Synthesis of mesoporous γ -Fe₂O₃ supported palladium nanoparticles and investigation of their roles as magnetically recyclable catalysts for nitrobenzene hydrogenation

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ABSTRACT

The mesoporous γ -Fe₂O₃ (maghemite) supported palladium catalysts (written as Pd/meso- γ -Fe₂O₃) are synthesized using impregnation and one-step sol-gel methods and characterized by PXRD, BET, TEM, EDX, and XPS. The synthesized Pd/meso- γ -Fe₂O₃ catalysts are applied in nitrobenzene hydrogenation reactions under 50 °C and 1 atm and their catalytic activities are compared with Pd/comm-Fe₂O₃, Pd/meso-SiO₂, and Pd/meso-C catalysts, in order to study the effect of the catalyst support. The TOF number of a 1% Pd/meso- γ -Fe₂O₃-im catalyst is highest among all the synthesized catalysts, attributed to the well dispersed Pd nanoparticles on the iron oxide support of large surface area, large pore size, and an interconnected network. All the mesoporous γ -Fe₂O₃ nanoparticle catalysts show characteristics of superparamagnetic behavior and thus can be easily retrieved by an external magnetic field. Significant catalyst activity decay is observed with 1% Pd/meso- γ -Fe₂O₃-im catalyst due to Pd leaching. However, improvement in activity of the recycled catalyst is observed when the one-step sol-gel synthesis method is used.

1. INTRODUCTION

Aniline is an important precursor for the manufacture of polyurethane, indigo, and other industrial chemicals. The common industrial method for aniline production is through catalytic hydrogenation of nitrobenzene ^[1,2]. In the process, carbon supported noble metal catalysts are widely used ^[2–10]. However, improvement of the catalyst is limited by some obstacles. The first obstacle is attributed to the use of an inactive carbon support. Although active carbon provides a high surface area, Pd cannot be anchored as efficiently as some basic supports, such as hydrotalcite ^[1]. Moreover, active carbon cannot act as effectively as basic supports (metal oxide support) to bond nitrobenzene strongly by a noble metal-support interface ^[11–13], which will promote the reaction rate of the catalytic hydrogenation reaction. The second obstacle exists when small pore size and pore volume catalyst supports are used, restricting the dispersion of Pd nanoparticles and diffusion of reactants ^[14–18]. The third obstacle is the difficulty of recycling the catalysts. Since the noble metal catalysts are very expensive, separation and recycling of the catalyst are desirable ^[19–27]. Magnetically separable catalysts are attractive heterogeneous catalysts due to their facile recycling process ^[28–30].

A great deal of effort has been put to overcome these obstacles in order to synthesize effective catalysts for the nitrobenzene hydrogenation reaction. Improvement of the carbon support has been studied in the literature. Torres et al. ^[31] found that carbon supports treated with ozone and hydrogen peroxide could reinforce noble metal dispersion and hydrogenation capacity, compared with untreated ones. This is because treated carbon supports, which have weak acid sites formed on the surface, have stronger interaction with the noble metal precursors. Banerjee et al. ^[14] studied the immobilization of noble metals into mesoporous materials. They encapsulated Pd nanoparticles into mesoporous MCM-48 matrix, which could catalyze hydrogenation reactions under aerobic conditions. The excellent activity of the catalyst was mostly due to their large surface area, better metal dispersion, and interpenetrating network of three dimensional pores of MCM-48. Liu et al. ^[17] dispersed bimetallic nanoparticles (PtPd/AuPd/AuPt) into mesoporous metal oxides ($\text{TiO}_2/\text{Al}_2\text{O}_3/\text{SiO}_2/\text{ZrO}_2$) by a one-step sol-gel method. The use of mesoporous metal oxides as catalyst supports had two functions: one was to protect nanoparticles from aggregation and improve their thermal stability; the other was to enhance the catalytic activity by providing acid/base and redox sites or desired interfaces. Moreover, researchers studied the

nitrobenzene hydrogenation reaction over magnetically supported palladium catalysts. Yi et al.^[21] synthesized silica-coated magnetic nanoparticles as the support for Pd nanoclusters. The synthesized catalysts could be easily recycled by an external magnet and reused at least 5 times with 100% conversion in nitrobenzene hydrogenation. Although the studies mentioned above focused on overcoming each obstacle in catalysis for nitrobenzene hydrogenation separately, a catalyst with properties that can improve (1) the functionality of the catalyst support, (2) the mesoporosity and porous network of the support, and (3) the recyclability of the catalyst are all still under exploration.

University of Connecticut (UCT) materials are a series of mesoporous materials recently developed using a sol-gel based inverse micelle method^[32]. They contain tunable structural properties such as surface area, pore volume and size, and interconnected mesopores formed between randomly packed nanocrystals^[32]. UCT materials have shown excellent activities in many applications^[33,34]. Mesoporous γ -Fe₂O₃ (UCT-64), an aggregate of nanoparticles, is a member of this family. Mesoporous γ -Fe₂O₃ has properties, such as monomodal pore size distribution, large surface area, and interconnected mesopores, all of which can contribute to an active support for an effective hydrogenation catalyst.

In this study, synthesis of mesoporous γ -Fe₂O₃ supported Pd catalysts and their application in nitrobenzene hydrogenation are investigated, trying to overcome the three main obstacles discussed above at the same time. In particular, iron oxide support is proposed to act as a base which can adsorb nitrobenzene to initiate the first step of heterogeneous catalysis, adsorption. The aggregated maghemite nanoparticles exhibit superparamagnetic behavior, which enables easy recycling of the catalysts. The interconnected mesoporous network enhances the Pd dispersion and diffusion of reactants and products. The catalytic performance of Pd/meso- γ -Fe₂O₃ catalyst is compared with a commercial Fe₂O₃ supported Pd catalyst, mesoporous SiO₂ supported Pd catalyst and mesoporous carbon supported Pd catalyst. The turnover frequency numbers of catalysts are calculated as an indicator of the activity of a catalyst for the nitrobenzene hydrogenation reaction. Finally, the recyclability of Pd/meso- γ -Fe₂O₃ catalysts is studied.

2. EXPERIMENTAL SECTION

2.1 Preparation of catalysts

Pd/meso- γ -Fe₂O₃ by impregnation method

For the synthesis of the mesoporous γ -Fe₂O₃ support, a solution was prepared by adding 0.01 mol iron nitrate, 0.12 mol 1-butanol, 0.019 mol nitric acid, and 2.04×10^{-4} mol poly(ethylene glycol)-block-poly(propylene glycol)-block-poly(ethylene glycol) (P123, $M_n \sim 5800$). The clear solution was placed in the oven at 100 °C and then heated to 150 °C for 12 hours and 250 °C for 4 hours under an air atmosphere. The freshly made palladium nitrate aqueous solution with the same volume as the pore volume of the mesoporous γ -Fe₂O₃ support was added to mesoporous γ -Fe₂O₃. Then the Pd impregnated mesoporous γ -Fe₂O₃ was dried at 40 °C for 30 min to remove water and heated at 150 °C for 1 hour to remove the nitrate ions. Pd loading amounts on mesoporous γ -Fe₂O₃ were 1% and 2% in molar ratio. The catalysts synthesized in this way are written as 1% Pd/meso- γ -Fe₂O₃-im and 2% Pd/meso- γ -Fe₂O₃-im (listed in Table 1). Both catalysts were reduced under mild conditions in hydrogen before the reactions.

Pd/meso- γ -Fe₂O₃ by one-step sol-gel method

The palladium nitrate was added in the initial solution which contained 0.01 mol iron nitrate, 2.04×10^{-4} mol P123, 0.019 mol nitric acid, and 0.12 mol 1-butanol. All the following synthesis steps were the same as those for mesoporous γ -Fe₂O₃ [32]. Pd loadings of 1% and 2% molar ratio were used to synthesize Pd/meso- γ -Fe₂O₃ following the one-step sol-gel method. These catalysts are written as 1% Pd/meso- γ -Fe₂O₃-os and 2% Pd/meso- γ -Fe₂O₃-os (listed in Table 1). Both catalysts were reduced under mild conditions in hydrogen before the reactions.

Other Catalysts containing Pd by impregnation method

Commercial Fe₂O₃ (non-porous maghemite), mesoporous SiO₂, and mesoporous carbon were also used as the supports to synthesize Pd-containing catalysts. The Pd impregnation of these materials follows the exact same procedures as those of the Pd impregnated mesoporous γ -Fe₂O₃ catalysts. Mesoporous SiO₂ and mesoporous carbon were synthesized by the same inversed micelle method as the mesoporous mesoporous γ -Fe₂O₃ [32]. All the catalysts synthesized by the impregnation method with these supports were loaded with 1% Pd molar content. These catalysts are written as 1% Pd/comm-Fe₂O₃-im, 1% Pd/meso-SiO₂-im, and 1% Pd/meso-C-im, respectively (listed in Table 1). All the catalysts were reduced under mild conditions in hydrogen before the reactions.

2.2 Characterization

Ultima IV Rigaku X-ray diffractometer with Cu K α radiation ($\lambda=1.54 \text{ \AA}$) was used to analyze the catalysts. The beam voltage and current were 40 kV and 45 mA. The low-angle and high-angle powder X-ray diffraction (PXRD) patterns were obtained at scan rates of $0.5^\circ \text{ min}^{-1}$ and 2° min^{-1} , respectively. The peaks were indexed with the International Center for Diffraction Data (ICDD) PDF-2 database. Nitrogen isotherms were obtained in a Micrometitics ASAP 2020 Accelerated Surface Area and Porosimetry System. The samples were degassed at 120°C for 12 hours to remove adsorbed water and other species before analysis. The Barrett-Joyner-Halenda (BJH) method was used to calculate pore sizes and pore volumes by desorption isotherms. Transmission electron microscopy (TEM) images were taken in a JEOL 2010 instrument with an accelerating voltage of 200 kV and energy-dispersive X-ray spectroscopy (EDX) system. EDX spectra were acquired in the same JEOL 2010 instrument as well. X-ray photoelectron spectroscopy (XPS) was used to determine the surface properties of catalysts in a PHI 590 multiprobe system. Measurement of the dc magnetization were carried out for $-50 \text{ kOe} \leq H \leq +50 \text{ kOe}$ at a temperature $T=300 \text{ K}$ using a Quantum Design MPMS-5 superconducting quantum interference device (SQUID) magnetometer.

2.3 Nitrobenzene hydrogenation

Solvent ethanol (25 mL) with 25 mg catalyst was bubbled in an inert gas atmosphere (30 mL/min nitrogen) for 1 hour to create an inert gas atmosphere. Then the suspension was purged with 30 mL/min hydrogen for 0.5 hour at 50°C under reflux for *in-situ* reduction of catalysts. When the catalyst was ready, nitrobenzene (2.5 mmol) was injected into the solution to start the reaction. During the reaction, the vessel was kept at 50°C and 1 atm under reflux, very mild conditions as compared with those in the literature ^[3,18,35–37]. Samples were taken every 20 min to analyze the conversion of nitrobenzene and concentration of reaction intermediates and products. All the samples were filtered with a $0.45 \text{ }\mu\text{m}$ -PVDF syringe filter (Pall Corporation) and then analyzed as a function of time with an Agilent 7820A gas chromatograph with a 5975 MS detector (GC/MS system).

3. RESULTS

3.1 Characterization of catalysts

Figure S1 shows the low-angle PXRD patterns of mesoporous SiO₂, 1% Pd/meso-SiO₂-im, mesoporous carbon, 1% Pd/meso-C-im, commercial Fe₂O₃, 1% Pd/comm-Fe₂O₃-im, mesoporous γ -Fe₂O₃, 1% and 2% Pd/meso- γ -Fe₂O₃-im, and 1% and 2% Pd/meso- γ -Fe₂O₃-os catalysts. Mesoporous SiO₂, mesoporous carbon, and mesoporous γ -Fe₂O₃ catalysts show peaks in the low-angle PXRD patterns, reflecting meso-structures of these catalysts. After synthesis of Pd-containing catalysts using impregnation and one-step sol-gel methods, all the catalysts still show peaks in low-angle PXRD patterns, indicating that after impregnating or doping Pd into the mesoporous supports, the supports still maintain a meso-structure. The *d*-spacings of mesoporous SiO₂, mesoporous carbon, mesoporous γ -Fe₂O₃ are 38 Å (2.30°), 54 Å (1.65°), and 41 Å (2.14°), respectively. After Pd impregnation, the *d*-spacings of 1% Pd/meso-SiO₂-im and 1% Pd/meso-C-im catalysts shift to 23 Å (3.83°) and 24 Å (3.71°) while the peak positions of 1% and 2% Pd/meso- γ -Fe₂O₃-im catalysts do not change much. Although the peak positions of 1% and 2% Pd/meso- γ -Fe₂O₃-im catalysts in the low-angle PXRD patterns remain relatively unaffected, the change of the shape of peaks indicates that the impregnation of Pd nanoparticles has an impact on the structure of mesoporous γ -Fe₂O₃. The 1% and 2% Pd/meso- γ -Fe₂O₃-os catalysts both show peaks at a *d*-spacing of 41 Å (2.15°) in the low-angle PXRD patterns.

Figure S2 shows the high-angle PXRD patterns of mesoporous SiO₂, 1% Pd/meso-SiO₂-im, mesoporous carbon, 1% Pd/meso-C-im, mesoporous γ -Fe₂O₃, 1% and 2% Pd/meso- γ -Fe₂O₃-im, and 1% and 2% Pd/meso- γ -Fe₂O₃-os catalysts. Mesoporous SiO₂ and mesoporous carbon show broad peaks at 23.1° and 22.8°, respectively. After 1% Pd impregnation, a weak peak at $2\theta=33.8^\circ$ is observed in the high-angle PXRD pattern of mesoporous SiO₂, which matches well with PdO (standard PDF card 02-1432). After 1% Pd impregnation, weak peaks at $2\theta=33.8^\circ$, 42.3°, 55.2°, 61.0°, and 72.2° are observed in the high-angle PXRD pattern of mesoporous carbon, which also match well with PdO. The 1% and 2% Pd/meso- γ -Fe₂O₃ catalysts synthesized using the impregnation and one-step sol-gel methods match with maghemite (standard PDF card 39-1346) very well. The palladium peaks are too small to be observed in the high-angle PXRD patterns of Pd/meso- γ -Fe₂O₃ catalysts synthesized using the impregnation and one-step sol-gel methods. Using the Scherrer equation and the broadening of the (220), (311), (400), (422), (511), and (440) reflections, the particle sizes of 1% Pd/comm-Fe₂O₃-im, 1% Pd/meso- γ -Fe₂O₃-im, 2% Pd/meso- γ -Fe₂O₃-im, 1% Pd/meso- γ -Fe₂O₃-os, 2% Pd/meso- γ -Fe₂O₃-os catalysts are 25.8 nm, 11.9 nm, 11.9 nm, 12.8 nm, and 8.1 nm, respectively. The particle sizes of 1% Pd/meso-SiO₂-im

and 1% Pd/meso-C-im catalysts are not available because of their amorphous nature shown in high-angle PXRD patterns.

Table 1 lists the surface area and porosity of mesoporous SiO₂, 1% Pd/meso-SiO₂-im, mesoporous carbon, 1% Pd/meso-C-im, commercial Fe₂O₃, 1% Pd/comm-Fe₂O₃-im, mesoporous γ -Fe₂O₃, 1% and 2% Pd/meso- γ -Fe₂O₃-im, and 1% and 2% Pd/meso- γ -Fe₂O₃-os catalysts. The surface areas of 1% Pd/meso-SiO₂-im and 1% Pd/meso-C-im catalysts decrease after Pd impregnation compared with the original mesoporous SiO₂ and carbon. The pore sizes of 1% Pd/meso-SiO₂-im and 1% Pd/meso-C-im also changed after Pd impregnation compared with original mesoporous SiO₂ and mesoporous carbon due to the impregnation of palladium. The surface area, pore size, and pore volume of 1%, 2% Pd/meso- γ -Fe₂O₃-im and 1% Pd/meso- γ -Fe₂O₃-os catalysts are similar to the original mesoporous γ -Fe₂O₃ catalyst. The 1% and 2% Pd/meso- γ -Fe₂O₃-os catalysts have larger surface areas and pore volumes than the intrinsic mesoporous γ -Fe₂O₃ catalyst. The 2% Pd/meso- γ -Fe₂O₃-os catalyst has a larger pore size than 1% Pd/meso- γ -Fe₂O₃-os and intrinsic mesoporous γ -Fe₂O₃ catalysts. The BET isotherms of these catalysts are shown in Supporting Information Figure S3. All the N₂ isotherms of mesoporous samples before and after Pd loadings are Type IV isotherms, which indicate the mesoporosity of the structures.

Table 1: The structural parameters of catalysts containing Pd by the impregnation and one-step sol-gel methods.

	Surface area (m ² /g)	Pore size (Å)	Pore volume (cm ³ /g)
Mesoporous SiO ₂	442	18	0.01
1% Pd/meso-SiO ₂ -im	27	27	0.03
Mesoporous Carbon	424	32	0.04
1% Pd/meso-C-im	41	20	0.03
Commercial Fe ₂ O ₃	26	-	-
1% Pd/comm-Fe ₂ O ₃ -im	26	-	-
Mesoporous γ -Fe ₂ O ₃	99	54	0.14
1% Pd/meso- γ -Fe ₂ O ₃ -im	95	52	0.13
2% Pd/meso- γ -Fe ₂ O ₃ -im	99	56	0.14

1% Pd/meso- γ -Fe ₂ O ₃ -os	105	56	0.16
2% Pd/meso- γ -Fe ₂ O ₃ -os	118	71	0.23

- Not available

Figure 1 shows the TEM images of 1% Pd/meso-SiO₂-im, 1% Pd/meso-C-im, 1% Pd/comm-Fe₂O₃-im, 1% and 2% Pd/meso- γ -Fe₂O₃-im, and 1% and 2% Pd/meso- γ -Fe₂O₃-os catalysts. The support of the Pd/meso- γ -Fe₂O₃ catalyst is spherical, “hedgehog-like”, or “pin-cushion” aggregates that consist of radially oriented nanoparticles. In circled areas of the TEM images, Pd/Fe or Pd/Si or Pd/C ratios are different from the ratios in bulk areas. The Pd/Fe or Pd/Si or Pd/C ratios of circled areas and bulk from EDX spectra are listed in Table 2. The dispersion of Pd nanoparticles in the mesoporous γ -Fe₂O₃ matrix can be observed by TEM images at the thin region of the sample (Figure S4 (a)) and the dark spots are proved to be Pd nanoparticles by the inserted HRTEM image. The bulk Pd/Fe ratios of 1% Pd/comm-Fe₂O₃-im, 1% and 2% Pd/meso- γ -Fe₂O₃-im, and 1% and 2% Pd/meso- γ -Fe₂O₃-os catalysts are 0.026, 0.023, 0.054, 0.024, and 0.048, respectively. The bulk Pd/Fe₂O₃ ratios of 1% Pd/comm-Fe₂O₃-im, 1% and 2% Pd/meso- γ -Fe₂O₃-im, and 1% and 2% Pd/meso- γ -Fe₂O₃-os catalysts are 0.013, 0.012, 0.027, 0.012, and 0.024, respectively. So the actual Pd concentrations in these five catalysts are close to Pd concentrations we used for synthesis.

Figure 1: TEM images of (a) 1% Pd/meso-SiO₂-im, (b) 1% Pd/meso-C-im, (c) 1% Pd/comm-Fe₂O₃-im, (d) 1% Pd/meso- γ -Fe₂O₃-im, (e) 2% Pd/meso- γ -Fe₂O₃-im, (f) 1% Pd/meso- γ -Fe₂O₃-os, and (g) 2% Pd/meso- γ -Fe₂O₃-os catalysts. (scale bar 20 nm) .

Figure S5 shows XPS spectra of the Pd 3d region of 1% Pd/meso-SiO₂-im, 1% Pd/meso-C-im, 1% Pd/comm-Fe₂O₃-im, 1% and 2% Pd/meso- γ -Fe₂O₃-im, and 1% and 2% Pd/meso- γ -Fe₂O₃-os catalysts after the *in-situ* reduction. To analyze XPS spectra, the peaks were deconvoluted to all the possible Pd species, like Pd, PdO, PdO₂, Pd(NO₃)₂, or combinations of these possible Pd species. The most reasonable peak fittings are shown in Figure S5. From the deconvolution of the curves, the most possible species existing in the catalysts after *in-situ* reduction is Pd(0). The spectra show two main peaks at around 335.5 eV and 340.7 eV, which can be ascribed to Pd 3d_{5/2} and Pd 3d_{3/2}, respectively. The Pd/Fe ratios from XPS survey that give the surface compositions of catalysts are listed in Table 2. The Pd/Fe ratios on the surface of 1% Pd/comm-Fe₂O₃-im, 1% and 2% Pd/meso- γ -Fe₂O₃-im, and 1% Pd/meso- γ -Fe₂O₃-os catalysts are similar to the bulk. Only for 2% Pd/meso- γ -Fe₂O₃-os catalyst is the Pd/Fe ratio on the surface much higher than that in the bulk.

Table 2: Pd/Fe ratio or Pd/Si or Pd/C ^a by EDX and XPS survey

	Circled area _b	Bulk ^b	Surface ^d
1% Pd/meso-SiO ₂ -im	17.8	0.029	-
1% Pd/meso-C-im	-	0.112 ^c	-
1% Pd/comm-Fe ₂ O ₃ -im	-	0.026	0.012
1% Pd/meso- γ -Fe ₂ O ₃ -im	-	0.023	0.011
2% Pd/meso- γ -Fe ₂ O ₃ -im	0.179	0.054	0.051
1% Pd/meso- γ -Fe ₂ O ₃ -os	0.213	0.024	0.029
2% Pd/meso- γ -Fe ₂ O ₃ -os	0.106	0.048	0.219

^a Pd/Fe ratio applies to 1% Pd/comm-Fe₂O₃-im, 1% Pd/meso- γ -Fe₂O₃-im, 2% Pd/meso- γ -Fe₂O₃-im, 1% Pd/meso- γ -Fe₂O₃-os, and 2% Pd/meso- γ -Fe₂O₃-os catalysts; Pd/Si ratio applies to 1% Pd/meso-SiO₂-im. Pd/C ratio applies to 1% Pd/meso-C-im catalyst.

^b “Circled area and bulk” refer to different regions in TEM images and both ratios were obtained from EDX detector which is attached TEM.

^c Pd/C ratio of 1% Pd/meso-C-im is obtained with an EDX detector attached to a scanning electron microscope by putting the sample on a copper tape. This ratio is for reference only, because it can be affected by the environment.

^d Surface composition ratio was obtained from XPS survey analysis. The surface compositions of 1% Pd/meso-SiO₂-im and 1% Pd/meso-C-im catalysts are not available because of the low signal to noise ratio of Pd in these two samples.

- Not available.

Figure 2 shows magnetization hysteresis loops obtained at 300 K for mesoporous $\gamma\text{-Fe}_2\text{O}_3$, 1% Pd/meso- $\gamma\text{-Fe}_2\text{O}_3$ -im, 2% Pd/meso- $\gamma\text{-Fe}_2\text{O}_3$ -im, 1% Pd/meso- $\gamma\text{-Fe}_2\text{O}_3$ -os, and 2% Pd/meso- $\gamma\text{-Fe}_2\text{O}_3$ -os catalysts. The saturated magnetization values of 1% and 2% Pd/meso- $\gamma\text{-Fe}_2\text{O}_3$ -im catalysts are 51.3 emu/g and 50.8 emu/g, respectively. The saturated magnetization values of 1% and 2% Pd/meso- $\gamma\text{-Fe}_2\text{O}_3$ -os catalysts are 46.0 emu/g and 48.0 emu/g, respectively. For comparison, the saturation magnetization for mesoporous $\gamma\text{-Fe}_2\text{O}_3$ is 52.4 emu/g. The magnetization curves show no remanence or coercivity at 300 K (room temperature), suggesting superparamagnetic behavior required for magnetic separation ^[38].

Figure 2: Magnetization hysteresis loops obtained at 300 K for: (a) mesoporous $\gamma\text{-Fe}_2\text{O}_3$, (b) 1% Pd/meso- $\gamma\text{-Fe}_2\text{O}_3$ -im, (c) 2% Pd/meso- $\gamma\text{-Fe}_2\text{O}_3$ -im, (d) 1% Pd/meso- $\gamma\text{-Fe}_2\text{O}_3$ -os, and (e) 2% Pd/meso- $\gamma\text{-Fe}_2\text{O}_3$ -os catalysts. The absence of remanence and coercivity at room temperature is necessary for magnetic separation.

3.2 Nitrobenzene hydrogenation

Figure 3 shows the catalytic conversions of nitrobenzene hydrogenation reactions using 1% Pd/meso- SiO_2 -im, 1% Pd/meso-C-im, 1% Pd/comm- Fe_2O_3 -im, 1% and 2% Pd/meso- $\gamma\text{-Fe}_2\text{O}_3$ -im, and 1% and 2% Pd/meso- $\gamma\text{-Fe}_2\text{O}_3$ -os catalysts. Among all the 1% Pd impregnated catalysts, the 1% Pd/meso- $\gamma\text{-Fe}_2\text{O}_3$ -im provides a faster reaction rate (100% conversion within 80 min) than 1% Pd/comm- Fe_2O_3 -im, 1% Pd/meso- SiO_2 -im, and 1% Pd/meso-C-im catalysts. When 1% Pd/comm- Fe_2O_3 -im, 1% Pd/meso-C-im, 1% Pd/meso- SiO_2 catalysts are used, 64%, 100%, and 4% conversions of nitrobenzene are reached after 120 min reaction time, respectively. Moreover, the

rate of reaction over 2% Pd/meso- γ -Fe₂O₃-im catalyst is greater than that of 1% Pd/meso- γ -Fe₂O₃-im catalyst. For the catalysts synthesized by one-step sol-gel method, 100% conversion is reached within 80 min with the 2% Pd/meso- γ -Fe₂O₃-os catalyst whereas only 76% nitrobenzene is converted after 120 min reaction time when 1% Pd/meso- γ -Fe₂O₃-os catalyst is used. A blank experiment was performed with intrinsic mesoporous γ -Fe₂O₃ without Pd loading (shown in Figure S6).

Figure 3: Catalytic performance of catalysts containing Pd synthesized by the impregnation and one-step sol-gel methods for nitrobenzene hydrogenation.

Figure 4 shows the turnover frequency (TOF) numbers of 1% Pd/meso-SiO₂-im, 1% Pd/meso-C-im, 1% Pd/comm-Fe₂O₃-im, 1% and 2% Pd/meso- γ -Fe₂O₃-im, and 1% and 2% Pd/meso- γ -Fe₂O₃-os catalysts for the nitrobenzene hydrogenation reaction. The TOF number is defined as the moles of nitrobenzene converted per Pd site per hour. The TOF numbers are calculated based on the reaction time at 50% conversion except 1% Pd/meso-SiO₂. The TOF number of 1% Pd/meso-SiO₂ is calculated based on the conversion at the largest reaction time (120 min) because of the low conversion on this catalyst. The values in the “bulk” column of EDX data of Table 2 are used to calculate actual Pd active sites in the catalysts since the amounts of Pd on the surfaces of some catalysts are not available from XPS surveys. The TOF numbers of Pd/meso- γ -Fe₂O₃ catalysts synthesized by the impregnation method (1% Pd/meso- γ -Fe₂O₃-im, TOF 982 h⁻¹;

2% Pd/meso- γ -Fe₂O₃-im, TOF 474 h⁻¹) and one-step sol-gel method (1% Pd/meso- γ -Fe₂O₃-os, TOF 686 h⁻¹; 2% Pd/meso- γ -Fe₂O₃-os, TOF 626 h⁻¹;) are all larger than those of 1% Pd/meso-SiO₂-im (TOF 12 h⁻¹), 1% Pd/meso-C-im (TOF 12 h⁻¹) catalysts, and 1% Pd/comm-Fe₂O₃-im catalyst (TOF 411 h⁻¹) catalysts. Among Pd/meso- γ -Fe₂O₃ catalysts synthesized by the impregnation and one-step sol-gel methods, 1% Pd/meso- γ -Fe₂O₃-im has the largest TOF number. The TOF numbers of 2% Pd/meso- γ -Fe₂O₃-im, 1% Pd/meso- γ -Fe₂O₃-os, and 2% Pd/meso- γ -Fe₂O₃-os catalysts are similar to each other. If the TOF value of our best catalyst, 1% Pd/meso- γ -Fe₂O₃-im, is calculated by the surface Pd content instead of bulk Pd content, the TOF value will be 2166 h⁻¹. This is better than the reported TOF value of 5-Pd/SiO₂ catalyst (292 h⁻¹) from Yan et. al.^[39] and comparable with the TOF values of Pd/hydrotalcites catalysts (2500 h⁻¹) from Sangeetha et. al.^[11].

Figure 4: TOF numbers of catalysts containing Pd synthesized by the impregnation and one-step sol-gel methods for nitrobenzene hydrogenation.

3.3 Catalyst recyclability

Figure 5 shows the recyclability of 1% Pd/meso- γ -Fe₂O₃-im, 2% Pd/meso- γ -Fe₂O₃-im, 1% Pd/meso- γ -Fe₂O₃-os, and 2% Pd/meso- γ -Fe₂O₃-os catalysts. With the 1% Pd/meso- γ -Fe₂O₃-im catalyst, only 2% conversion is reached after 120 min in the 2nd cycle of reaction. With the 2%

Pd/meso- γ -Fe₂O₃-im catalyst, 61% conversion is reached after 120 min in the 2nd cycle of reaction and only less than 4% conversion is reached after 120 min in the 3rd cycle of reaction. In contrast, Pd/meso- γ -Fe₂O₃ catalysts synthesized by the one-step sol-gel method perform better in recyclability than Pd/meso- γ -Fe₂O₃ catalysts synthesized by the impregnation method. With the 1% Pd/meso- γ -Fe₂O₃-os catalyst, 27% conversion can be reached after 120 min in the 2nd cycle of reaction and 4% conversion is reached after 120 min in the 3rd cycle of reaction. With the 2% Pd/meso- γ -Fe₂O₃-os catalyst, 100% conversion can be reached within 90 min in the 2nd cycle of reaction while 88% and 50% conversions are reached in the 3rd and 4th cycles of reaction, respectively.

Figure 5: Recyclability of (a) 1% Pd/meso- γ -Fe₂O₃-im catalyst, (b) 2% Pd/meso- γ -Fe₂O₃-im catalyst, (c) 1% Pd/meso- γ -Fe₂O₃-os catalyst, and (d) 2% Pd/meso- γ -Fe₂O₃-os catalyst.

Figure S7 shows the high-angle PXRD patterns of 1% Pd/meso- γ -Fe₂O₃-im, 2% Pd/meso- γ -Fe₂O₃-im, 1% Pd/meso- γ -Fe₂O₃-os, and 2% Pd/meso- γ -Fe₂O₃-os catalysts before and after reactions. The high-angle PXRD patterns were collected from recycled catalysts after the last cycle of recyclability experiments. Consistent PXRD patterns are shown between initial 1% Pd/meso- γ -Fe₂O₃-im catalyst, 2% Pd/meso- γ -Fe₂O₃-im, 1% Pd/meso- γ -Fe₂O₃-os, 2% Pd/meso- γ -

Fe₂O₃-os catalysts and their recycled catalysts. This means all the Pd/meso- γ -Fe₂O₃ catalysts maintain their crystal structures after recyclability experiments.

4. DISCUSSION

4.1 Structure of catalysts

From Figure S1, after impregnation, the *d*-spacings of mesoporous SiO₂ and mesoporous carbon catalysts change from 18Å to 27Å and from 32Å to 20Å, respectively. At the same time, there is a decrease in the surface areas of mesoporous SiO₂ and mesoporous carbon catalysts after impregnation (Table 1). The pore sizes of mesoporous SiO₂ and mesoporous carbon are close to micropores since the mesopore range is 2-50 nm and the micropore range is < 2nm according to IUPAC. The decrease in *d*-spacings of mesoporous SiO₂ and carbon shown in XRD patterns and structural parameters of impregnated catalysts suggests that the Pd nanoparticles accommodate inside the mesopores because a lot of space in the mesoporous network is occupied after impregnation. Since the pore sizes of these materials are small, the impregnation process could affect the structure of the materials. The Pd nanoparticles occupied a lot of space in the micro/mesopores of mesoporous SiO₂ and carbon catalysts. The decrease of surface area of the catalysts synthesized by the incipient wet impregnation method was also observed by Sangeetha et al. ^[1]. For the 1% Pd/comm-Fe₂O₃-im catalyst, the surface areas and low-/high-angle PXRD patterns are almost the same as the intrinsic commercial Fe₂O₃ catalyst, because the non-porous structure of commercial Fe₂O₃ leads to the existence of Pd nanoparticles on the outer surface. For the Pd/meso- γ -Fe₂O₃-im catalysts, compared with intrinsic mesoporous Fe₂O₃, the pore sizes, surface areas and pore volumes of the structure are preserved because of large pore size of the mesoporous γ -Fe₂O₃ support. On the high-angle PXRD patterns, all the peaks are retained as well, due to the low Pd loading. However, in low-angle PXRD patterns, the shape of the pattern changes more significantly when more Pd is impregnated on the support. This means the impregnation of Pd will also affect the *d*-spacing of mesoporous γ -Fe₂O₃. For Pd/meso- γ -Fe₂O₃-os catalysts, low-angle and high-angle PXRD patterns stay the same as in the intrinsic mesoporous γ -Fe₂O₃. When the mesoporous γ -Fe₂O₃ catalyst is doped with 1% Pd, the surface areas, pore sizes, and pore volumes of the catalyst remain similar to the intrinsic mesoporous γ -Fe₂O₃. However, when mesoporous γ -Fe₂O₃ is doped with 2% Pd, the surface areas, pore sizes, and pore volumes become larger than those of intrinsic mesoporous γ -Fe₂O₃. This is attributed to

the change of the mesoporous $\gamma\text{-Fe}_2\text{O}_3$ structure caused by the large amount of Pd content. As shown in another study^[32], calcination causes the aggregation of nanoparticles, which will result in a decrease of surface area. The large amount of Pd content prevents the aggregation of iron oxide nanoparticles during the calcination, so the 2% Pd/meso- $\gamma\text{-Fe}_2\text{O}_3$ -os catalyst has a larger surface area than the intrinsic mesoporous Fe_2O_3 catalyst. When a large amount of Pd is added into the initial solution, the formation of micelles is disturbed to some extent, which likely makes the micelle formation incomplete. The pores formed from incomplete micelles are not stable. They could merge with other pores during calcination, leading to a larger pore size and pore volume than in the intrinsic mesoporous $\gamma\text{-Fe}_2\text{O}_3$.

The Pd/Fe or Pd/Si or Pd/C ratios in the circled area, in the bulk, and on the surface of all the Pd containing catalysts are shown in Figure 1 and Table 2. For 1% Pd/comm- Fe_2O_3 -im and 1% Pd/meso- $\gamma\text{-Fe}_2\text{O}_3$ -im catalysts, no region with particularly high Pd/Fe ratio is observed. The Pd nanoparticles in these catalysts are not gathering in a small region of the iron oxide support and are dispersed relatively better than those in other catalysts. For 2% Pd/ meso- $\gamma\text{-Fe}_2\text{O}_3$ -im, 1% Pd/ meso- $\gamma\text{-Fe}_2\text{O}_3$ -os, 2% Pd/meso- $\gamma\text{-Fe}_2\text{O}_3$ -os, and 1% Pd/meso-SiO₂-im catalysts, Pd/Fe or Pd/Si ratios in the circled region are higher than those in the bulk. The Pd nanoparticles are not well dispersed in these supports. Comparing 1% and 2% Pd/meso- $\gamma\text{-Fe}_2\text{O}_3$ -im catalysts, the mesoporous $\gamma\text{-Fe}_2\text{O}_3$ cannot impregnate Pd nanoparticles homogeneously when the Pd loading amount is 2%. Comparing 1% Pd/meso- $\gamma\text{-Fe}_2\text{O}_3$ -im and 1% Pd/meso- $\gamma\text{-Fe}_2\text{O}_3$ -os catalysts, the one-step sol-gel method cannot disperse Pd nanoparticles very well, because, when the Pd/meso- $\gamma\text{-Fe}_2\text{O}_3$ catalysts are synthesized by the one-step sol-gel method, the Pd nanoparticles change the structure of the iron oxide support, leading to the gathering of Pd nanoparticles in the circled region. For all the Pd containing catalysts except 2% Pd/meso- $\gamma\text{-Fe}_2\text{O}_3$, the Pd/Fe ratios obtained by EDX are similar to those obtained by the XPS data. Pd nanoparticles stay in the bulk of the catalysts rather than gathering on the surface of catalysts. For 2% Pd/meso- $\gamma\text{-Fe}_2\text{O}_3$ catalyst, the Pd/Fe ratio on surface is much higher than that in the bulk. Part of the Pd nanoparticles is ejected out of the iron oxide support during the merging of pores during calcination. The Pd/C ratio in 1% Pd/meso-C-im catalyst is for reference only because of the carbon element in the ambient experiment environment.

4.2 Effect of supports – mesoporous SiO₂, mesoporous carbon, commercial Fe₂O₃ and mesoporous- γ -Fe₂O₃

Compared with the 1% Pd/comm-Fe₂O₃-im catalyst (Figure 3), 1% Pd/meso- γ -Fe₂O₃-im catalyst has much higher activity in nitrobenzene hydrogenation reactions. Since these two catalysts are both prepared by the impregnation method, the major difference between them exists in the support – one is a mesoporous support and the other is a non-porous support. The higher activity of the 1% Pd/meso- γ -Fe₂O₃-im catalyst is probably due to two reasons related to the mesoporous support: one is that the mesoporous support has a larger surface area, pore size, and pore volume, which can provide more sites and disperse Pd better than the non-porous materials; the other is that the mesoporous support can reduce the mass transport of reactants and/or products ^[40]. All the catalysts supported on mesoporous γ -Fe₂O₃ in this study have higher TOF numbers than commercial non-porous γ -Fe₂O₃. Compared with 1% Pd/meso-SiO₂-im and 1% Pd/meso-C-im catalysts, the activity of 1% Pd/meso- γ -Fe₂O₃-im catalysts for the nitrobenzene hydrogenation reaction is much higher. This is consistent with Ge et al. ^[41], who found that the basic sites (oxygen vacancies) of iron oxide support could help palladium catalysts reach higher activity in the glycerol hydrogenolysis reaction. The reason for oxide supported catalysts being more active in nitrobenzene hydrogenation reaction is possibly due to the large surface area and phases of iron oxide nanoparticles ^[42,43], or the strong interaction between palladium and iron oxide supports ^[41,44,45]. It is not fair to compare the Pd/meso- γ -Fe₂O₃-im with Pd/meso-SiO₂-im and Pd/meso-C-im catalysts, because of the significant decrease of surface areas of silica and carbon supports after Pd impregnation. It seems surface area and pore size have significant impact on the catalyst activity. Further studies focusing on the synthesis of Pd impregnated materials (include mesoporous γ -Fe₂O₃, silica, and carbon) with higher surface area and proper pore size are necessary. However, for comparison purposes, the Pd impregnated catalysts are synthesized under identical procedures in this study. The better catalytic performance of iron oxide support might be restricted to the current impregnation method. An exhaustive study on optimizing the synthesis conditions for the Pd impregnated mesoporous γ -Fe₂O₃, silica, and carbon individually and in comparison with their catalytic performance in nitrobenzene hydrogenation may be interesting as future work.

4.3 Effect of preparation method – impregnation method vs one-step sol-gel method

Comparing the 1% Pd/meso- γ -Fe₂O₃-im and 1% Pd/meso- γ -Fe₂O₃-os catalysts (Figure 4), the TOF number of 1% Pd/meso- γ -Fe₂O₃-im catalyst is about 30% higher than that of 1% Pd/meso- γ -Fe₂O₃-os catalyst. This is possibly because 1% Pd/meso- γ -Fe₂O₃-os catalyst has some Pd nanoparticles inside the iron oxide support which are not accessible to reactant. The Pd nanoparticles of 1% Pd/meso- γ -Fe₂O₃-im catalyst stay on the surface of the iron oxide support, which makes them more available for reaction than those inside the iron oxide support. One possible reason for the high TOF number of 1% Pd/meso- γ -Fe₂O₃-im catalyst is that the Pd nanoparticles are well dispersed in the support due to a large pore size and interconnected network of mesoporous γ -Fe₂O₃ (Figure 1 and Table 2). No apparent aggregation of Pd nanoparticles in 1% Pd/meso- γ -Fe₂O₃-im catalysts occurs (Figure 1 and Table 2). Compared with 2% Pd/meso- γ -Fe₂O₃-im and 2% Pd/meso- γ -Fe₂O₃-os catalysts, the TOF numbers are similar while the low TOF number of 2% Pd/meso- γ -Fe₂O₃-im catalyst is due to the aggregation of Pd nanoparticles in the support; the low TOF number of 2% Pd/meso- γ -Fe₂O₃-os catalyst is because not all the Pd nanoparticles are accessible to reaction which is discussed in detail in Section 4.4. Another reason for high activity of 1% Pd/meso- γ -Fe₂O₃-im catalysts could be also due to the leached homogeneous Pd nanoparticles ^[46,47]. From a recyclability perspective, the one-step sol-gel method helps to improve the noble metal leaching problem which is further discussed in Section 4.6.

4.4 Effect of Pd loading amount

From Figure 3, the reaction rate of nitrobenzene hydrogenation reaction becomes faster when the Pd amount in the catalysts increases. This is reasonable in the sense that Pd is well-known as an effective catalyst for reactions related to hydrogen in a variety of reactions ^[48]. However, in this study, the reaction rate of 2% Pd/meso- γ -Fe₂O₃-im catalyst is only slightly faster than that of 1% Pd/meso- γ -Fe₂O₃-im catalyst. The TOF number of 2% Pd/meso- γ -Fe₂O₃-im catalyst is almost half of that of the 1% Pd/meso- γ -Fe₂O₃-im catalyst. As discussed in Section 4.1, in the 2% Pd/meso- γ -Fe₂O₃-im catalyst, there is aggregation of Pd nanoparticles, which makes not all the Pd nanoparticles accessible for reaction. This is why although the Pd impregnation amount is doubled in 2% Pd/meso- γ -Fe₂O₃-im catalyst, the activity only increases a small amount.

From Figure 3, 2% Pd/meso- γ -Fe₂O₃-os catalyst has better catalytic performance than 1% Pd/meso- γ -Fe₂O₃-os catalyst. However, from Figure 4, the TOF numbers of nitrobenzene

hydrogenation reaction on 1% and 2% Pd/meso- γ -Fe₂O₃-os catalysts are similar. This means that the better performance of 2% Pd/meso- γ -Fe₂O₃-os catalyst is mainly due to the larger amount of Pd. Although Pd/meso- γ -Fe₂O₃ synthesized by the one-step sol-gel method cannot disperse Pd nanoparticles homogeneously, the overall effectiveness of Pd nanoparticles in the catalysts is similar.

4.5 Selectivity of Pd/meso- γ -Fe₂O₃ catalysts

All the Pd containing catalysts used in this study have > 97% selectivity to aniline after reactions, because the reaction mainly follows a direct pathway. The nitrobenzene hydrogenation reaction has two possible reaction pathways^[49]: one is the direct route; the other is the condensation route. The direct route of nitrobenzene hydrogenation will occur when the hydrogenation over the catalysts is sufficiently fast to prevent condensation of phenylhydroxylamine with nitrosobenzene. In the direct route, the reactions catalyzed by the Pd containing catalysts follow this path: nitro compound $\rightarrow$ (nitroso compound $\rightarrow$) hydroxylamine $\rightarrow$ aniline derivative^[50]. In the condensation route, the condensation of hydroxylamine and nitroso intermediates is the step to form impurities. A typical GC spectrum of a sample solution during nitrobenzene hydrogenation reaction is shown in Figure S8. Typical MS spectra of impurities hydroxylamine and N-ethylaniline are shown in Figure S9. In the GC spectrum, only trace amounts of hydroxylamine and N-ethylaniline are observed in the reaction solution which are intermediates and products of possible aldol condensation side reactions, respectively^[51]. The product of the reaction (aniline) is further confirmed by nuclear magnetic resonance spectroscopy (Figure S10). For side reactions, trace amounts of acetaldehyde in the ethanol solvent react with the product aniline following an aldol condensation reaction mechanism. The product of this aldol condensation reaction is N-ethylideneaniline. Then N-ethylideneaniline is reduced by hydrogen to form N-ethylaniline. The proposed pathways of nitrobenzene hydrogenation and aldol condensation side reaction are shown in Figure 6.

Figure 6: The proposed pathways of nitrobenzene hydrogenation reaction (upper row) and possible side reaction by aldol condensation (lower row).

4.6 Recyclability of Pd/meso- γ - Fe_2O_3 catalysts

The 1% and 2% Pd/meso- γ - Fe_2O_3 -im catalysts have an obvious decay in catalytic performance in the 2nd cycle of reaction (Figure 5 (a) and (b)). This is due to serious leaching of palladium. The leaching problem in this study is confirmed by TEM images. The TEM images of the catalyst with highest TOF values (1% Pd/meso- γ - Fe_2O_3 catalyst) before and after the reaction are shown in Figure S4. Before the reaction, Pd nanoparticles are well dispersed in the iron oxide matrix. The dark spots in Figure S4 (a) are proven to be Pd nanoparticles by matching Pd (111) lattice spacings in the inserted HRTEM images. But after the reaction, there's no evidence of Pd nanoparticles in the selected region (shown in the EDX pattern). This indicates that part of the Pd nanoparticles leached out during the reaction. Agglomeration of Pd nanoparticles on Pd/meso- γ - Fe_2O_3 catalysts cannot be observed by TEM. When the sizes of Pd particles are large, the contrast of the Pd particles becomes similar to those of overlapped iron oxide nanoparticles.

Leaching of the effective metals during experiments has been observed on catalysts synthesized by the impregnation method in many studies ^[4,8,15,39,52,53]. In the literature, there are several approaches that can mitigate leaching from the perspective of modifying synthesis methods. Webb et al. ^[54] loaded palladium on functionalized mesoporous silica by a grafting approach. The catalysts can be highly active and recyclable for Suzuki–Miyaura coupling reaction under

certain reaction conditions. Su et al. ^[55] synthesized ruthenium nanoparticles by impregnating ruthenium into mesoporous materials then thermally reducing ruthenium to ruthenium nanoparticles. The nanoparticles showed high activity and stability in hydrogenation of monoaromatics with less leaching. Banerjee et al. ^[14] synthesized Pd-MCM-48 using tetra-n-octylammonium bromide as a capping and stabilizing agent of Pd nanoparticles during typical Stober syntheses of MCM-48. The synthesized catalysts can be used at least ten times for hydrogenation of olefins with minimal loss of activity. Ge et. al ^[56] synthesized core-shell nanocomposite catalysts using superparamagnetic Fe₃O₄ as a core and protecting noble metal nanoparticles by mesoporous silica shell. The catalysts with protection of mesoporous silica shell showed high activity after 6 cycles of reduction of 4-nitrophenol.

In this study, the one-step sol-gel method is investigated to help mitigate the noble metal leaching problem ^[57]. With the same Pd loading amount, Pd/meso- γ -Fe₂O₃-os catalysts have better recyclability than Pd/meso- γ -Fe₂O₃-im catalysts. From Figure 5 (d), in the 1st and 2nd cycle of reaction, 100% nitrobenzene is converted within 80 min over 2% Pd/meso- γ -Fe₂O₃-os catalyst. In the 3rd cycle of reaction, although there is some decay in catalytic performance, 88% conversion of nitrobenzene can still be reached after 120 min reaction time over the 2% Pd/meso- γ -Fe₂O₃-os catalyst. Overall, the catalysts synthesized by the one-step sol-gel method can help improve the recyclability of the catalyst compared to the catalysts synthesized by impregnation methods.

5. CONCLUSIONS

Magnetically recyclable Pd/meso- γ -Fe₂O₃ catalysts have been successfully synthesized by impregnation and one-step sol-gel methods. The catalysts are designed to have large surface areas, pore sizes, and pore volumes, which promote the dispersion of Pd nanoparticles. All of the synthesized catalysts have very high selectivity for the aniline product in the nitrobenzene hydrogenation reaction. Higher Pd loading accelerates the reaction catalyzed by Pd/meso- γ -Fe₂O₃ catalysts using the impregnation and one-step sol-gel methods. Among all the synthesized catalysts using the impregnation method, the 1% Pd/meso- γ -Fe₂O₃-im catalyst has the highest activity and highest TOF number due to its large surface area, pore size, pore volume, and

interconnected network of the iron oxide support. The 2% Pd/meso- γ -Fe₂O₃-im catalyst has similar reaction rate with the 1% Pd/meso- γ -Fe₂O₃-im catalyst due to Pd nanoparticle aggregation. The 1% Pd/meso- γ -Fe₂O₃-im catalyst has a higher activity than 1% Pd/meso- γ -Fe₂O₃-os catalyst because of more accessible Pd nanoparticles on the surface of the mesoporous Fe₂O₃ support in the Pd/meso- γ -Fe₂O₃-im catalyst. The Pd/meso- γ -Fe₂O₃ catalysts synthesized by impregnation method have a decay in performance after the 1st run of the reaction due to the leaching of Pd nanoparticles. The one-step sol-gel synthesis method can help improve the recyclability of the Pd/meso- γ -Fe₂O₃ catalysts by preventing leaching, compared to the impregnation method.

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