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Solid-state CTAB-assisted synthesis of mesoporous Fe₃O₄ and Au@Fe₃O₄ by mechanochemistry

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ABSTRACT

Mesoporous iron oxides have shown excellent performance in many research areas such as catalysts, biosensors, enzyme immobilization, heavy metal adsorption, and drug delivery. The state-of-the-art synthesis methods are mostly wet chemistry processes. This paper reports a solvent-free approach for the rapid synthesis of mesoporous Fe₃O₄ (specific surface area up to 170 m²/g) and Au@Fe₃O₄ (highly dispersed Au nanoparticles, average particle size: ~4 nm). With different amounts of added template agent, cetyltrimethylammonium bromide (CTAB), the pore structure could easily be adjusted. More importantly, the mesoporous Fe₃O₄ exhibited good catalytic activity in carbon monoxide (CO) oxidation, outperforming commercially purchased Fe₃O₄ with 100% CO conversion at around 274 °C vs. 490 °C for the commercial product.

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1. Introduction

Carbon monoxide (CO) pollution, generated by incomplete combustion of fossil fuels (e.g., coal and oil), automobile exhaust, and industrial waste gases, has become a health and environmental problem that cannot be ignored because of its high toxicity to the human nervous system. Increasing concerns have prompted chemists to design and develop various catalysts for CO oxidation [1,2] in air purification, pollution control, and fuel cell technologies. In particular, mesoporous catalysts, including the widely used mesoporous transition metal oxides and noble metals, tend to exhibit superior catalytic activities in some kinds of CO catalytic oxidation [3–7]. Research on highly efficient catalysts as well as the design and optimization of the preparation technology of porous catalysts to complete the oxidation process more effectively is of great significance for basic research as well as for the chemical industry.

Among various metal oxides, ferroferric oxide (Fe₃O₄) has

been considered as one of the most promising materials for mesoporous catalysts or supports because of its intriguing properties such as low cost, high chemical and thermal stabilities (remaining stable during sintering), widespread availability, nontoxicity, and environment friendly features [8–12]. Furthermore, the introduction of mesopores into this iron oxide gives rise to a material with more exposed catalytic sites and improved surface functionalities [13]. The enlarged surface areas make this material a promising candidate for application in heterogeneous catalysis. Recent attempts have also focused on the preparation of metal oxides loaded with precious metals (Pd, Pt, Au, etc.) [14–18] for catalytic oxidation of CO. In addition, the pore structure (pore sizes and pore volumes), particle size of the noble metal, and surface area are also the major factors that determine the final catalytic properties. These properties lead to a synergetic effect on the activity of the catalyst in CO oxidation, which is normally higher than that of commercially purchased catalysts.

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In general, the typical synthesis strategy of mesoporous materials involves soft templating pathways and hard templating approaches [19,20]. The common loading processes for noble metals include precipitation [21], sedimentation, impregnation, etc. [22,23]. Unfortunately, most of these are wet chemical processes with inherent disadvantages such as the requirement for complex steps, the use of excessive solvent, the production of liquid waste, and time- and energy-consuming drying treatments (most require drying or solvent evaporation) [24]. Mechanochemical synthesis has shown advantages in the synthesis of porous solid materials because it benefits from intermolecular interactions that utilize the frictional heat and mechanical momentum generated by the ball milling process. Researchers have already introduced mechanochemistry into the preparation of metal organic frameworks (MOFs) [25–30], ordered mesoporous carbon (OMC) [31,32], covalent organic frameworks (COFs) [33–35], zeolites [36–38], etc.

Herein, solid-state synthesis, a green strategy, is proposed to synthesize mesoporous Fe_3O_4 and $\text{Au@Fe}_3\text{O}_4$ catalysts. In this process, the spontaneous organic-inorganic self-assembly between reactants (e.g., iron nitrate as precursor, and cetyltrimethylammonium bromide (CTAB) as the template) is accomplished with mechanical ball milling in the solid phase, replacing solvent-based technology. Then, sintering is utilized to obtain mesoporous iron oxide powders and noble-metal-loaded catalysts under an air atmosphere. No further wet chemical processes are required. Finally, to further evaluate the catalytic activity of these catalysts, their catalytic performance in a CO oxidation reaction was monitored. It is apparent that such a strategy is comparable to traditional templating methods in industrial manufacturing because it involves easy, solvent-free, less time- and energy-consuming, and environment-friendly preparation [39]. However, some existing deficiencies of current solid-state synthesis strategy still need to be addressed, which will be discussed later.

2. Experimental

2.1. Materials and instruments

The principal materials for mechanochemical synthesis of mesoporous Fe_3O_4 are as follows: CTAB (Macklin, purity 99%), ferric nitrate nonahydrate ($\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, J&K, purity 98%), ferroferric oxide (Fe_3O_4 , General Reagent, 70.5–74.2 wt%), and chloroauric acid (Energy, purity 98%). All the reagents were used as purchased without any further purification. The compressed gas mixture (carbon monoxide, 1%; O_2 , 20%; and the remainder, N_2) that we used was commercially purchased from Shanghai Weichuang Standard Reference Gas Analytical Technology Company. The analytical techniques and/or instruments used for the experimental work and their operating parameters include: powder X-ray diffraction (XRD) (PANalytical Empyrean diffractometer, operating at 45 kV and 40 mA, 0.02° per step for scanning step), N_2 adsorption-desorption isotherms (TriStar 3000 volumetric adsorption analyzer, Micromeritics Instrument Corp), scanning transmission electron microscopy (STEM) with high-angle annular dark field

Fig. 1. The typical synthesis process of mesoporous Fe_3O_4 .

(HAADF) capability (The Nion Co., operating at 200 kV, inner angle 80 mrad).

In order to characterize the CO catalytic oxidation, the concentrations of CO and CO_2 in the quartz tube were analyzed by a Buck Scientific 910 gas chromatograph. A dual molecular sieve/porous polymer column (Alltech CTR1) and a thermal conductivity detector were also employed.

2.2. Typical solid-state preparation for mesoporous Fe_3O_4 and $\text{Au@Fe}_3\text{O}_4$

In a typical run (Fig. 1), we added a moderate amount of metal salts (ferric nitrate nonahydrate, 1.0 g) and CTAB (0.2 g) into a 25-mL vibrating zirconia ball mill, where they were mixed and ground by using a planetary ball mill (constant frequency, 30 Hz) for 0.5 h without the addition of any solvent; this process gives rise to the mechanochemical self-assembled mixture. We then transferred the obtained mixtures to a muffle furnace; the heating rate was set at 2 °C/min to the carbonization temperature of 300 °C and that temperature was maintained for 2 h to ensure the complete pyrolysis of CTAB into gaseous products. Evidence from the thermal gravimetric analysis (TGA) profiles for $\text{Fe}_3\text{O}_4\text{@CTAB}$ 0.4 and 0.8 confirmed the complete CTAB decomposition at a temperature of ~250 °C (Fig. 2). Finally, we turned off the heat and allowed the products to cool down naturally to room temperature in the oven. For the preparation of mesoporous Fe_xO_y loaded with precious metals (e.g., Au), chloroauric acid (10–20 mg) was added during the initial ball milling process.

Fig. 2. TGA plots of $\text{Fe}_3\text{O}_4\text{@CTAB}$ 0.4 and 0.8 in an air atmosphere.

Fig. 3. XRD patterns of as-synthesized $\text{Fe}_3\text{O}_4\text{@CTAB}$ (0.1–1.0).

The as-prepared samples are denoted as $\text{Fe}_x\text{O}_y\text{@0.1}$, $\text{Fe}_x\text{O}_y\text{@0.2}$, $\text{Au@Fe}_x\text{O}_y\text{-10 mg}$, $\text{Au@Fe}_x\text{O}_y\text{-20 mg}$, etc., where the root expression such as “ $\text{Fe}_x\text{O}_y\text{@0.1}$ ” corresponds to 0.1 g of CTAB being used as a template. The designation “ $\text{Au@Fe}_x\text{O}_y\text{-10 (20) mg}$ ” refers to adding 0.2 g CTAB and 10 (20) mg chloroauric acid.

3. Results and discussion

3.1. Mesoporous Fe_3O_4

To explore the crystallinity of as-synthesized Fe_3O_4 samples with surfactant CTAB, XRD was performed. As shown in Fig. 3, while the amount of CTAB as template was adjusted within the

Fig. 4. N_2 sorption isotherm at -196°C and pore size distribution in the mesoporous $\text{Fe}_3\text{O}_4\text{@CTAB-0.2}$ sample.

range from 0.1 to 1.0 g, the phase transformation from ferric nitrate to Fe_3O_4 at 300°C was verified with the diffraction peaks solely assigned to Fe_3O_4 (JCPDS 72-2303). The different intensity diffraction peaks at $2\theta = 30^\circ\text{--}45^\circ$ and $50^\circ\text{--}65^\circ$ were attributed to the (220), (311), (400), (422), (511), and (440) facets, respectively. The average crystallite sizes (14–23 nm) of as-prepared iron oxide samples calculated by the (311) peak at 35.4° were small (Table 1), which is consistent with the broad diffraction peaks in the XRD patterns.

In order to understand the pore structure, N_2 gas sorption characterization was carried out at -196°C . The Brunauer-Emmett-Teller (BET) surface area of $\text{Fe}_3\text{O}_4\text{@0.2}$ (Fig. 4) was $146\text{ m}^2/\text{g}$, and the Barrett-Joyner-Halenda (BJH) adsorption average pore width (4 V/A) was 5.0 nm. Furthermore, as shown in Fig. 5, N_2 adsorption/desorption isotherms of as-synthesized $\text{Fe}_3\text{O}_4\text{@CTAB}$ (0.1–1.0) measured at liquid nitrogen temperature (-196°C) showed characteristic type IV isotherms of mesoporous materials with obvious hysteresis loops, and the nitrogen uptake kept increasing rapidly above $P/P_0 > 0.1$, indicating that the samples contained a high degree of mesoporosity. According to the calculated N_2 adsorption parameters (Table 1), the BET surface areas and total pore volumes increased going from $\text{Fe}_3\text{O}_4\text{@0.1}$ to $\text{Fe}_3\text{O}_4\text{@0.8}$ and

Fig. 5. N_2 adsorption-desorption isotherms of $\text{Fe}_3\text{O}_4\text{@0.1}$ –1.0 samples at -196°C and pore size distributions calculated by the Barrett-Joyner-Halenda (BJH) method.

Table 1

Calculated pore parameters for the obtained mesoporous Fe₃O₄@CTAB via N₂ adsorption and average crystallite sizes calculated by the Scherrer equation from the XRD results.

Sample	Pore volume ^a (cm ³ /g)	S _{BET} (m ² /g)	PSD ^b	Crystallite size (nm)
Fe ₃ O ₄ @0.1	0.19	112	Broad	14.2
Fe ₃ O ₄ @0.2	0.20	146	Narrow	20.9
Fe ₃ O ₄ @0.4	0.21	101	Narrow	17.9
Fe ₃ O ₄ @0.8	0.23	170	Broad	22.5
Fe ₃ O ₄ @1.0	0.12	118	Narrow	16.5

^a BJH adsorption cumulative volume of pores. ^b Pore size distribution.

reached their maximum value (0.23 cm³/g, 170 m²/g) when 0.8 g of CTAB was added. Correspondingly, the BJH adsorption average pore size varied in the range of 4.3–7.5 nm. This allows us to conclude that textural properties (specific surface areas, pore volume, and pore size distribution) of mesoporous Fe₃O₄ can easily be tuned by changing the amount of added soft template species. Such high values clearly suggest the rich porosity, which could validate the great potential application of these materials in heterogeneous catalysis.

3.2. Catalytic behavior of mesoporous Fe₃O₄

The catalytic CO oxidation reaction was carried out in a fixed-bed reactor. The catalyst loaded was 30 mg and the feed gas of 1% CO balanced with dry air (20% O₂ and 79% N₂) passed through the catalyst at a gas hourly space velocity (GHSV) of 30 400 mL h⁻¹ g_{cat}⁻¹. The gas phase analysis was carried out every five minutes with gradual heating according to the program. The activity estimation of the catalyst was based on the CO conversion calculated by the percentages of CO₂ and CO after the reaction.

Figure 6 demonstrates the superior CO oxidation activity of the mesoporous iron oxide, as compared with commercial ferroferric oxide. While the commercially purchased Fe₃O₄ (as the standard material) enabled the 100% CO conversion at around 490 °C, the CO conversion of mesoporous Fe₃O₄ samples can reach 100% even at a relatively low temperature (e.g., Fe₃O₄@0.8, 274 °C). The significantly enhanced catalytic activi-

Fig. 6. Conversion curves for CO oxidation on various catalysts at GHSV = 30 400 mL h⁻¹ g_{cat}⁻¹. Fe₃O₄-C denotes commercially purchased Fe₃O₄.

Fig. 7. Effect of reaction time on CO oxidation. Reactions were carried out at 240 °C (GHSV = 30 400 mL h⁻¹ g_{cat}⁻¹) on Fe₃O₄@0.4.

ty should be attributed to the larger specific surface area, pore volume, and more exposed active sites. Moreover, based on the evolution of the conversion rate curves, mesoporous Fe₃O₄ showed very weak CO oxidation catalytic activity below 135 °C, with the catalytic behavior not starting until 150 °C. The Fe₃O₄@CTAB with a larger specific surface area was significantly more effective, indicating that the catalytic activity is closely related to surface area.

The catalytic stability of as-prepared mesoporous iron oxide on the catalytic oxygenation of CO at 240 °C is displayed in Fig. 7. It can be observed that as the reaction time was prolonged, Fe₃O₄@0.4 maintained a high CO conversion reaching up to 80% at 48 h. The CO conversion value is in agreement with the result in Fig. 6, indicating excellent catalysis stability.

Encouraged by the interesting activity of mesoporous Fe₃O₄ catalysts, we undertook a study of CO oxidation reaction at varying gas hourly space velocities (GHSV) in the range of 14400–121600 mL h⁻¹ g_{cat}⁻¹ (Fig. 8). As evidenced by the fact that the flow rate did not show any significant effect on the final 100% CO conversion temperature, the catalytic activity of the Fe₃O₄@0.8 sample was stable at different GHSV levels. On the other hand, Fe₃O₄@0.8 did show a lower initial activation temperature (~127 °C) for CO oxidation at the higher feed gas space velocity.

Fig. 8. Light-off curves of CO oxidation on mesoporous Fe₃O₄@0.8 under different GHSV values (mL h⁻¹ g_{cat}⁻¹).

Fig. 9. XRD patterns of as-synthesized Au@Fe₃O₄-10mg, 20mg.

3.3. Au@Fe₃O₄

In an effort to expand the scope of this mechanochemical solvent-free method, the assembly of iron salt (1 g), CTAB (0.2 g) and HAuCl₄ (10 mg or 20 mg; labelled Au@Fe₃O₄-10mg and Au@Fe₃O₄-20mg, respectively) was carried out by ball milling for 30 min, followed by thermal treatment at 300 °C in air.

To gain an insight into the phase morphologies of Au species, Au@Fe₃O₄ samples were examined by XRD. The diffraction pattern indicated the phases of metallic Au (PDF #01-1172) and Fe₃O₄ (Fig. 9). Hence, it is worth emphasizing that the introduction of Au does not affect the crystal structure of the catalyst carrier, thereby providing a simple approach to load gold nanoparticles onto a mesoporous Fe₃O₄ support. In addition, the diffraction peak of Au was relatively wide, indicating that the average particle size was small.

Fig. 11. A STEM-HAADF image of the Au@Fe₃O₄-20mg sample.

The porosity of Au@Fe₃O₄ by N₂ sorption was examined at −196 °C. The N₂ adsorption isotherms (Fig. 10) both afforded an increasing uptake with $P/P_0 > 0.1$, indicating the possible formation of mesopores. The pore size distribution provided additional evidence that the porosity was dominated by mesopores of 2–10 nm. Moreover, increasing the amount of Au on mesoporous Fe₃O₄ did not clearly affect the pore volume and specific surface area of catalysts (65 to 63 m²/g and 0.258 to 0.152 cm³/g, respectively).

Because of the relatively low Tammann temperature and high surface energy, Au nanoparticles are usually prepared by solution-based methods [22,23]. It is noteworthy that no solvents were used during our entire synthesis process. To verify the structural details of Au@Fe₃O₄-20mg, STEM mapping analysis was carried out in HAADF mode. As seen in Fig. 11, Au na-

Fig. 10. N₂ adsorption isotherms of Au@Fe₃O₄-10mg and Au@Fe₃O₄-20mg at −196 °C and the corresponding pore size distribution by the BJH model.

noparticles with an average size of ~ 4 nm were highly dispersed on the mesoporous iron oxides. Hence, the current solvent-free assembly by mechanochemistry seems not only to direct mesopores but also control the size of Au nanoparticles and prevent the growth or coalescence of the nanoparticles.

4. Conclusions

In contrast to existing synthesis methods (soft templating pathways and hard templating approaches) for mesoporous iron oxides, there remains a need for a sustainable method that can consume less solvents, fewer steps, and less time. This work demonstrates a solid-state CTAB-assisted synthesis of mesoporous Fe_3O_4 and suggests a possible method for loading noble metal nanoparticles onto mesoporous metal oxide by mechanochemistry. The specific surface area of $\text{Fe}_3\text{O}_4@0.8$ can reach up to $170 \text{ cm}^2/\text{g}$ by adjusting the addition of CTAB, resulting in an enhanced CO oxidation activity compared with commercially purchased Fe_3O_4 . During the investigation of noble-metal-loaded catalysts, the as-prepared $\text{Au}@ \text{Fe}_3\text{O}_4$ samples have been explored by XRD, BET, and SEM analysis. Highly dispersed Au nanoparticles on Fe_3O_4 supports, with small particle sizes around 4 nm, were identified. The potential applications and synergistic effects will be studied in detail in ongoing work.

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Graphical Abstract

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Solid-state CTAB-assisted synthesis of mesoporous Fe_3O_4 and $\text{Au}@ \text{Fe}_3\text{O}_4$ by mechanochemistry

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Structurally adjustable mesoporous Fe_3O_4 and $\text{Au}@ \text{Fe}_3\text{O}_4$ were rapidly fabricated via mechanochemistry. Meso- Fe_3O_4 showed excellent catalytic performance for the CO catalytic oxidation reaction, and the Au nanoparticles were highly dispersed.

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CTAB辅助的机械化学法合成介孔Fe₃O₄和Au@Fe₃O₄催化剂

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摘要: 一氧化碳(CO)是化石燃料、汽车尾气和工业废气不完全燃烧所产生的污染物, 对人体神经系统具有高毒性, 因此CO污染已成为一个不可忽视的健康和环境问题。介孔催化剂在CO催化氧化中表现出优越的催化活性, 在多相催化领域具有广阔的应用前景, 尤其是介孔过渡金属氧化物和贵金属作为催化剂得到了广泛的应用。无论是从基础研究的角度, 还是从化工的角度, 研究高效催化剂, 设计优化多孔催化剂的制备工艺, 更好地完成CO催化氧化过程都具有重要意义。目前已有设计和开发各种CO氧化催化剂应用在空气净化和燃料电池技术领域, 以及制备负载贵金属(Pd、Pt、Au)的金属氧化物应用于催化氧化的相关报道。在各种金属氧化物中, 氧化铁因成本低、化学稳定性和热稳定性高(抗烧结性能稳定)、资源丰富、无毒环保和耐久性好被认为是最有前途的介孔催化剂或载体材料之一。介孔的引入使氧化铁具有更多的暴露催化位点, 介孔催化剂的孔隙结构(孔隙尺寸、孔隙体积和表面积)以及负载的贵金属颗粒大小等都会对催化剂CO氧化活性产生协同效应。

介孔材料的典型合成策略包括软模板法和硬模板法, 负载贵金属的方法有沉淀法和浸渍法等。这些方法大部分为湿法化学过程, 步骤复杂, 溶剂用量过多, 干燥处理耗时耗能。而机械化学法利用球磨过程产生的摩擦热和机械动量促进分子间相互作用, 在多孔固体材料的合成中更具优势。研究人员已将机械化学合成方法引入到金属有机骨架(MOF)、有序介孔碳(OMC)、共价有机骨架(COF)及沸石等材料的制备过程。在此, 我们研究组提出溴化十六烷基三甲基铵(CTAB)辅助的机械化学法合成介孔Fe₃O₄和Au@Fe₃O₄的新型合成策略, 实现以硝酸铁为前驱体, CTAB为模板的反应物之间的有机-无机自组装, 在空气中烧结后制备出介孔氧化铁及其负载的贵金属催化剂。

XRD表征结果表明, 采用不同CTAB用量所得产物均是Fe₃O₄; N₂吸附-脱附测试数据显示, 合成的介孔Fe₃O₄比表面积可高达170 m²/g; XRD和SEM表征结果显示, Au@Fe₃O₄的Au纳米粒子高度分散, 平均粒径为4 nm左右。进一步研究了不同CTAB用量合成的催化剂在不同空速下催化CO氧化反应转化率的变化。发现通过调整模板剂CTAB的用量可以很好地调节孔结构, 与商业购买的Fe₃O₄ (CO在490 °C左右完全转化)相比, 介孔Fe₃O₄在CO催化氧化反应中表现出良好的催化活性, 在274 °C即达到100%的CO转化率, 且稳定性很好, 48 h内未出现转化率降低的现象。上述结果表明, CTAB辅助机械化学法合成介孔Fe₃O₄和Au@Fe₃O₄在CO催化氧化反应中发挥了重要作用, 且催化剂制备过程简单, 无溶剂参与, 快速、高效、环保。该方法也为后续研究工作——将小粒径的贵金属纳米粒子负载到介孔金属氧化物且实现高度分散提供了一种潜在的合成策略。

关键词: 机械化学; 介孔材料; 介孔催化剂; 一氧化碳氧化; 氧化铁

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