Preparation and characterization of stable Ru nanoparticles embedded on the ordered mesoporous carbon material for applications in Fischer–Tropsch synthesis

Kun Xiong [a], Jinlin Li [a,*], Kongyong Liew [a], Xiaodong Zhan [b,**]

[a] Key Laboratory of Catalysis and Materials Science of the State Ethnic Affairs Commission & Ministry of Education, South-Central University for Nationalities, Wuhan, China
[b] SynuTech LLC, 2422 S Umbrella Pl., Broken Arrow, OK 74012, USA

ABSTRACT

A novel Ru–OMC catalyst was prepared by autoreduction reaction between a ruthenium precursor and a carbon source at 1123 K. Ruthenium nanoparticles were embedded on the carbon walls of the ordered mesoporous carbon material. Characterization tools including power X-ray diffraction (XRD), nitrogen adsorption–desorption, and transmission electron microscopy (TEM) were used to scrutinize the catalysts. The catalyst activity for Fischer–Tropsch synthesis (FTS) was carried out in a fixed bed reactor. For comparison, Ru catalysts supported on ordered mesoporous carbon (OMC), active carbon (AC), and carbon nanotubes (CNT) were prepared using conventional impregnation method and evaluated at the same FTS reaction conditions. The Ru–OMC catalyst exhibited highly ordered mesoporous structure and large surface area, indistinguishable with those of the OMC material. On this catalyst, Ru nanoparticles were actually embedded on the carbon walls, forming an intimate contact with the carbon supports. It is proposed that this feature might create certain electron-deficient sheets on the interfacial contact, which facilitates the transfer of spilled-over hydrogen and improves hydrogen disassociation on the catalyst surface.

© 2010 Elsevier B.V. All rights reserved.

1. Introduction

Fischer–Tropsch synthesis (FTS) technology for the production of liquid fuels by natural gas, coal, and biomass has received extensive attention [1]. Although iron and cobalt are the more common metals for FTS [2,3], Ru catalysts possessing higher intrinsic activity produce higher molecular weight hydrocarbons, and have been widely utilized for mechanism studies. Thus, Ru catalysts are usually used as the model catalysts for the development of promising novel FTS catalysts.

Catalysts for FTS using various supports such as alumina [4,5], titania [6], silica [7,8], carbon materials [9–11], have been reported by many research groups. It has been found that the support has significant influence on the reducibility, activity, and selectivity properties of the active phase [12,13]. Alumina is an interesting support for cobalt FTS catalyst since it possesses high surface area, favorable mechanical properties, and good stability within a wide temperature range. Yet, that metal–support interaction formed during the catalyst preparation and activation processes resulting

in a decrease of catalytic activity is not an uncommon phenomenon [14]. Similarly, titania also forms a strong interaction with active metal phase leading to rapid catalyst deactivation [15]. Silica material, on the other hand, has been used as support due to its high surface area and weak interaction with the metals. Periodic mesoporous silica materials, such as MCM-41, SBA-15, and KIT-6 types, have been employed due to their well-defined periodic mesopore, narrow pore size distribution, high surface area and large pore volume. The utilization of such novel materials [16–18] as supports may make it possible to design new catalysts with high product selectivity and stability for FTS. However, some authors [19] reported that the surface silanol groups (SiOH) on SBA-15 material could interact with cobalt oxides, resulting in low reducibility at low temperatures, while cobalt supported on SBA-15 modified by silylation could enhance the reducibility of cobalt oxides and increase the FTS activity. It thus appears that the metal–support interaction is complex when investigating the effects of the pore structure of the support and the active metal phase on the catalytic properties of a catalyst for FTS.

In contrast, carbon materials are considered to be more inert than the conventional oxide materials. The inertness of the carbon surface facilitates the reduction of the metal precursor to the zero-valence state. Furthermore, carbon materials usually possess many specific features, such as high surface area, rich porosity,

---

and good stability at high temperatures in inert or reducing atmospheres [20]. Recently, ordered mesoporous carbon (OMC) has received much attention because of its unique structure, high surface area, and physicochemical property as a novel support [21]. Lu et al. [22] reported that Pd–OMC catalyst showed high catalytic performance and good stability for the oxidation of alcohols to aldehydes. They proposed that it was likely that Pd nanoparticles confined/stabilized by the carbon framework and the silica walls that averted particle aggregation, movement, and pore blocking. Recent studies [23] also showed that Fe_xO_y/C spheres embedded with highly dispersed iron oxide nanoparticles displayed remarkable stability and selectivity in FTS. It is hence expected that metal nanoparticles embedded on carbon walls may display high activity and stability for FTS because of the intimate contact between the metal and the support, albeit there are few reports so far in open literatures on the use of OMC as a FTS catalyst support. A careful examination of these novel catalysts might help understand the catalytic mechanism of FTS.

In this work, the Ru–OMC catalyst was prepared by a co-impregnation method as detailed in the next section. The catalyst was characterized using transmission electron microscopy (TEM), X-ray diffraction (XRD), and N_2 adsorption–desorption. The catalytic performance of Ru–OMC catalyst for FTS was determined in a fixed bed reactor. The results were compared with some other reference catalysts supported on ordered mesoporous carbon (OMC), active carbon (AC), and carbon nanotubes (CNT), i.e., Ru/OMC, Ru/AC, and Ru/CNT, respectively.

2. Experimental section

2.1. Catalyst preparation

Ordered mesoporous carbon (OMC) was synthesized according to the method reported in literature with slight modifications [24] using SBA-15 as a hard template. Furfuryl alcohol (FA) dissolved in ethanol was used as carbon precursor with oxalic acid added to the FA solution as a polymerization catalyst. The SBA-15 silica synthesized according to Zhao et al. [25] was impregnated with the FA solution, followed by polymerization at 363 K for 6 h and at 423 K for 3 h in air, and then at the same temperature in a vacuum oven for 3 h. Afterwards, the composites were carbonized at 1123 K for 3 h under N_2 atmosphere in a quartz tube. Finally, the black powders were treated with 5% HF solution to remove the template, washed with deionized water, and dried at 363 K overnight before serving as a support for metal impregnation.

The Ru–OMC catalyst was obtained using the method similar to that for OMC. The only difference was that the SBA-15 silica was impregnated with an FA solution containing $Ru(NO)(NO_3)_3$. The mass content of Ru in the Ru–OMC catalyst is 3.53 wt% by using an inductive-coupled plasma atomic emission spectroscopy (ICP-AES). For purpose of comparison, three conventionally impregnated catalysts, i.e., Ru/OMC, Ru/AC, and Ru/CNT, with the same Ru loading (3 wt%), were prepared using incipient wetness impregnation method. The catalysts were dried at 393 K for 12 h, followed by calcination at 623 K for 5 h under a N_2 atmosphere.

2.2. Catalyst characterization

The X-ray diffraction (XRD) patterns were determined using a Bruker-D8 diffractormeter with monochromatized Cu-Kα radiation ($\lambda = 1.54056$ Å) operated at 40 kV and 40 mA and collected by a Vantec-1 detector.

Nitrogen adsorption–desorption experiment was conducted at 77 K with a Quantachrome Autosorb-1-C-MS. Before the measurement, the samples were outgassed at 473 K for over 6 h. The surface area was obtained using the Brunauer–Emmett–Teller (BET) model for adsorption data in a relative pressure ranging from 0.05 to 0.30. The total pore volume was determined from the aggregation of N_2 vapor adsorbed at a relative pressure of 0.99. The pore size distribution was acquired from the desorption branches of the isotherms using the Barrett–Joyner–Halenda (BJH) model.

Transmission electron microscopy (TEM) images of the samples were obtained with a FEI Tecnai G20 instrument. The samples were prepared by directly suspending in ethanol with ultrasonic treatment. A copper microscope grid covered with perforated carbon was dipped into the solution.

The reduction profiles of the catalysts were measured by hydrogen temperature programmed reduction (H_2-TPR) experiments employing a Zeton Altamira AMI-200 unit. The catalysts (ca. 0.05 g) were placed in a U-shape quartz reactor, with a thermocouple for continuous temperature measurement. Samples were first pretreated at 423 K in a flowing high purity argon to drive away the water or impurities before cooled down to 323 K. Afterwards, an Ar gas stream containing 10% H_2 (30 cm^3 min^{-1}) was switched on and the temperature was raised from 323 to 1073 K at a rate of 10 K min^{-1}. The temperature was held at 1073 K for 30 min. Hydrogen consumption was monitored using a thermal conductivity detector (TCD).

2.3. Fischer–Tropsch synthesis (FTS)

Fischer–Tropsch synthesis reaction was conducted in a fixed bed reactor (id = 12 mm) at 503 K and 1.0 MPa. The catalyst (ca. 1.0 g) was not diluted and reduced in high purity H_2 with a GHSV of 3 SL h^{-1} g^{-1} at atmosphere pressure. The reactor temperature was increased from ambient to 373 K at 2 K min^{-1}, followed by increasing to 723 K at 1 K min^{-1} and held for 10 h at that temperature. Subsequently, the reactor was cooled down to 373 K before switching to syngas (H_2/CO = 2, 2 SL h^{-1} g^{-1}) and the pressure was increased to 1.0 MPa. The reactor temperature was increased to 503 K in 14 h at which the reaction was carried out. The products were collected in a hot trap (373 K) and a cold trap (271 K). The outlet gases were analyzed online by an Agilent MicroGC 3000A. The oil product was analyzed with an Agilent 6890N GC and the solid wax with an Agilent 7890A GC.

3. Results and discussion

3.1. X-ray diffraction (XRD)

As shown in Fig. 1(a), the small-angle XRD patterns observed for OMC, Ru–OMC, and Ru/OMC all reveal a main (1 0 0) diffraction peak and weak peaks at (1 1 0) and (2 0 0) similar to the $p6mm$ hexagonal symmetry of the SBA-15 template, consistent with the previous reports [24,26]. For the Ru–OMC catalyst, the intensity of the diffraction peaks was not apparently decreased after introduction of the ruthenium species, indicating that the ordered mesostructure of OMC has been retained. In contrast, a slight decrease in the intensity of diffraction peaks of the Ru/OMC catalyst was observed after loading of Ru particles on the synthesized OMC. Nevertheless, it imposed insignificant impact on the overall structure and the physical properties of the catalyst. Fig. 1(b) shows the wide-angle X-ray diffraction patterns of OMC and other carbon-supported Ru catalysts. It is interesting to note that there is neither Ru nor RuO_2 diffraction peaks in the XRD patterns of Ru/OMC, Ru/AC, and Ru/CNT, probably due to that the size of the Ru nanoparticles upon impregnation is too small to be captured with XRD. However, the Ru–OMC catalyst showed clear peaks at 38.3°, 42.2°, and 44.0°, which can be assigned to (1 0 0), (0 0 2), and (1 0 1) diffractions of bulk hexagonal Ru, respectively (ICDD-JCPDS