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Direct conversion of syngas to ethanol over Rh/Mn-supported on modified SBA-15 molecular sieves: Effect of supports

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ABSTRACT

SBA-15 molecular sieves with a tunable pore size (SBA-15-HCl, SBA-15-HPMo, SBA-15-HPW, and SBA-15-HSiW) were synthesized through adding heteropoly acids to a template and extending crystallization time. Loaded with $RhCl_3$ and $Mn(NO_3)_2$, SBA-15-HPMo catalyzed well the direct conversion of syngas to ethanol. In the first 2 h the CO conversion over the Rh–Mn/SBA-15-HPMo catalyst was up to 100%. Average CO conversion over the SBA-15-HPMo-supported catalyst increased significantly from 4.2 to 21.9% and selectivity to ethanol from 9.3 to 12.8% compared with the amorphous silica-supported one. The enhanced redox property of the encapsulated Rh and Mn oxides within the mesoporous channels, and multi-dispersed centers formed by confined metal particles contributed to improved catalytic performances.

1. Introduction

The finite resources of fossil fuels along with environmental concerns have stimulated a broad intensive search for alternative energy sources [1,2]. As a fuel [3,4], ethanol has found widespread use. Syngas (a mixture of CO and H_2) conversion over Rh-based catalysts to ethanol offers a good alternative because other C_2 oxygenate by-products (for example, acetaldehyde and acetic acid) can be readily hydrogenated to ethanol, and syngas can be conveniently manufactured from natural gas and coal at present and from biomass in the future [5]. However, the catalytic conversion of syngas to ethanol remains challenging, and no commercial process exists as of today although the research on this topic has been ongoing for 90 years [6]. A growing consensus regarding ethanol synthesis from syngas is that supported Rh has a great potential for the reaction, but suitable supports and promoters are needed to enhance the reactivity of Rh [7–10].

Most previous works have been performed over SiO_2-supported systems [6,11–13], and examples of other supports studied include Al_2O_3 [14], TiO_2 [15], NaY [16], ZrO_2 [17] and CeO_2 [18]. Mesoporous molecular sieves SBA-15 with two-dimensional hexagonally ordered arrays of channels, discovered by Zhao et al. [19], has attracted much attention for potential applications as versatile catalysts and catalyst supports [20], template [21] and separation materials [22] because of its appealing textural properties and high surface area, and appreciable thermal and hydrothermal stability. However, to our knowledge, no detailed study of the effect of SBA-15 on Rh/Mn-supported catalysts on the activity of ethanol synthesis from syngas has been reported. Small amounts of heteropoly acid can significantly enhance the crystallization process for SBA-15 formation [23]. Here, four kinds of mesoporous molecular sieves (SBA-15-HCl, SBA-15-HPMo, SBA-15-HPW, and SBA-15-HSiW) were synthesized by different methods or materials. The effect of SBA-15s on CO conversion and product selectivities was explored in order to significantly improve the performance of catalysts for the synthesis of ethanol from syngas and as-prepared catalysts exhibit good activity and selectivity.

2. Experimental

2.1. Materials and catalyst synthesis

2.1.1. Materials

Nonionic triblock copolymer $EO_{20}PO_{70}EO_{20}$ (P123) (Mn 5800) was purchased from Aldrich. Phosphomolybdic acid (AR), phosphotungstic acid (AR) and silicotungstic acid (AR) with a principal composition of $H_3PO_4 \cdot 12MoO_3 \cdot 24H_2O$, $H_3PO_4 \cdot 12WO_3 \cdot 24H_2O$ and $H_4SiO_4 \cdot 12WO_3 \cdot 24H_2O$ (abbreviated to HPMo, HPW and HSiW), were obtained from J & K Chemical. Tetraethoxysilane (TEOS) (AR) and concentrated hydrochloric acid (c-HCl, 36 wt.%) were provided by Shanghai Chemical Regent Company of China. SiO_2 (20–40 mesh, BET surface area about 200 m^2/g) was purchased from Haiyang Chemicals Plant of Qingdao. $RhCl_3 \cdot 3H_2O$ (AR) was purchased from Beijing Chemical

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Agents Plant. $Mn(NO_3)_2$ (AR) were obtained from Tianjin Tianhe Chemical Agent Plant.

2.1.2. Synthesis of SBA-15

2.1.2.1. Synthesis of SBA-15-HCl. A modified procedure for SBA-15 preparation [19] giving better reproducibility of hexagonal porous array was adopted. In a typical procedure, 2.0 g of Pluronic P123 was dissolved with stirring in 60 ml of 2 M HCl for 6 h at 311 K, followed by addition of 4.5 ml of TEOS with stirring at 311 K for 24 h. The mixture was aged at 373 K for 24 h. After cooling to room temperature, the solid product was recovered by filtering , washing and drying in air at 311 K for 48 h. Calcination at 823 K in air for 8 h (with a slow temperature increase of 1 K/min) completed the preparation. The preparation procedure was modified to reduce the microporosity; this was achieved according to the literature [24] by increasing the duration of the hydrothermal treatment at 373 K to 48 h instead of 24 h before recovery by filtration.

2.1.2.2. Synthesis of SBA-15-HPMo, SBA-15-HPW, and SBA-15-HSiW. A modified procedure was used to prepare SBA-15-HPMo, SBA-15-HPW, and SBA-15-HSiW samples [23]. Heteropoly acids were used as promoters. In a typical synthesis batch, 3.0 g of P123 was dissolved in 78.75 ml of distilled water with vigorously stirring at room temperature for 3 h, then the calculated amounts of heteropoly acids (0.48 g HPMo for SBA-15-HPMo, 0.7423 g HPW for SBA-15-HPW, and 0.7428 g HSiW for SBA-15-HSiW, and the molar ratio of Si/Mo, Si/W and Si/HSiW was all the same, 12.4) was added into the solution. After P123 and heteropoly acids were dissolved completely, 6.9 ml of zTEOS and 0.56 ml c-HCl (36 wt.%) were added dropwise to the above mixture solution. The chemical composition of the reaction mixture was: 3 g P123: 0.031 mol TEOS: 0.00021 mol heteropoly acids: 0.0065 mol HCl: 4.37 mol H_2O. Subsequently, the mixture was stirred at 313 K for 24 h and thermally treated at 373 K for 48 h. The reaction products were filtered, washed and dried at 318 K for 48 h. Finally, the samples were calcined at 823 K in air for 8 h (with a slow temperature increase of 1 K/min). Compared with the conventional synthesis method [19], the toxic liquid acid HCl concentration of the reaction mixture solution is only 3.6% and the total H^+ originated from both HCl and heteropoly acid dissociation is about 4%.

2.1.3. Catalyst synthesis

Catalysts were prepared by impregnating SBA-15 or SiO_2 with an aqueous solution of $RhCl_3 \cdot 3H_2O$ and/or $Mn(NO_3)_2$ and/or HPMo via the incipient wetness technique. The impregnated powders are dried at 333 K overnight. Rhodium loading of all the catalysts was 5.0 wt.%. The weight ratio of Rh:Mn was 1:1.

2.2. Catalyst characterization

2.2.1. N_2 adsorption–desorption

N_2 adsorption–desorption isotherms were obtained at 77 K on an Omnisorp-100CX apparatus (USA). Prior to analysis, all samples were degassed in a high vacuum for 2 h at 523 K. BET surface areas were calculated from the linear part of the BET plot. Pore size distribution (PSD) were calculated by the Barret–Joyner–Halenda model, and the total pore volumes were estimated from the N_2 uptake at $P/P_0 = 0.994$.

2.2.2. X-ray powder diffraction (XRD)

XRD patterns were recorded on a Rigaku D/max 2550PC diffractometer (Rigaku, Japan) using Cu Ka radiation, operating at 40 kV and 300 mA.

2.2.3. Transmission electron microscopy (TEM)

TEM images were obtained on a JEM-2010HR microscope (JEOL, Japan). Samples for TEM studies were prepared by dipping a carbon-coated copper grid into a suspension of a mesoporous material in ethanol that was pre-sonicated for 10 min.

2.2.4. Temperature programmed reduction (TPR)

TPR experiments were carried out on a Micromeritics TPD/TPR 2900 apparatus. The catalyst (about 40 mg) was pretreated under dry air at 383 K for 1 h. The TPR profile was recorded by heating the sample from room temperature to 973 K at a rate of 10 K/min under a H_2/Ar (10% *v*/*v*) flow.

2.2.5. Temperature programmed surface reaction (TPSR) of adsorbed CO

TPSR experiments were performed on America Micromeritics Autochem 2920 with a U-shaped quartz reactor connected to a Baltzer Prisma QMS 200 TM quadropole mass spectrometer. The experimental procedure was as follows: About 50 mg catalyst was placed in a quartz reactor and reduced in H_2/Ar by heating to 533 K at 10 K/min and held for 1 h, followed by flushing with an Ar flow for 1 h at the same temperature. The samples were then cooled to 323 K in a stream of argon. CO was adsorbed by flowing a CO/He (5% *v*/*v*) mixture at 298 K for 30 min. Physisorbed CO was purged with Ar for 30 min. Finally, the temperature was linearly increased from 298 to 923 K at a heating rate of 10 K/min under a H_2/Ar (10% v/v) flow. The signals of H_2 ($m/z = 2$), CO ($m/z = 28$), CH_4 ($m/z = 16$), H_2O ($m/z = 18$), and Ar($m/z = 40$) were simultaneously recorded with the mass spectrometer.

2.3. Catalytic measurements

CO hydrogenation reactions were performed using a high-pressure fixed-bed microreactor (stainless steel 316, 200 mm length and 4 mm internal diameter). First, 0.5 g catalysts were reduced in situ at 673 K (heating rate of 1 K/min) for 16 h in a flow of H_2/N_2 (1:9) at a rate of 100 ml/min. The reactor was then cooled down and the gas flow was switched to 75 $cm^3\ min^{-1}$ (or other flow rate) of syngas (molar ratio $H_2/CO = 2$). The system was pressurized at 1.0 MPa and heated to desired temperatures at a heating ramp of 10 K/min. Temperature was measured with a type-K thermocouple buried in the catalytic bed. Flow rates were controlled using a Brooks 5850 TR Series mass flow controllers. All experimental variables were carefully controlled to ensure identical reaction conditions when testing catalysts. Some recommendations and criteria proposed by Pérez-Ramirez et al. [25] were followed to ensure accurate measurements.

Product analysis was performed on-line with a gas chromatograph (GC 2014 Japan) equipped with TCD and FID detectors. The identification of reaction products and gas chromatograph calibration were accomplished using gas chromatography-mass spectrometry (GC-MS) and quantitative standard solutions from AccuStandard.

3. Results and discussion

3.1. CO hydrogenation results

The effects of the flow rate of syngas on the conversion and selectivity of Rh–Mn/SBA-15-HPMo catalyst are summarized in Table 1. As expected, CO conversion decreased with increasing flow rate. Obviously, the product selectivities are also affected. Three examples in Table 1 illustrate that increasing syngas flow rate from 60 to 90 $cm^3\ min^{-1}$ decreased the average CO conversion from 25.0 to 17.5% while simultaneously increasing the ethanol selectivity from 8.6% to maximum volume 12.8% at flow rate of 75 $cm^3\ min^{-1}$ and then decreasing to 11.6%. Methanol synthesis involves CO molecular adsorption, liquid hydrocarbon synthesis involves CO dissociative adsorption, while highly efficient synthesis of ethanol requires a good balance between the molecular adsorption CO and dissociative adsorption CO. When the flow rate is low, contact time between CO and catalysts is long, the concentration of dissociative adsorption CO is high, and that of molecular adsorption CO is low. When the flow rate is high, the concentration of dissociative adsorption CO is low, and that of molecular adsorption CO is high. So the ethanol selectivity passes through a maximum with increasing flow rate. The methanol