



Short communication

Highly efficient β -SiC-supported 0.5% Rh-based catalyst for CO hydrogenation to C_2 oxygenates

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ABSTRACT

β -SiC was used as a support for a 0.5% Rh-based catalyst for CO hydrogenation to C_2 oxygenates for the first time. The β -SiC was acid etched and/or calcined at high temperature before use. The results show that the pretreatments had little effect on the textural and crystal properties of SiC, but calcination markedly increased the number of surface oxygen-containing groups. The pretreatment significantly increased the catalytic activities of SiC-supported Rh—Mn—Li/SiC catalysts in CO hydrogenation. An Rh efficiency of 97.2 g/g-Rh/h was achieved, the highest value reported in the literature to date. Possible reasons for this enhancement are suggested.

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1. Introduction

Ethanol is attracting increasing interest for use as a clean fuel or an additive to gasoline. Food prices are soaring globally and crude oil resources are finite, therefore alternative techniques for ethanol production other than grain fermentation and oil need to be developed. Syngas (a mixture of CO and H_2) can be conveniently manufactured from coal, natural gas, or biomass, and CO hydrogenation over Rh-based catalysts to C_2 oxygenates (ethanol, acetaldehyde, and acetic acid) offers a good alternative because acetaldehyde and acetic acid can be readily hydrogenated to ethanol [1,2]. Suitable supports are crucial in enhancing the activity of Rh, and a wide range of solid materials have been used as supports, including SiO_2 [3,4], Al_2O_3 [5], TiO_2 [6], carbon materials [7], and SBA-15 [8]. SiO_2 -supported Rh—Mn—Li catalysts are still considered to be the most promising for this transformation. However, there are challenges associated with this process, because of the high loading, scarcity, and low activity of Rh. New support materials with special properties therefore still need to be developed.

Because of its superior thermal conductivity, excellent mechanical strength, and high chemical inertness, β -SiC with a medium specific surface area (10–40 m^2/g) is an ideal catalyst support candidate under demanding conditions such as high temperature, highly endothermic or exothermic reactions, and strong acidic or basic solutions [9];

examples are reforming [10,11], methanation [12], Fischer–Tropsch synthesis (FTS) [13–17], isomerization [18], dehydrogenation [19], and hydrogenation, even under visible-light irradiation [20]. However, to the best of our knowledge, the use of SiC to support Rh-based catalysts for CO hydrogenation has not yet been reported, and few authors have investigated catalysts with Rh loadings below 1%.

CO hydrogenation over Rh-based catalysts is highly exothermic (similar to FTS) and structure sensitive, therefore the removal of reaction heat at high CO conversions and control of the formed Rh particle size are major concerns. However, conventional SiO_2 and Al_2O_3 are insulating materials and cannot effectively prevent hot spot formation within the catalyst bed, and their surface areas are relatively high (100 m^2/g and above). They are therefore not good choices for supporting low Rh loadings. In this study, to reduce the Rh loading as much as possible and to effectively eliminate the reaction heat, we used β -SiC, which has good thermal conductivity, loaded with 0.5% Rh—Mn—Li in CO hydrogenation. Before impregnation, the SiC was etched with HNO_3 solution to reduce metal impurities that might poison Rh and/or calcined to increase the amount of surface groups for anchoring metal species.

2. Experimental

2.1. Catalyst preparation

SiC (SiC-0, SICAT Company) was treated with 10% HNO_3 solution at 100 °C for 3 h (SiC-1) or calcined at 950 °C for 6 h (SiC-2). SiC-1 was calcined at 950 °C for 6 h (SiC-3). Catalysts were prepared by impregnating

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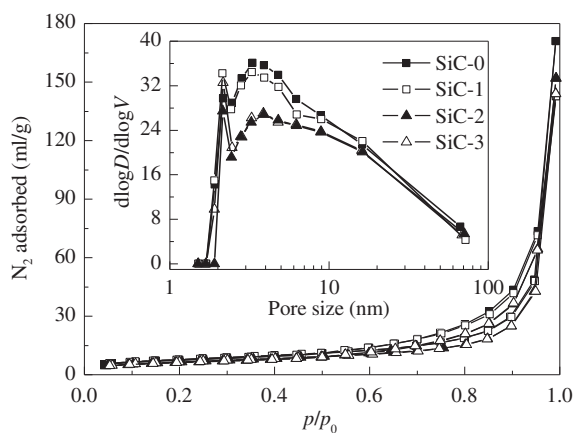


Fig. 1. N_2 adsorption–desorption isotherms and pore size distributions (inset) of SiC samples. SiC-1: SiC-0 pretreated with 10% HNO_3 ; SiC-2: SiC calcined at 950 °C for 6 h; SiC-3: SiC-1 calcined at 950 °C for 6 h.

the SiC samples (20–40 mesh) with an aqueous solution containing $RhCl_3$, $MnCl_2$, and $LiCl$ in specified amounts. After drying at room temperature overnight, the samples were kept at 110 °C for 4 h and 350 °C for 4 h. The Rh, Mn, and Li contents were controlled to be 0.5, 0.5, and 0.02 wt%, respectively.

2.2. Catalyst characterization

N_2 adsorption–desorption isotherms were recorded at -196 °C using a Quantachrome Autosorb-1 analyzer. The samples were degassed at 350 °C for 3 h before analysis. The specific surface area (S_{BET}) was calculated using the multi-point Brunauer–Emmett–Teller (BET) method. The total pore volume was obtained from the accumulated volume of adsorbed N_2 at $p/p_0 = 0.99$. The average pore size was calculated from the desorption branch using the Barrett–Joyner–Halenda method. The X-ray diffraction (XRD) patterns of the samples were recorded with a PANalytical X'Pert-Pro diffractometer operated at 40 kV and 40 mA, using Ni-filtered $Cu K_{\alpha}$ ($\lambda = 0.15406$ nm) radiation. Fourier-transform infrared (FT-IR) spectra of the SiC samples were recorded in air using a Thermo Scientific Nicolet iS50FT-IR spectrometer. Typically, 32 scans were collected at a 4 cm^{-1} spectral resolution in the range 4000–400 cm^{-1} . Temperature-programmed H_2 reduction (H_2 -TPR) and pulsed H_2 chemisorption experiments were performed using an Altamira Instruments AMI-300 U instrument. The sample was flushed with Ar at 300 °C for 0.5 h, cooled to 50 °C, and heated to 800 °C (10 °C/min) in 10% H_2 /Ar. The H_2 -TPR profiles were obtained using a thermal conductivity detector (TCD). Before H_2 chemisorption, the catalyst samples were reduced in situ with 10% H_2 /Ar at 350 °C for 1 h, purged with He at 350 °C for 30 min, and cooled to 50 °C. The samples were repeatedly dosed with 10% H_2 /Ar until the TCD signal reached a constant value.

2.3. Catalyst evaluation

CO hydrogenation reactions were performed in a fixed-bed microreactor (Φ 6 mm). The catalyst (1 mL) was reduced in situ with pure H_2 at 330 °C for 1 h and cooled to 305 °C, followed by introduction of syngas ($H_2/CO = 2$, gas hourly space velocity = 8000 h^{-1}) to

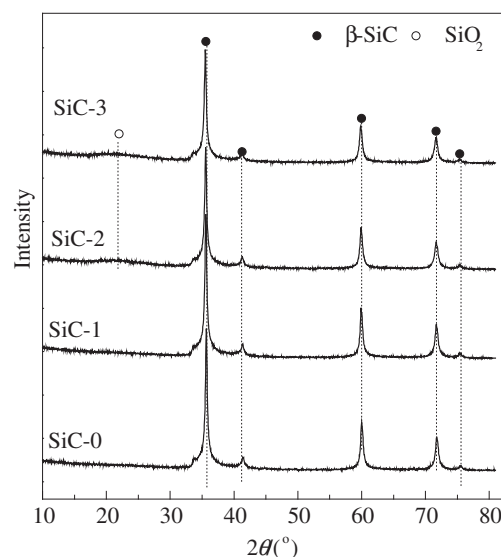


Fig. 2. XRD patterns of various SiC supports.

5.0 MPa. The effluent from the reactor was passed through a condenser and analyzed online using an Agilent 7890 gas chromatograph with a TCD. The produced oxygenates dissolved in water in the condenser. After the reaction had stabilized, the liquid products were collected for 4 h and analyzed off-line using an Agilent 7890 gas chromatograph with a flame ionization detector, and *n*-pentanol as an internal standard. The CO conversion, product selectivity, and space–time yields (STY, g/kg-cat/h) of the C_2 oxygenates were calculated using a previously reported method [5]. The Rh efficiency (g/g-Rh/h) was defined as the mass of C_2 oxygenates produced per unit mass of Rh metal per hour [3, 21]. The error was estimated to be 5%–8% for all data collected.

3. Results and discussion

3.1. Effects of pretreatment on SiC properties

First, the acid-treated SiC samples were analyzed using X-ray fluorescence spectroscopy (results not shown). The results indicated that the metal impurity contents were almost unchanged. This is not in accord with previously reported results [16]; this is probably because different acid-etching conditions were used and our SiC sample was of high purity. Fig. 1 shows the N_2 adsorption–desorption isotherms and pore size distributions of the SiC samples and Table 1 summarizes their textural properties. No meaningful differences among the isotherms were observed. The four SiC samples contained mainly mesopores (centered at 2.1 and 3.9 nm) and small amounts of

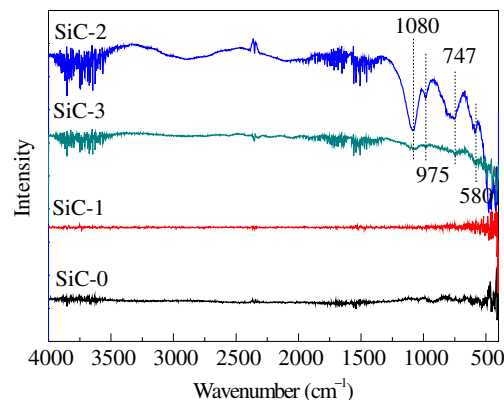


Fig. 3. FT-IR spectra of SiC samples.

Table 1
Textural properties of SiC samples.

Sample	S_{BET} (m^2/g)	Pore volume (ml/g)	Average pore size (nm)
SiC-0	26.5	0.27	8.53
SiC-1	27.4	0.22	8.61
SiC-2	22.4	0.24	8.55
SiC-3	22.6	0.22	8.61

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