

# CATALYTIC CONVERSION OF CARBON DIOXIDE

## 1. SUBJECT SETTING

Carbon dioxide is well-known greenhouse gases. As reported by the International Energy Agency (IEA) the total anthropogenic CO<sub>2</sub> emissions in 2007 were around  $29 \times 10^9$  metric tons. Electricity and heat generation combined with the use of hydrocarbon-based fuels in transportation have been the largest contributors of CO<sub>2</sub>, creating almost two-thirds of global emissions. According to IEA statistics, coal has been the dominant source for world electricity and heat generation at 41%, while the share of gas was 23%.

CO<sub>2</sub> is a cheap, nontoxic and abundant C1 feedstock and its chemical utilization is a challenge and important topic. Thus, any efficient reactions using CO<sub>2</sub> as a reagent have positive ramifications on efforts towards carbon management. However, CO<sub>2</sub> is a thermodynamically stable compound, and then its reduction requires high energy substances or electro reductive processes. Such an inert property of CO<sub>2</sub>, together with the lower reactivity in various reactions, is probably the major reasons why currently the toxic carbon monoxide, as a C1 building unit for many processes, is used mostly in industry.

The total amount of carbon dioxide used in industry is approximately  $115 \times 10^6$  metric tons per year. Its utilization as a technological fluid, where carbon dioxide is not chemically converted and thus can be recovered at the end, is estimated at  $18 \times 10^6$  metric tons per year. The generation of energy used for CO<sub>2</sub> transformation, if based on hydrocarbon raw materials, ironically still produces large amounts of CO<sub>2</sub>. In addition the result in organic chemicals in which CO<sub>2</sub> is incorporated as the result of these transformations release CO<sub>2</sub> at the end of their use. However, despite the fact that, currently, the usage of CO<sub>2</sub> in the chemical industry cannot reduce significantly the global CO<sub>2</sub> levels, it is believed that the full potential of the fixation of CO<sub>2</sub> into value added products has not yet been completely explored. The direct use of no hydrocarbon based energy sources for reduction of CO<sub>2</sub> would change the above

perspective and allow recycling of carbon dioxide via chemicals and liquid fuels. Thus, the further development of industrial processes that are utilizing CO<sub>2</sub> for high-demand products is of importance.

The potential of homogeneous catalysis for CO<sub>2</sub> fixation has been discussed in recent reviews. Valuable chemicals including the production of carbonates, carbonate's, urethanes, lactones, pyrones, and formic acid and its derivatives could be synthesized by homogeneous catalysts. Heterogeneous catalysis can offer several technical advantages such as stability, separation, handling and reuse of the catalyst and reactor design. Despite CO<sub>2</sub> activation by heterogeneous catalytic routes were still limited, efforts have been made towards the synthesis of dimethyl carbonate, cyclic carbonates, and synthetic gas (CO, H<sub>2</sub>) as well as methanol synthesis from CO<sub>2</sub> hydrogenation.

The objective of this thesis aims at development of various efficient catalysts for the process of conversion of carbon dioxide to syngas and valuable produce. The first way is about catalytic conversion of carbon dioxide to syngas, which is the main feedstock for many reactions; the second way is about catalytic conversion of carbon dioxide downstream product to another more valuable product, which is also a way of conversion carbon dioxide.

## **2. METHODOLOGY**

The methodology of this thesis is to develop and prepare the different catalysts which possess high catalytic activity and more stability in catalytic reaction. In this process, we also analyze the structure, physical property and chemical property of the catalysts using Nitrogen adsorption-desorption analysis, XRD analysis, H<sub>2</sub>-TPR analysis, TEM analysis, SEM analysis, TG-DTA analysis and so on. It is also very important to get the physical chemical property of the spent catalyst to analysis the reason of different catalytic performance of the catalysts using TPH analysis, Raman spectra, XPS analysis, et al.

### **3.EXPERIMENTAL**

#### **3.1. CATALYST PREPARATION**

##### **3.1.1 CNTS CATALYST**

Raw multi-wall carbon nanotubes (inner diameter: 4-10 nm, Chengdu, China) (denoted as raw CNTs) were firstly refluxed in concentrated HNO<sub>3</sub> (65 wt. %) at 120 °C for 14 h, and then washed with deionized water until pH=7. The sample was dried at 120 °C overnight (denoted as acid-treated CNTs). And then the obtained sample was further calcined at 900 °C under Ar atmosphere for 3 h (denoted as heat-treated CNTs). For the preparation of catalysts with Ni particles inside CNTs, catalyst was prepared by an improved wetness impregnation method. A certain amount of Ni(NO<sub>3</sub>)<sub>2</sub> were dissolved in the ethanol solvent. Above treated CNTs with open ends was impregnated with the nickel solution and then vacuumed for 0.5 h. After ultrasonic treatment for 0.5 h, the sample was impregnated with deionized water and dried at 60 °C overnight. By this method, the particles could be easily deposited inside CNTs (denoted as I-Ni/CNTs). In order to prepare the catalyst with Ni catalytic site on the exterior surface of nanotubes, dimethyl benzene was used to fill the pore of nanotubes. The volume of the solvent was equal to the pore volume of CNTs. Then the nickel nitrate solution was added to the pore-filled support. After ultrasonic treatment for 0.5 h, the sample was dried at 60 °C overnight (denoted as O-Ni/CNTs). For the comparison of catalytic activity with the Ni/CNTs, the Ni/AC (active carbon) catalyst was prepared by wet impregnation method. A specified amount of Ni (NO<sub>3</sub>)<sub>2</sub> was dissolved in deionized water. The amount of solution was equal to total volume of AC. Subsequently, the impregnated Ni/AC sample was treated by ultrasonic for 0.5 h and dried at 60 °C overnight.

All the samples were calcined in Ar at 450 °C for 3 h. Before the reaction, the catalyst was reduced at 500 °C for 2 h under a flow of 5 % hydrogen of 40 ml/min. The loading of Ni for all catalysts was 10.0 wt. %.

##### **3.1.2 MESOPOROUS ALUMINA CATALYSTS**

The mesoporous alumina (MA) was synthesized by using aluminum

iso-propoxide as a precursor, surfactant (EO)<sub>20</sub>(PO)<sub>70</sub>(EO)<sub>20</sub> triblock copolymer (Pluronic P123, from Sigma Aldrich) as a template under the evaporation induced self-assembly approach, according to the similar method reported in literature<sup>[32]</sup>. In a typical synthesis, an appropriate amount of P123 was dissolved in ethanol under constant stirring. Then fixed amounts of aluminum iso-propoxide and nitrate acid were added in the solution, and was further stirred for 5h. The solvent was then evaporated for 72h at 60 °C. The final sample was calcined at 700 °C for 5h with a heating rate of 10 °C/min.

A mesoporous alumina (denoted as MA) was also prepared by the same method as above without adding nickel precursor. Nickel impregnated MA catalyst (denoted as Ni/MA) was synthesized via incipient-wetness impregnation using Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O as a nickel precursor. The impregnated sample was dried at 120 °C overnight, followed by calcining at 700 °C for 4 h. Nickel loading was fixed at 6 wt% in both NiMA and Ni/MA catalysts.

The catalysts were prepared by incipient wetness co-impregnation of mesoporous alumina with aqueous solution of Ni(NO<sub>3</sub>)<sub>2</sub> and Pd(NO<sub>3</sub>)<sub>2</sub>. The sample was then dried at 120°C overnight and calcined at 450 °C for 3h. The loadings of Ni and Pd for all catalysts were fixed to 6.0 wt. % and 0.5 wt. %, respectively. The sample denoted as Ni/MA, Pd/MA or PdNi/MA corresponding to the loading metal.

### 3.1.3 HT CATALYSTS

Hydrotalcite-like samples of the catalyst were synthesized by the co-precipitation method. 0.03 mol (7.69 g) Mg(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O, 0.01 mol (3.75 g) Al(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O and the fixed amount of La(NO<sub>3</sub>)<sub>3</sub>·H<sub>2</sub>O (AR) were dissolved in deionized water of 400 mL at the molar ratios of Mg: Al: La=3:1:0, 3:1:0.1, 3:1:0.4, 3:1:0.7, 3:1:1, respectively. Then an aqueous solution of Na<sub>2</sub>CO<sub>3</sub> and NaOH (2:1, Na<sup>+</sup>: 1.5 mol/L) was slowly dropped at a constant rate of 3 mL/min into the solution of nitrates under vigorous stirring until the pH value reached 10. The slurry was continuously stirred for 0.5 h and then kept at room temperature for 20 h. The slurry

was then filtrated and washed with deionized water until the pH value reached 7.0. The resulting cake was dried at 80 °C for 10 h to obtain the HTLcs samples. Finally, the catalysts were calcined in air at 650 °C for 5 h with a heating rate of 10 °C/min. The obtained HTLcs samples and composite oxide catalysts were denoted as xLa-HTLcs before calcination and xLHTs after calcination, respectively, where x represented the added molar amount of La.

## 3.2 CATALYTIC REACTION TESTS

### 3.2.1 DRY REFORMING REACTION

Dry reforming experiments were carried out in fixed-bed quartz reactor (6 mm i.d.) under atmospheric pressure. A reactant gas stream that consisted of CH<sub>4</sub>, CO<sub>2</sub> and Ar with a molar ratio of 4.5:4.5:1 was used. The W/F was fixed at 1 g h/mol. Before the reaction, the catalyst was reduced in situ at 700 °C for 2h under a flow of 5% hydrogen of 40ml/min. The reforming methane with CO<sub>2</sub> was carried at 750 °C. The effluent gases being cooled through an ice trap were analyzed with two gas chromatographs. CO, CO<sub>2</sub> and CH<sub>4</sub> were analyzed by a Shimadzu GC-8A with a Porapak Q column and a thermal conductivity detector (TCD). H<sub>2</sub> was analyzed by a Shimadzu GC-320 with an activated carbon column and a TCD. The conversions of CO<sub>2</sub> and CH<sub>4</sub>, and the molar rate of H<sub>2</sub>/CO were calculated as following equations:

$$\text{CH}_4 \text{ conversion, vol\%} = \frac{(\text{CH}_4/\text{Ar})_{\text{in}} - (\text{CH}_4/\text{Ar})_{\text{out}}}{(\text{CH}_4/\text{Ar})_{\text{in}}} \times 100$$

$$\text{CO}_2 \text{ conversion, vol\%} = \frac{(\text{CO}_2/\text{Ar})_{\text{in}} - (\text{CO}_2/\text{Ar})_{\text{out}}}{(\text{CO}_2/\text{Ar})_{\text{in}}} \times 100$$

$$\text{H}_2/\text{CO ratio} = \frac{\text{H}_2 \text{ generation rate}}{\text{CO generation rate}}$$

### 3.2.2 DPC SYNTHESIS REACTION

The catalytic activities of the composite oxides xLHTs for the DPC synthesis via transesterification were evaluated in a one-neck round bottom flask with a rotary evaporator. The freshly prepared powder catalysts were placed in the flask along with liquid reactant of DMC/n-propanol with an initials molar ratio of 1:3. The reaction

was conducted at  $90\pm 2$  °C at an atmospheric pressure. The reaction time was 6 h. The dosage of the catalyst was defined as weight percentage of the reactants. The co-product of methanol was evaporated and separated from reaction system during the reaction.

The products were analyzed on a SP-2100 gas chromatography with a flame ionization detector (FID) and a separation column packed with polyglycol 20M. The column was temperature-programmed from 100 °C to 150 °C.

### **3.3 CATALYST CHARACTERIZATION**

Nitrogen adsorption measurements were carried out at -196 °C under a Quantachrome Instruments AUTOSORB-1, and BET surface area and the pore size distribution were determined from the isotherms. The samples were outgassed at 200 °C for 2 h before each test. The samples were characterized by H<sub>2</sub> temperature programmed reduction (H<sub>2</sub>-TPR) using BELCAT-B-TT (BELJAPAN INC.) in a flow system using 5 % H<sub>2</sub>/Ar mixture gases with 10 °C/min temperature ramp and with a flow rate of 30 mL/min. The power X-ray diffraction patterns were measured using Rigaku Corporation Instruments RinT2200V/PC with monochromatized Cu/K $\alpha$  radiation. High resolution transmission electron micrographs (HRTEM) were obtained with a JEOL JEM-2100 UHR transmission electron microscope operated at 200 kV. Raman spectra were recorded with a Raman spectrometer using a laser excitation line at 514.5 nm. X-ray photoelectron spectroscopy (XPS) study was conducted using ESCALAB 250Xi spectrometer equipped with a monochromatized Al K $\alpha$  source focused to a spot size of 0.2 mm. The position of the C 1s peak (284.5 eV) was used to correct the binding energies for all catalysts for possible charging effects. The carbon deposition was characterized by thermogravimetric analysis using Shimadzu DTG-60 instrument. The spent catalyst was heated in a platinum sample cell in the air atmosphere from room temperature to 750 °C at a ramp rate of 10 °C/min. Thermogravimetric analysis (TGA) system was performed with DTG-60 instrument under air atmosphere (50 ml/min) with a heating rate of 10°C/min from room temperature to 800 °C to estimate thermal decomposition behavior of catalyst. The

basicity of catalysts was studied by the temperature programmed desorption (TPD) with CO<sub>2</sub>. The TPD of CO<sub>2</sub> was carried out between 50 and 700 °C under a helium flow (30ml/min) with a heating rate of 10°C/min. Before the test, the samples were pretreated under helium atmosphere at 500 °C for 1 h, then, cooled to 50 °C, and exposed to pure CO<sub>2</sub> (30 ml/min) for 0.5 h. The Fourier transform infrared spectroscopy (FT-IR) spectra were recorded using the KBr pellet technique on a FT-IR spectrometer in the 4000–400 cm<sup>-1</sup> range. SEM images were obtained at an amplifying time of 5000 on a JEOL JSM-6360LV instrument.

## **4. CONCLUSIONS**

### **4.1 Effect of catalytic site position: nickel nanocatalyst selectively loaded inside or outside carbon nanotubes for methane dry reforming**

Ni nanoparticles loaded inside or outside CNTs were selectively prepared via wet chemical method. The TEM images and XPS characterization demonstrated that nickel nanoparticles loaded inside or outside CNTs catalysts were obtained as designed. H<sub>2</sub>-TPR indicated that the nickel nanoparticles inside the CNTs were easy to be reduced. The effects of catalytic sites position at interior or exterior surface of CNTs on catalytic activity were researched by CO<sub>2</sub> reforming of CH<sub>4</sub>. The reaction results showed that the catalytic activity of I-Ni/CNTs was higher than that of O-Ni/CNTs catalyst. Furthermore, the I-Ni/CNTs catalyst also exhibited high stability. All these can be ascribed to the electric density difference between interior and exterior surface of CNTs and the confinement effect of CNTs. The analysis of spent catalysts indicated that amorphous carbon formed on the catalyst with Ni particles inside CNTs channels, while another type of graphite carbon appeared on the catalyst with Ni particles outside CNTs channels.

### **4.2 Development of Ni-Pd bimetallic catalysts supported on ordered mesoporous alumina for utilization of carbon dioxide and methane by dry reforming reaction**

Bimetallic PdNi catalyst supported on ordered mesoporous alumina was prepared

by co-impregnation method for methane dry reforming. Characterization results indicated that the catalysts had uniform mesoporous structure and the metallic particles were well dispersed on the surface of MA. TPR results displayed that trace Pd significantly enhanced the reducibility of catalyst. The catalytic data demonstrated that Pd promoted Ni catalyst had higher catalytic activity compared to monometallic Ni/MA and Pd/MA catalysts. The TEM and coke analysis results indicated that different carbon species were formed according to the active metal, which was the key reason for catalyst deactivation. The trace Pd addition could prevent the formation of filament carbon, which caused the breakage of catalyst and pressure drop in the reactor.

#### **4.3 Development methane combined dry reforming for utilization of carbon dioxide over mesoporous nickel-alumina composite catalyst**

A mesoporous Ni-Al composite oxide catalyst (NiMA) prepared by a single-step surfactant-templating method and a nickel supported on mesoporous Al<sub>2</sub>O<sub>3</sub> catalyst (Ni/MA) prepared by impregnation were tested in methane dry reforming. Both catalysts exhibited high BET surface area, large pore volume and narrow pore size distribution. NiMA catalyst showed superior textural properties when compared with Ni/MA catalyst. Nickel species were well dispersed in the form of surface nickel aluminate phase for both catalysts. During the reduction and reaction, nickel aluminate was gradually reduced to generate highly dispersed nanosized nickel particles. Both catalysts showed good catalytic performance in methane dry reforming, due to the small nickel crystalline and strong metal to support interaction, since highly dispersed nickel species could suppress coking and strong SMSI could resist sintering. However, NiMA catalyst exhibited better catalytic performance than Ni/MA catalyst. This can be explained by higher nickel dispersion and stronger nickel-alumina interaction for NiMA than those for Ni/MA. Hence, NiMA catalyst prepared by one step template method could be served as a superior catalyst candidate for carbon dioxide reforming of methane.



#### **4.4 Synthesis of dipropyl carbonate from carbon dioxide downstream product over calcined hydrotalcite-like compounds containing La**

The Mg-Al and La-Mg-Al composite oxide catalysts were prepared via calcining the precursors of hydrotalcite-like compounds (HTLcs) from co-precipitation method and they exhibited high catalytic activities for the DPC synthesis via transesterification from DMC and propanol. When the HTLcs precursor with a La: Mg: Al molar ratio of 0.7:3:1 was calcined at 650°C, the obtained catalyst displayed the best catalytic activity. Under the stipulated reaction conditions, the maximum conversion of DMC and selectivity of DPC reached above 98% and 95.4%, respectively.

The catalyst characterization results suggested that the La content played an important role in tuning the structural and morphological properties of the catalysts. The platelet surface became rough and fluffy along with the La content increasing and it no longer had the platelet structure when La content reached 1.0. It was also found that the moderate strength basic sites enhanced with the La content increasing and it reached to the highest desorption temperature when the x rose to 0.7. As the La content x increased to 1.0, the chelating bidentate carbonate sites disappeared and the moderate basic sites were replaced by bridging bidentate carbonate sites. The moderate strength basic sites were the catalytic centers in this reaction.

## **5. LIST OF PUBLICATIONS**

### **Papers**

1. Effect of catalytic site position: Nickel nanocatalyst selectively loaded inside or outside carbon nanotubes for methane dry reforming, **Qingxiang Ma**, Ding Wang, Mingbo Wu, Tiansheng Zhao, Yoshiharu Yoneyama, Noritatsu Tsubaki, Fuel, 108(2013): 430-438.
2. Synthesis of dipropyl carbonate over calcined hydrotalcite-like compounds containing La, **Qingxiang Ma**, Tiansheng Zhao, Ding Wang, Wenqi Niu, Peng Lv, Noritatsu Tsubaki, Applied Catalysis A: 464-465(2013):142-148.
3. Methane

reforming with carbon dioxide over mesoporous nickel–alumina composite catalyst, Kai Tao, Lei Shi, **Qingxiang Ma**, Ding wang, Chunyang Zeng, Chunlong Kong, Mingbo Wu, Liang Chen, Shenghu Zhou, Yibo Hu, Noritatsu Tsubaki, Chemical Engineering Journal, 221(2013):25-31.

4. Facile solid-state synthesis of Cu–Zn–O catalysts for novel ethanol synthesis from dimethyl ether (DME) and syngas (CO + H<sub>2</sub>), Ding Wang, Guohui Yang, **Qingxiang Ma**, Yoshiharu Yoneyama, Yisheng Tan, Yizhuo Han, Noritatsu Tsubaki, Fuel, 109( 2013): 54-60.

5. Confinement Effect of Carbon Nanotubes: Copper Nanoparticles Filled Carbon Nanotubes for Hydrogenation of Methyl Acetate, Ding Wang, Guohui Yang, **Qingxiang Ma**, Mingbo Wu, Yisheng Tan, Yoshiharu Yoneyama, Noritatsu Tsubaki, ACS Catalysis, 2(2012):1958-1966.

#### **Conference:**

1. Promoted Ni/CNTs catalyst for methane reforming of CO<sub>2</sub>. The 10th International Novel Gas Conversion Symposium. Doha, Qatar, 2013.