



New insights into the effects of Mn and Li on the mechanistic pathway for CO hydrogenation on Rh-Mn-Li/SiO₂ catalysts



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ABSTRACT

It has been reported widely that Rh-Mn-Li/SiO₂ catalysts can exhibit high selectivity to C₂⁺ oxygenates during CO hydrogenation, with promoters of Mn and Li playing an important role in this behavior. In this study, a series catalysts of Rh-Mn-Li/SiO₂ with different amounts of Mn and Li were prepared, and the new insights into the effects of Mn and Li on the mechanistic pathway for C₂⁺ oxygenates synthesis from syngas were investigated. The XPS analysis showed that Rh existed mainly as metallic Rh after reduction, however partially positively charged Rh^{δ+} atoms appeared on the surface of Mn-containing catalyst due to the interaction of Rh-Mn. The results of H₂-TPR indicated that both of Li and Mn can inhibit the reduction of Rh₂O₃. With the increase in the ratio of Mn/Rh, the most effective interaction, associated to the presence of two reduction centers of Rh₂O₃, was obtained when the ratio of Mn/Rh = 1. *In situ*-FTIR was used to probe the effects of Mn and Li on CO adsorption and hydrogenation. With regards to the CO adsorption, the doping of Mn can enhance the CO adsorption ability of Rh and weaken the CO-Rh bond strength very effectively when the amount of Mn reached 1.5 wt.%. Improved capacity of CO adsorption is conducive to increase of CO conversion, while the weakening of CO-Rh bond is beneficial to the CO insertion reaction, thus contributing to the generation of C₂⁺ oxygenates. Moreover, the low amount of Li (≤0.075 wt.%) can also enhance the CO adsorption, resulting in the improvement of reactivity. On the other hand, Mn and Li promoted dissociation of H₂, which is favorable to an increase in the rate of hydrogenation. But an opposite effect appeared at high content of Mn (>1.5 wt.%). As the optimized results, when Rh, Mn, Li content was 1.5 wt.%, 1.5 wt.% and 0.075 wt.%, the catalyst for CO hydrogenation of C₂⁺ oxygenates achieved the best performance of C₂⁺ oxygenates synthesis.

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1. Introduction

The search for processes to provide alternative feedstock for fuels has been promoted by the increasing concerns about global climate change, depletion of fossil fuel resources, and rising crude oil prices. Ethanol has attracted increasing attention as a clean fuel or an additive to gasoline [1,2]. Direct catalytic synthesis of C₂ oxygenates (e.g., ethanol, acetaldehyde and acetic acid) from syngas, which can be derived from biomass, coal, or natural gas, is one of the most promising technologies [3,4]. However, developing an efficient and selective catalyst for C₂ oxygenates synthesis has been a major challenge.

Over the last thirty years, Rh-based catalysts have been found to display unique efficiency and selectivity in C₂ oxygenates synthesis from syngas [5–9]. Since single Rh component exhibits a poor activity and mainly leads to formation of hydrocarbon products, with methanol being the primary oxygenate, efforts have been centered on improving the dispersion of Rh and modification of Rh with additives and supports in order to selectively synthesize C₂ oxygenates [10–12]. So far, the catalyst of Rh-Mn-Li/SiO₂ was found to give an excellent activity and C₂ oxygenates selectivity [13], with promoters of Mn and Li playing an important role in this behavior.

Considerable investigations heretofore have been reported to interpret the role of Mn and Li. Sachtler et al. [14] concluded that the improved activity of Mn promoted Rh/SiO₂ catalysts was due to the formation of a tilted CO adsorption mode on the Rh surface. The tilted adsorbed CO dissociated more easily, thereby increasing the CO hydrogenation activity. Wang et al. [15] proposed that the interaction between Rh and Mn formed a new active site of

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(Rh_x⁰Rh_y⁺)-O-Mⁿ⁺, wherein a portion of the Rh was present in the Rh⁺ oxidation state, the promoter Mn (Mⁿ⁺) was in close contact with these Rh species, and the formation of this active site was conducive to the C₂ oxygenates synthesis. With respect to Li, it is believed that addition of Li can restrain CO dissociation, thereby improving the selectivity of oxygenates [16]. Chuang et al. [17] reported that the effect of Li promoter was attributed to electron-donation, which inhibited the hydrogenation ability of the catalyst and hence promoted the formation of oxygenates. Although a lot of experiments and reasoning were focused on the interaction mechanism among Rh, Mn, and Li, the synergistic promoting roles of Mn and Li cannot be confined to one of the theories mentioned above due to the varied experimental conditions and complex reaction scheme.

In the present study, to further probe the promoting mechanisms of Mn and Li, the catalytic activities of Rh/SiO₂ catalysts promoted with various amounts of Mn and Li for CO hydrogenation were compared. Considering that the catalytic performance of the Rh-Mn-Li/SiO₂ catalyst for the synthesis of C₂ oxygenates from CO hydrogenation was enhanced greatly when a commercial SiO₂ was replaced by a monodispersed SiO₂ prepared by the Stöber method [18,19], the monodispersed SiO₂ was employed in serving as the support for Rh-based catalysts. The techniques of XPS and H₂-TPR were used to relate to the structure-activity relationships of the catalysts. Furthermore, new insights into the effects of Mn and Li on the mechanistic pathway for CO hydrogenation were demonstrated by diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS).

2. Experimental

2.1. Catalyst preparation

SiO₂ was prepared by the Stöber method [20] as follows. The mixture solution of 21 mL tetraethylorthosilicate (TEOS) (99.5%, SCRC) and 50 mL anhydrous ethanol (99.7%, SCRC) was added slowly into the solution of 76 mL NH₃·H₂O (26 vol%, SCRC) and 200 mL anhydrous ethanol. Then, this synthesized solution was aged for 4 h and separated centrifugally at 7000 rpm. Finally, the collected product was washed with de-ionized water three times and dried at 70 °C for 12 h. Before used, it was calcined in static air at 350 °C for 4 h.

RhCl₃ hydrate (Rh ~36 wt.%, Fluka), Mn(NO₃)₂·6H₂O (99.99%, SCRC), Li₂CO₃ (99.5%, SCRC), and SiO₂ mentioned above were used in catalyst preparations. Catalysts were prepared by co-impregnation to incipient wetness of silica (1.0 g) with an aqueous solution of RhCl₃ hydrate and aqueous solutions of precursors of the promoters, followed by drying at 90 °C for 4 h, and then at 120 °C overnight before being calcined in air at 350 °C for 4 h. The specific content of various metals are listed in related tables and figures. For example, the catalyst referred to as 1.5Rh-1.5Mn-0.075Li/SiO₂ indicated that the weight percents of Rh, Mn and Li were 1.5 wt.%, 1.5 wt.%, and 0.075 wt.%, respectively. Elemental analysis by inductively coupled plasma (ICP) revealed good agreement between the expected and experimental values. In addition, the possible chloride composition in the catalyst after calcination was also detected by ICP, and the absence of chloride was confirmed.

2.2. Reaction

CO hydrogenation was performed in a fixed-bed micro-reactor with length ~350 mm and internal diameter ~5 mm. The catalyst (0.3 g) diluted with inert α-alumina (1.2 g) was loaded between quartz wool and axially centered in the reactor tube, with the temperature monitored by a thermocouple close to the catalyst

bed. Prior to reaction, the catalyst was heated to 400 °C (heating rate ~3 °C/min) and reduced with 10% H₂/N₂ (total flow rate = 50 mL/min) for 2 h at atmospheric pressure. The catalyst was then cooled down to 300 °C and the reaction started as gas flow was switched to a H₂/CO mixture (molar ratio of H₂/CO = 2, total flow rate = 50 mL/min) at 3 MPa. All post-reactor lines and valves were heated to 150 °C to prevent product condensation. The products were analyzed on-line (Agilent GC 6820) using a HP-PLOT/Q column (30 m, 0.32 mm ID) with detection with an FID (flame ionization detector) and a TDX-01 column with a TCD (thermal conductivity detector). The conversion of CO was calculated based on the fraction of CO that formed carbon-containing products according to: %Conversion = (∑n_iM_i/M_{CO})-100, where n_i is the number of carbon atom in product i, M_i is the percentage of product i detected, and M_{CO} is the percentage of carbon monoxide in the syngas feed. The selectivity of a certain product was calculated based on carbon efficiency using the formula n_iC_i/∑n_iC_i, where n_i and C_i are the carbon atom number and molar concentration of the *i*th product, respectively.

2.3. Catalyst characterization

The X-ray powder diffraction (XRD) spectra of samples were obtained on a Rigaku D/MAX-III A X-ray diffractometer with CuKα (λ = 0.15418 nm). The specific surface area (S_{BET}), pore volume (V_p), and pore diameter (D_p) of sample were obtained by N₂ adsorption at -196 °C on a Micromeritics ASAP 2020 apparatus. The metal loadings of the catalysts were determined by ICP-OES (PerkinElmer Optima 7000DV).

The amount of hydrogen adsorption of various catalysts was calculated on the basis of H₂-TPD profiles. For H₂-TPD measurements, the catalyst (0.1 g) was reduced in-situ for 2 h at 400 °C in 10% H₂/N₂, and then was held at 400 °C for another 30 min before being cooled down to room temperature in He flow. The next step was H₂ adsorption at room temperature for 0.5 h, and then the gas was swept again with He for 3 h. Subsequently, the sample was heated in a flowing He stream (50 mL/min) up to ~500 °C at a rate of 10 °C/min, while the desorbed species was detected with a TCD detector. The uptake of H₂ was used to calculate Rh metal dispersion and particle size, assuming that each surface metal atom adsorbs one H atom, i.e. H/RH_{surface} = 1.

Photoelectron spectra (XPS) were acquired with an ESCALAB 250Xi spectrometer in the pulse-count mode at a pass energy of 20 eV using an Al Kα (hν = 1486.6 eV) X-ray source. Kinetic energies of photoelectrons were measured using a hemispherical electron analyzer working in the constant pass energy mode. The background pressure in the analysis chamber was kept below 7 × 10⁻⁹ mbar during data acquisition. The powder samples were pressed into copper holders and then mounted on a support rod placed in the pretreatment chamber. Samples were reduced in situ at 400 °C for 1 h under 200 mbar H₂ pressure. The binding energies were calibrated relative to the C 1s peak from carbon contamination of the samples at 284.9 eV to correct for contact potential differences between the sample and the spectrometer. The XPS data were signal averaged for 20 scans and were taken in increments of 0.1 eV with dwell times of 50 ms.

H₂ temperature-programmed reduction (TPR) was carried out in a quartz microreactor. 0.1 g of the as-prepared sample was first pretreated at 350 °C in O₂/N₂ (molar ratio of O₂/N₂ = 1/4) for 1 h prior to a TPR measurement. During the TPR experiment, H₂/N₂ (molar ratio of H₂/N₂ = 1/9) was used at 50 mL/min and the temperature was ramped from room temperature to 500 °C at 10 °C/min while the effluent gas was analyzed with a TCD.

CO adsorption was studied using a Nicolet 6700 FT-IR spectrometer equipped with a Harrick diffuse reflectance infrared Fourier transform (DRIFT) cell with CaF₂ windows. Prior to exposure to the

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