Ordered mesoporous carbon supported uniform rhodium nanoparticles as catalysts for higher alcohol synthesis from syngas

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HIGHLIGHTS

- Mesoporous carbon supported specially size-controlled Rh nanoparticles catalysts was designed for syngas-to-alcohol (STA).
- Thus-obtained catalysts are much more active than the catalyst prepared using impregnation for STA.
- Rh NPs in OMC were uniformly sintered within the range of the optimum size for STA during reaction.
- The size-confined Rh NPs in OMC enhanced the CO insertion and reduced methane formation.

GRAPHICAL ABSTRACT
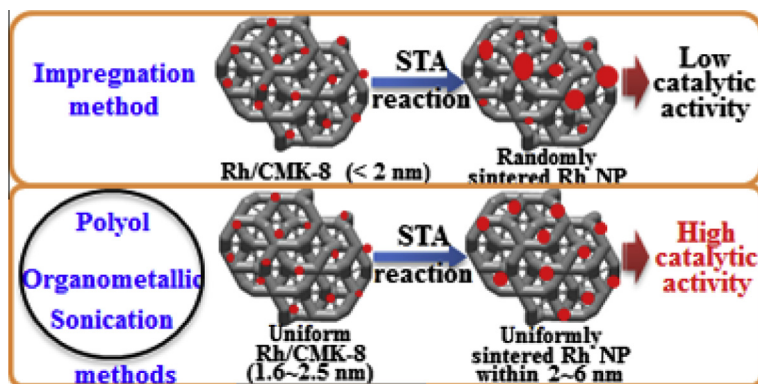
ABSTRACT

Structurally well-defined ordered mesoporous carbon (OMC)-supported uniform and specifically size-controlled Rh nanoparticle (NP) catalysts with low Rh content were prepared by three different methods (polyol, organometallic, and sonochemical) for higher alcohol synthesis from syngas. During the reaction, the size-confined Rh NPs in OMC were uniformly sintered, and the size of the aggregated Rh NPs was within the optimum metal size range for syngas-to-alcohol (STA) reaction. The catalytic reactions and TEM analyses clearly show that the uniform Rh NPs with a specific size in the OMC supports increase the STA catalytic performance by enhancing the CO insertion and reducing methane formation. Moreover, additional chain growth reactions for the synthesis of C_3 and C_4 alcohols could be produced by the use of uniform Rh nanoparticles on OMC supports.

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1. Introduction

Higher alcohols (C_2–C_4 alcohols) can be used in many potential applications: energy carriers, alternative fuels, fuel additives, and basic materials or intermediates for value added chemicals [1,2]. Higher alcohol synthesis from syngas (syngas-to-alcohol, STA) via catalytic thermochemical conversion has attracted interest to address present possible and future situations, such as continuing unstable oil prices, depletion of petroleum, reduction of greenhouse gas emissions, and new accessibility of nonconventional natural gas (shale gas) [1–4]. Over the past few decades, many researchers have made efforts to develop an efficient catalyst with satisfactory higher alcohol selectivity and yield. Since the mid-1970s, Rh-based catalysts have proven to be an attractive option for STA reaction due to the high selectivity of C_{2+}

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oxygenates [5,6]. However, the application and commercialization of Rh-based STA catalysts are still inadequate due to the high loading (>4–5 wt%) and high cost of Rh [7]. Therefore, it is essential to design a new catalyst with a lower Rh metal loading to reduce the catalyst cost while maintaining or improving high productivity and selectivities for higher alcohols.

Recently, a carbon support was found to be a good candidate in an Rh-based catalyst for the improvement of catalytic performance due to the favorable thermal and electron conductive properties and confinement of the active metal in carbon pores [8–12]. Among these carbon supports, ordered mesoporous carbon (OMC) supports have been investigated as a good candidate for STA reaction due to their unique physicochemical properties, such as high surface area, large pore volume, and uniform periodic pore structure and pore size distribution [13]. However, the Rh/OMC catalyst with a low Rh loading did not improve the catalytic activity of STA reaction much because the Rh particle size in OMC is not precisely and uniformly controllable in the range of the optimum Rh size from ca. 2 to 6 nm [12,14]. The optimum Rh size provides a high production of C_{2+} alcohols and oxygenates, but the low metal loaded Rh/OMC exhibits tiny Rh nanoparticles measuring less than ∼1–2 nm due to the high surface area of the OMC support. During STA reaction, the tiny nanoparticles remain or are randomly sintered to form a large Rh nanoparticle with non-uniform distribution. Herein, we employed uniform and specifically size-controlled Rh nanoparticles (NPs) to prepare the promoted Rh/OMC catalyst with a low Rh loading for high-performance STA reaction.

2. Experimental

2.1. Catalyst preparation

2.1.1. IM-OMC
The IM-OMC catalyst was prepared by a simple incipient wetness method using ethanol as a solvent. The Rh metal and promoters (Mn, Li, and Fe) were added in a weight ratio of Rh:Mn:Li:Fe = 1:1:0.075:0.05 according to previous literature [15]. The detailed preparations for KIT-6 silica template, OMC supports (CMK-8 and CMK-9), and Rh/OMC catalysts are described in Supplementary Information S1.2.

2.1.2. PO-OMC
Rh NPs in the range of ca. 1.8–2.5 nm were firstly synthesized by the one-step polyol synthesis method [16]. The Rh NPs were impregnated into OMC support with ethanol as a solvent. After impregnation of Rh NPs, the promoters (Mn, Li, and Fe) were added to the Rh/OMC sample by the simple incipient wetness method in the same manner as IM-OMC sample.

2.1.3. OM-OMC
The OM-OMC catalyst was prepared using organometallic Rh complex compound ($Rh_2Cl_2C_2O_4$) with carboxylate-functionalized OMC (COOH-OMC) support as following the previous literature for preparation of Rh/MWCNT catalyst [17]. The promoters were introduced after formation of Rh metal complex-OMC in the ethanol solution.

2.1.4. SN-OMC
The SN-OMC catalyst was synthesized through the sonochemical one-pot method, which is a similar preparation of Rh/MWCNT as a catalyst for hydrogenation of arenes [18]. $RhCl_3$ and COOH-OMC sonicated for 20 min with borane morpholine complex

as a mild reducing agent. The promoters were also added by the same method as PO-OMC sample.

2.2. Characterization

Powder X-ray diffraction (XRD) patterns were recorded on a Rigaku Multiplex instrument using Cu Kα radiation (λ = 0.15406 nm) operated at 40 kV and 40 mA (1.6 kW). The transmission electron microscopy (TEM) images and energy-dispersive X-ray spectroscopy (EDS) elemental mapping image were taken from the thin edges of the particles supported on a porous carbon grid using a Philips Tecnai G220 device operated at 200 kV. The nitrogen adsorption isotherms were measured at −196 °C on a Micromeritics Tristar 3000 volumetric adsorption analyzer. The Brunauer–Emmett–Teller (BET) equation was used to calculate the apparent surface area from the adsorption data obtained at P/P_0 between 0.05 and 0.2. The total volume of micropores and mesopores was calculated from the amount of nitrogen adsorbed at P/P_0 = 0.95, assuming that the adsorption on the external surface was negligible compared with that in the pores. The pore size distributions (PSDs) were calculated by analyzing the adsorption branch of the N_2 sorption isotherm using the Barrett–Joyner–Halenda (BJH) method. The actual methal loadings of the catalysts were verified using inductively coupled plasma atomic emission spectrometries (ICP-AES, Spectro Ciros Vision). X-ray photoelectron spectrometric (XPS) experiments were performed on a KRATOS Analytical AXIS Nova electron spectrometer. The surface acidity and basicity of the catalysts was measured by temperature programmed desorption of ammonia and carbon dioxide (NH_3-TPD and CO_2-TPD) using a BEL-CAT TPD analyzer with TCD detector.

2.3. Catalytic test

The CO hydrogenation was performed in a lab-made fixed bed reactor system. In order to avoid reactions due to the stainless steel reactor, the reactor was designed with an 8 mm inner diameter and a 35 cm long copper tube inside the stainless steel tube. The end of the tube was welded to seal all gaps between the stainless steel tube and copper tube. Before reaction test, the empty reactor performed for the blank test, and no reactions were occurred. A type K thermocouple (Omega) and PID controller controlled the reaction temperature. Syngas (H_2/CO = 2) was fed into the catalytic reactor at 60 ml/min using a mass flow controller (MFC). The catalyst (0.3 g) was loaded in the middle of the reactor and quartz wool was used to fill the length of the reactor. After the reduction, the temperature of the reactor was cooled to room temperature for removal of the adsorbed H_2 gas using N_2 as a sweep gas. The CO hydrogenation reaction was performed with 12,000 h^{-1} of gas hourly space velocity (GHSV) at 320 °C under 3 MPa. The reactor was heated to reaction temperature with syngas flow, and then pressurized reactor at the reaction temperature. The effluent products were maintained at 190 °C through line heating and measured using an online gas chromatograph (6100GC, Young Lin Instrument Co.) equipped with a thermal conductivity detector (TCD) and a flame ionization detector (FID). The H_2, CO, CO_2, and CH_4 content in the effluent product were detected using a TCD with two capillary columns in series: Molecular sieve 5A column (3.175 mm id × 1.83 m) and Porapak-Q column (3.175 mm id × 1.83 m). The alcohols, other oxygenates, and hydrocarbons were also detected using an FID with two capillary columns in series: DB-FFAP (0.320 mm id × 30 m) column and HP-PLOT-Q column (0.530 mm id × 30 m). Possible products from the reaction were identified by GC–MS, firstly, and then GC calibration was performed with standard gases and liquids for obtain the response factors of each