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Ruthenium nanoparticles encapsulated inside porous hollow carbon spheres: A novel catalyst for Fischer–Tropsch synthesis

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ABSTRACT

Two novel Ru Fischer–Tropsch (FT) catalysts were made that were supported on the inside of two hollow carbon spheres that differed in terms of their shell porosity. Mesoporous Stober spheres were made and Ru deposited on the silica. The Ru/silica spheres were encapsulated with carbon deposited by CVD (toluene) or from resorcinol/formaldehyde. Removal of the silica gave Ru@HCS ($d_{Ru} = 5.5$) and Ru@MHCS (3.2 nm) that had carbon shells ($d = ca. 20$ nm) with different physicochemical properties as evidenced by the TEM, nitrogen adsorption–desorption, TGA, Raman spectroscopy and XRD measurements. FT studies were performed on the two catalysts (10 bar; 190/220/250 °C; 2/1 ratio H₂/CO). Classical Fischer–Tropsch data was obtained indicating that the catalysts could access the reactants and that FT products could escape from the inside of the spheres (acting as a nanoreactor). Activity data indicated diffusion control of CO/H₂ into the nanoreactor and selectivity data indicated an alpha value of 0.74–0.78 (220 °C). Typical product selectivity associated with small Ru particles was observed and the methane content increased with reaction temperature. No substantial Ru sintering occurred below 220 °C. It is thus seen that the porosity of the two hollow carbon architectures is suitable for the FT polymerization reaction.

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1. Introduction

Carbon monoxide hydrogenation reactions are an important set of reactions used extensively in the chemical and fuels industry. Two examples include: (i) the Fischer–Tropsch synthesis (FTS) in which carbon monoxide derived from natural gas, coal or biomass [1,2] is converted into liquid hydrocarbons for energy generation and chemicals [1,3,4] and (ii) the selective methanation reaction used to purify hydrogen that contains CO, for use as a fuel in proton exchange membrane fuel cells [3,5]. Generally FT CO hydrogenation reactions have been performed on supported metal catalysts using metals such as Co, Fe, Ru and Ni [6–8]. Even though Ru is not cheap relative to other metals, its unique catalytic properties, in particular its high activity in CO hydrogenation reactions and its good stability under different reactions conditions make it a valuable and useful CO hydrogenation catalyst [9–11].

Most studies on the CO hydrogenation reaction using supported Ru catalysts have been performed on supports such as silica, alumina, titania and various shaped carbon materials [12–15]. These supports are solid materials with the catalyst particles typically placed on the external support surface, or at best in the pores of the support as found in zeolites or mesoporous materials [16,17]. Preparation and characterization of stable Ru nanoparticles embedded on ordered mesoporous carbon materials have also been applied in FTS [18].

In the last decade the possibility of making hollow supports with the metal placed inside the support has become possible [19,20]. The support can then be considered as a nanoreactor [21–23]. Two types of carbon nanoreactors can be envisaged. These are (i) carbon nanotubes (CNTs); various studies have shown metal particles placed inside CNTs have different catalytic properties to metals placed outside the CNT. The reactant access to the metal particles is determined by the diameter of the CNT (typically >3 nm) [24–26], (ii) hollow carbon spheres (HCSs); in this case metal nanoparticles are placed inside hollow carbon spheres to form a core-shell or rattle type catalyst. Access to metals placed in these types of nanoreactors is determined by the porosity of the carbon

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shell which can be mesoporous (2–50 nm) or microporous (<2 nm) [27,28].

The HCSs have emerged as a support material having potential for application as a nanoreactor in heterogeneous catalysis studies. This is because of the relative chemical inertness of carbon which minimizes the metal support interactions, hence allowing easier reducibility and increased metal catalytic activity [29,30]. The compartmentalization of the metal nanoparticles can also limit sintering [27,28] and lead to containment of fragmented catalyst particles [31]. The facile ability to control the HCS pore size distribution can be exploited to control access of reactants to metal active sites as well as removal of the products from the hollow core [32–35]. This concept of performing catalytic reactions inside nanoreactors has been demonstrated [28] but to date, no reports on the applications of Ru@HCS for gas phase CO hydrogenation reactions (e.g. Fischer–Tropsch synthesis or selective methanation of CO) have been reported.

Here we report on the synthesis of Ru@HCS that relies on a hard template method using monodisperse silica spheres as sacrificial templates, a procedure that has proven to be invaluable in the synthesis of hollow nanoreactors [28,36,37]. These resulting Ru@HCS structures were tested for CO hydrogenation reactions under typical Fischer–Tropsch conditions. The objective was to determine whether these types of supports could be used in FT synthesis viz. (i) Will the carbon shell porosity affect the catalyst activity/selectivity? (ii) Does sintering of the catalysts occur during the reaction? (iii) Can the carbon nanoreactor shell survive the FT catalytic reaction conditions?

2. Experimental procedure

2.1. Synthesis of modified Stöber spheres

The silica spheres were made by classical procedures using CTAB/TEOS (see Supplementary section) [38,39].

2.2. Synthesis of 0.5% Ru/mSiO₂

Mesoporous silica spheres (mSiO₂, 4g) were dispersed in 250 mL of deionized water by ultra-sonication. To this mixture was added 0.4 g of urea and 2 mL of 0.1 M RuCl₃ solution and the mixture was then sonicated for 30 minutes. Homogenous deposition precipitation of Ru was performed at 95 °C for 12 h. The product (ca. 0.5% loaded Ru/SiO₂) was then collected by filtration, washed with deionized water and then dried at 100 °C overnight.

2.3. Synthesis of Ru@MHCS

Ru/mSiO₂ (2 g) and ammonia solution (25%; 1.5 mL) were dispersed in 100 mL of ethanol in a 250 mL beaker. Resorcinol (0.75 g), formaldehyde solution (37%; 1.5 mL), TEOS (1 mL) and CTAB (1 g) mixture in ethanol (50 mL), was added to the first solution and the total mixture then stirred at room temperature for 20 h to form the resorcinol–formaldehyde (RF) polymer around the silica spheres. The red product (Ru/mSiO₂@RF) was then collected by centrifugation (4000 rpm, 10 min), washed with acetone and dried at 100 °C for 2 h. Carbonization of the Ru/mSiO₂@RF was performed at 900 °C for 2 h under a flow of argon gas (25–30 mL/min) in a horizontal furnace reactor. The silica was then removed by etching at ambient temperature with HF (5% in deionized water) to give Ru@MHCS.

2.4. Synthesis of Ru@HCS

The uncalcined Ru/mSiO₂ was placed inside a horizontal tube furnace which was heated to 900 °C at 10 °C/min under argon. When the desired temperature was reached the argon gas

(100 mL/min) was bubbled through toluene, at room temperature, for 2 h to coat the Ru/mSiO₂ composite with a carbon shell. HF solution (5%; 100 mL) was added to the carbon coated Ru/mSiO₂ (to produce Ru/mSiO₂@C) and the silica template removed at room temperature over 12 h. The material was purified by centrifugation and repeated washing using deionized water and then dried at 100 °C to give Ru@HCS

The two catalysts (Ru@HCS and Ru@MHCS) were both heated at 250 °C under nitrogen gas at 30 mL/min for 2 h prior to use and characterization.

2.5. Preparation of Ru supported on hollow carbon sphere catalysts

The mSiO₂ was prepared as described above and then coated by carbon using the procedures described in Section 2.3 and 2.4 (but without Ru) and the silica removed by HF to give MHCS and HCS. Ru/HCS and Ru/MHCS were then prepared by loading 5% Ru onto the hollow carbon spheres by classical homogenous deposition precipitation (see Supplementary section). The two catalysts (Ru/HCS and Ru/MHCS) were heated at 250 °C under nitrogen gas at 30 mL/min for 2 h prior to use and characterization.

All characterization techniques used are reported in the Supplementary section (Supp section 1.4)

3. Results and discussion

The general synthesis scheme used to make the Ru supported on hollow carbon spheres is shown in Fig. 1. Two different carbon sources were used to modify the surface porosity of the final nanoreactor, but otherwise both methods used similar protocols.

3.1. Silica spheres and hollow carbon spheres

The silica spheres were prepared by a modified Stober method. The spheres were then covered by a mesoporous layer using CTAB/TEOS. The covered spheres revealed a uniform particle size (ca. 620 nm) and good dispersion typical of silica spheres prepared by the modified Stöber method [38,39]. It is notable that the mesoporous silica layer on the spheres is uniformly distributed around the silica particle (Fig. 2). Ru nanoparticles were then loaded on the silica spheres and the silica was then coated with carbon using two different methods. Removal of the silica from both samples gave the hollow carbon shells with different porosities and physicochemical properties which encapsulated the Ru particles.

In the first case the silica spheres were completely covered by the resorcinol–formaldehyde polymer which was carbonized to form Ru/mSiO₂@C as confirmed using SEM-EDS mapping (Fig. S1). The C L α 1 (densely blue) map clearly showed evidence of total coating by carbon, based on a random sampling of individual silica spheres that had been coated with the carbon layer. In the second case the Ru/mSiO₂ was coated by carbon from a toluene source. A uniform coating was also observed for the composite consistent with other studies (Fig. S2) [32,36,40].

The hollow carbon spheres from both methods were obtained by etching the silica with HF (5% in water). The hollow morphology of these spheres is visible using transmission electron microscopy showing that the silica material had been removed (Fig. 3). TGA analysis also confirmed the removal of the SiO₂ (Fig. 4(B)). EDS scans (Figs. S3 and S4) of these hollow materials also confirmed that thorough washing of the carbon material after etching ensured that all the fluoride ions were removed. The Ru@MHCS carbon shell showed a shell thickness of 17.8 ± 3.4 nm while the carbon layer thickness for Ru@HCS was observed to be 19.1 ± 4.6 nm (Figs. S3 (b) and S4 (b)).

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