF时,其分解温度为500 °C^[24],低于本文值.

图3为Zr-MOF和 Ru@Zr-MOF 样品的XRD谱.由图可见,两种样品的晶体结构基本一致,表明Ru的负载没有改变晶体结构.另外,在 Ru@Zr-MOF 的谱图上也未发现Ru纳米颗粒的衍射峰,这主要是由于Ru纳米颗粒较小而且分布比较均匀.元素分析表明,Zr-MOF材料中C, H和N的含量分别为27.53%, 2.71%和1.11%,其中N元素的存在源于溶剂和表面活性剂的部分残留.

图4为 Ru@Zr-MOF 和 Ru/Zr-MOF 催化剂的TEM照片.可以看出,用超临界 CO_2 -甲醇制备的 Ru@Zr-MOF 催化剂中Ru纳米粒子比较均匀地分散在Zr-MOF载体中,且粒径较小,平均粒径约为2.3 nm;而采用水浸渍法负载制备的 Ru/Zr-MOF 中Ru金属颗粒分布不均匀,且有明显的聚集.这主要是因为超临界 CO_2 具有粘度低、扩散性好和表面张力为零等特殊性质,因而能将Ru前驱体均匀负载到载体的各个部位,升高温度后甲醇能将 Ru^{3+} 还原为Ru金属粒子^[35].

图5为Zr-MOF和 Ru@Zr-MOF 样品的 N_2 吸附-脱附等温线.可以看出,两个样品的吸附-脱附等温线基本一致,表明样品Ru的负载没有明显改变Zr-MOF的孔结构.它们的等温曲线介于IV和I型之间,表明同时具有介孔和微孔的结构.这主要是由于在制备过程中加入了螯合剂和表面活性剂的缘故.Zhou等^[21]利用螯合剂CA和表面活性剂CTAB制备了具有介孔和微孔结构的Cu-MOFs材料,并证实只有螯合剂和表面活性剂同时存在时才能得到介孔和微孔结构,这主要是由于螯合剂起到了金属有机骨架和表面活性剂的联接作用.

图6为Zr-MOF样品的孔径分布图.其中微孔和介孔分布曲线分别用HK和BJH方法得到.由图可见,Zr-MOF样品同时具有微孔和介孔结构.Zr-MOF和 Ru@Zr-MOF 样品的BET比表面积和孔体积分别为235 m^2/g , 0.13 cm^3/g 和273 m^2/g , 0.37 cm^3/g .在催化剂制备过程中,由于超临界 CO_2 -甲醇是良好的溶剂,可除去MOF材料孔中部分残余的溶剂、 H_2BDC 和表面活性剂分子;同时负载的Ru纳米粒子尺寸很小,比表面积很大,因此,Ru的负载使得Zr-MOF样品的比表面积有所增加.

图7为 Ru@Zr-MOF 的完整XPS谱.可以看出,谱中

没有Cl元素,表明200℃时在超临界CO₂-甲醇流体中能将RuCl₃完全还原为金属Ru.

图8为Ru@Zr-MOF催化剂的Ru 3d XPS谱. 由图可见,尽管Ru 3d_{3/2}电子结合能(284.6 eV)受到C 1s的影响而变得比较模糊,但是284.8和279.3 eV处仍有Ru 3d_{3/2}和Ru 3d_{5/2}能级的两个能谱峰,且没有Ru–O的能谱峰,说明Ru物种以Ru⁰形式存在于催化剂Ru@Zr-MOF中.

3.2. 苯及其苯同系物的加氢催化反应

芳香烃的加氢反应在石油化工和精细化工中占有非常重要的地位^[38],如可用于降低柴油中芳香烃浓度,从而提高柴油的质量. 本文将超临界CO₂-甲醇中制备的Ru@Zr-MOF催化剂和水溶液中制备的Ru/Zr-MOF催化剂用于苯及苯同系物的加氢反应(见图式1)中,催化反应结果列于表1. 可以看出,对于苯加氢,Ru@Zr-MOF在较低的温度(40℃)和H₂压力(2 MPa)下具有很高的催化活性(实验1). 比较实验2和实验3发现,Ru@Zr-MOF的催化活性明显高于Ru/Zr-MOF的活性,这主要是由于Ru@Zr-MOF中Ru纳米金属颗粒在载体上的分散更为均匀,颗粒尺寸较小(约2.3 nm),而Ru/Zr-MOF中Ru金属颗粒分布不均匀,且有明显的聚集. 表1还考察了反应压力和温度对反应性能的影响. 结果表明,提高反应压力(实验1和2)和温度(实验2,8和9)都有利于提高反应速率. 催化剂Ru@Zr-MOF的重复使用结果(实验4~7)表明,Ru@Zr-MOF重复使用4次后,其催化活性不变,说明具有较高的重复使用性能. 如图1所示,反应4次后

Ru@Zr-MOF的FT-IR谱与反应前基本一致

表中还给出了Ru@Zr-MOF和Ru/Zr-MOF催化剂上苯同系物加氢反应结果. 由表可见,在110℃和6 MPa H₂的反应条件下,两种催化剂对甲苯、乙苯以及叔丁基苯加氢都具有高的催化活性,且Ru@Zr-MOF的催化活性明显更高. 还可以看出,随着取代基碳链的增加,反应速率有所下降,这主要是由于受到苯环上取代基空间结构的影响.

在前期工作中^[36],我们曾在超临界CO₂-甲醇溶液中将Ru负载于只有微孔结构的La-MOF表面上,在60℃和6 MPa的条件下苯加氢生成环己烷反应TOF值为2475 h⁻¹;而在相同反应条件下,本文的TOF值高达5260 h⁻¹以上(实验8). 主要原因在于Zr-MOF同时具有微孔和介孔,有利于反应物和产物的扩散以及反应的发生.

4. 结论

在螯合剂和表面活性剂的作用下,通过ZrOCl₂·8H₂O与对苯二甲酸反应制备了同时具有微孔和介孔结构的Zr-MOF,并在超临界CO₂-甲醇流体中,制备了负载型Ru@Zr-MOF催化剂. 结果表明,该催化剂中Ru纳米颗粒尺寸较小,且在载体中分散均匀;而采用浸渍法制备的Ru/Zr-MOF催化剂,Ru金属颗粒较大,且分布不均匀. 因此,在苯及其同系物加氢反应中,Ru@Zr-MOF催化活性明显更高. 用超临界流体制备这类新型负载催化材料具有明显的优势,显示了良好的发展前景.