



Methanation of carbon dioxide on metal-promoted mesostructured silica nanoparticles

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ABSTRACT

Metal-promoted mesostructured silica nanoparticles (MSN) have been studied for CO₂ methanation under atmospheric pressure. In term of activities, high activity was observed on Rh/MSN, Ru/MSN, Ni/MSN, Ir/MSN, Fe/MSN and Cu/MSN at and above 623 K. However, on an areal basis, Ni/MSN was the most active catalyst, while Ir/MSN was the poorest catalyst. The catalysts have also been studied for elucidation of the role of each metal, MSN and metal/MSN in CO₂ methanation by *in situ* FTIR spectroscopy studies. Firstly, CO₂ and H₂ was adsorbed and dissociated on metal sites to form CO, O and H atoms, followed by migration onto the MSN surface. The dissociated CO then interacted with oxide surfaces of MSN to form bridged carbonyl and linear carbonyl, while the presence of H atom facilitated the formation of bidentate formate. These three species could be responsible for the formation of methane. However, the bidentate formate species could be the main route to formation of methane. MSN support has been found to play an important role in the mechanism. MSN support served the sites for carbonyl species which act as precursors to methane formation. These results provided new perspectives in the catalysis, particularly in the recycling of CO₂.

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1. Introduction

The growing interest on greenhouse gas mitigation implies that CO₂ will be increasingly considered as a valuable feedstock for chemical industry instead of as a waste [1]. The valorization of carbon dioxide emissions could be one important part of the general strategy for reducing CO₂ emissions, and push chemical and energy companies towards a more sustainable use of the resources. There are several ways of adding value to CO₂, one of which is hydrogenation to form methane. Provided that hydrogen is generated from renewable energy sources such as water electrolysis [2], the methane produced by this reaction can be sent to chemical industry or can be utilized as an energy vector, which is an important advantage considering that the infrastructure for methane storage and transport is already present. CO₂ methanation has been investigated over a variety of supported metal catalysts, including Ni [3–11], Ru [12,13], Rh [14–17], Fe [18] and Cu [19]. Nickel catalysts were found to exhibit high activity for the reaction [4,5]. However, most of the studies concerning the methanation of CO₂ over

Ni catalysts have been focused on the reaction performed at high temperatures (>473 K) [7,8]. In addition to Ni catalysts, CO₂ methanation has been studied by several authors using different noble metals such as Ru, Pd and Rh over a variety of supports. Among them, Rh has been shown to be one of the most promising metal catalyst that is active in low-temperature of reactions [14,16].

There is still no consensus about the mechanistic path of CO₂ methanation, even though it is a comparatively simple reaction. Thus, its reaction mechanism appears to be difficult to establish. In general, the proposed mechanism in the previous work fall into two main categories. The first mechanism involves the conversion of CO₂ to CO prior to methanation [20–22]. The other involves the direct hydrogenation of CO₂ to methane without forming CO as an intermediate [23,24]. The present work tends to fall into the first category. However, there are still different opinions on the nature of the intermediate and the methane formation process. For example, Betta and Shellef demonstrated the presence of formate in the hydrogenation of CO on a Ru/Al₂O₃ catalyst by IR spectroscopy. It was claimed that the formate ion was formed directly on the alumina support and its formation did not require metallic Ru [25]. Karelavic et al. studied CO₂ adsorption and dissociation on a Rh/γ-Al₂O₃ system in the presence of H₂ by operando-diffuse reflectance Fourier transform infrared spectroscopy (DRIFTS) experiments.

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Their results showed that the linear Rh–CO species act as precursors of methane [14]. The mechanism of CO₂ methanation over Ni catalyst has been discussed by several authors [9,10,20,22]. One of the most cited mechanism proposes that the reverse water–gas-shift reaction, which generates CO from CO₂, is the first step. This reaction occurs on Ni surface and is followed by the methanation of CO. Falconer and Zagli studied the mechanism of CO₂ methanation over a Ni/SiO₂ catalyst, and reported that the carbon dioxide did not adsorb significantly on silica, leading them to conclude that this activated adsorption occurred on the nickel metal and not the support. Their conclusion was based on the capacity of CO₂, which did not adsorb significantly on SiO₂ [20]. Peebles et al. also suggested that CO₂ is quickly transformed into CO on the Ni surface [22]. However, the previously proposed mechanism leaves several questions unanswered regarding how the CO₂ is adsorbed and transformed into methane:

- (i) CO₂ methanation over unsupported Ni exhibited low yield of methane. Therefore, it is difficult to conclude that the CO that adsorbed on the Ni and/or metal surface was a precursor to methane.
- (ii) The technique used to elucidate the mechanism of CO₂ methanation was performed on a combination of metal and support, and it was difficult to determine the real function of the metal and the support. Therefore, each metal, support and metal/support combination should be tested in order to know the role of their presence.

Therefore, in this work, a series of metal-based catalyst supported on mesostructured silica nanoparticles (M/MSNs; M = Rh, Ru, Ni, Fe, Ir, Cu, Zn, V, Cr, Mn, Al and Zr) were prepared, and were applied for methane production from carbon dioxide and hydrogen gas in the temperature range of 373–723 K under atmospheric pressure. The effect of metal on the MSN was characterized by X-ray diffraction (XRD), nitrogen physisorption and infrared spectroscopy. To elucidate the mechanistic path of CO₂ methanation, *in situ* FTIR spectroscopy was used to observe the surface species during the reaction.

2. Experimental

2.1. Catalyst preparation

MSN was prepared by the sol–gel method according to the report by Karim et al. [26]. The surfactant cetyltrimethylammonium bromide (CTAB; Merck), ethylene glycol (EG; Merck) and NH₄OH solution (QRec) were dissolved in water with the following molar composition of CTAB:EG:NH₄OH:H₂O = 0.0032:0.2:0.2:0.1. After vigorous stirring for about 30 min at 353 K, 1.2 mmol of tetraethyl orthosilicate (Merck) and 1 mmol of 3-aminopropyl triethoxysilane (Merck) were added to the clear mixture to give a white suspension solution. This solution was then stirred for another 2 h, and the samples were collected by centrifugation at 20,000 rpm. The as-synthesized MSN were dried at 333 K and calcined at 823 K for 3 h in air to remove the surfactant. For unsupported Ni catalyst, it was prepared by calcination of Ni(NO₃)₂·6H₂O at 823 K for 3 h. For metal based MSN catalysts, they were prepared by impregnation of MSN powder with an aqueous solution of the corresponding metal salt precursor (RhCl₃, RuCl₃, Ni(NO₃)₂, IrCl₃, Fe(NO₃)₃, Cu(CO₂CH₃)₂, Zn(NO₃)₂, V(C₅H₇O₂)₃, Cr(NO₃)₃, MnCl₂, Al(NO₃)₃ and ZrOCl₂) (Merck, 99%). The resulting slurry was heated slowly at 353 K under continuous stirring and maintained at that temperature until nearly all the water being evaporated. The solid residue was dried in an oven at 383 K overnight before calcination at 823 K for 3 h in air. The metal loading of the

catalysts was 5 wt%. All metal based MSN samples were denoted as Rh/MSN, Ru/MSN, Ni/MSN, Ir/MSN, Fe/MSN, Cu/MSN, Zn/MSN, V/MSN, Cr/MSN, Mn/MSN, Al/MSN and Zr/MSN.

2.2. Characterization

The crystalline structure of the catalyst was determined by X-ray diffraction (XRD) recorded on a powder diffractometer (Bruker Advance D8, 40 kV, 40 mA) using a Cu K α radiation source in the range of $2\theta = 1.5\text{--}90^\circ$. The BET analysis of the catalyst was determined by N₂ adsorption–desorption isotherms using a Quantachrome Autosorb-1 instrument. The catalyst was outgassed at 573 K for 3 h before being subjected to N₂ adsorption. Pore size distributions and pore volumes were determined from the sorption isotherms using a non-localized density functional theory (NLDFT) method. In the FTIR measurements, pyrrole has been used as a probe molecule for the characterization of basic sites [3]. The methanation was also recorded by *in situ* FTIR spectroscopy to study the surface species formed during the reaction. All the measurements were performed on an Agilent Cary 640 FTIR spectrometer equipped with a high-temperature stainless steel cell with CaF₂ windows. Prior to the measurements, 30 mg of sample in the form of a self-supported wafer was reduced in H₂ stream (100 ml/min) at 773 K for 4 h and cooling to 303 K under He atmosphere. For pyrrole adsorption, the reduced catalyst was exposed to 2 Torr of pyrrole at 303 K for 30 min, followed by outgassing at 423 K for 30 min. All spectra were recorded at room temperature with a spectral resolution of 5 cm⁻¹ with five scans. Furthermore, the formation of surface species during the methanation was recorded by introducing of a mixture of CO₂ (4 Torr) and H₂ (16 Torr) to the catalyst at room temperature, followed by heating to 523 K. The spectra were recorded after equilibrium conditions have been reached. For CO₂ and H₂ adsorption studies, the sample was pretreated using the same procedure as above. The adsorption of CO₂ was done by exposing 4 Torr of CO₂ on sample at room temperature and subsequent heating to 523 K. While, the adsorption of H₂ was done by exposing 16 Torr H₂ at room temperature followed by heating in hydrogen from 303 to 573 K. For adsorption of CO₂, H₂ or the mixture of CO₂ and H₂ in the bare Ni catalyst, the Ni catalyst was mixed with KBr (Ni:KBr = 1:100) to increase the transparency of the sample.

2.3. Catalytic activity measurements

CO₂ methanation was conducted in a microcatalytic quartz reactor with an interior diameter of 8 mm at atmospheric pressure at temperature range of 373–723 K. The thermocouple was directly inserted into the catalyst bed to measure the actual pretreatment and reaction temperatures. The catalyst was sieved and selected in the 20–40 μm fraction. Initially, 200 mg of catalyst was treated in an oxygen stream ($F_{\text{Oxygen}} = 100 \text{ ml/min}$) for 1 h followed by a hydrogen stream ($F_{\text{Hydrogen}} = 100 \text{ ml/min}$) for 4 h at 773 K and cooled down to the desired reaction temperature in a hydrogen stream. After the temperature became stable, a mixture of H₂ and CO₂ was fed into the reactor at gas hourly space velocity (GHSV) of 50,000 ml g⁻¹ h⁻¹ and H₂/CO₂ mass ratio of 4/1. All gases were controlled with calibrated mass flow controllers (SEC-400 MK2, Stec Ltd., Japan). The CH₄ formation rate was measured in the temperature range of 373–723 K. The activity was monitored with decreasing temperature and back to verify stable catalyst conditions during these measurements. The composition of the outlet gases was analyzed with an on-line 6090N Agilent gas chromatograph equipped with a GS-Carbon PLOT column and a TCD detector. The lines from the outlet of the reactor to the GC were heated at 383 K to avoid condensation of the products. The moisture trap was installed at the outlet gas line of the reactor to prevent moisture

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