

In-situ XPS studies on Low temperature and high performance thermocatalytic CO₂ methanation at TMOS coated Ni@Pd nanoparticles

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Abstract

CO₂ methanation is a vital reaction for converting waste energy into alternative fossil fuels. Among existing catalysts, nickel is a promising player regarding its high selectivity and low cost. In this research, acidified carbon nanotube (A-CNT) supported Ni_{core}@Pd_{shell} nanoparticles (NPs) with surface decoration of Tetramethoxysilan (TMOS) is synthesized by two steps wet chemical reduction method as a thermocatalyst in the CO₂ reduction reaction (CO₂RR). Upon thermal reduction, the H₂ from TOMS decomposition or the feed gas triggers the polymerization of CO₂ into high carbon chain as C₃ products found in CO₂ and H₂ mixing gas.

Keywords: CO₂ reduction reaction, thermocatalyst, APXPS, wet chemical reduction method, methanation

Introduction

In recent years, searching for an alternative to non-renewable energies is a global environmental issue due to limited reserves of combustible fuels, such as coal, crude and natural gas. Therefore, to develop a technique converting CO₂ to useful fuels e.g. hydrocarbon is a powerful tool in response to this environmental issue, and the thermal reduction is one of the developing techniques, which can use waste heat as initiating energy in the industrial field. However, the temperature needed to activate the CO₂ reduction reaction is too high for practical use. For that reason, design a facile catalyst to lower the reaction temperature is quite important, moreover, to enhance the selectivity for the CO₂ reduction reaction.

Metal oxide supported Ni catalyst had shown lots of application on CO₂ related region as dry reforming of methane ($\text{CH}_4 + \text{CO}_2 \rightarrow 2\text{CO} + 2\text{H}_2$), CO₂ methanation ($\text{CO}_2 + 4\text{H}_2 \rightarrow \text{CH}_4 + 2\text{H}_2\text{O}$) and CO production [1-4]. Luisetto, I., et al. found that dry reforming of methane achieved the highest conversion efficiency of 97% at 800 °C by bimetallic Co-Ni/CeO₂ catalyst with a highly stable performance after 20 h [2]. At a lower temperature, Fakeeha, A. H., et al. studied the effect of Ni at different metal oxide support for dry reforming of methane, and the experiment showed that best performance of 5% Ni/Al₂O₃ converted CH₄ and CO₂ significantly at 700 °C [4]. As for CO₂ methanation, the striking conversion efficiency of nearly 100% CH₄ selectivity at 250 °C was reached with MgO doped Ni/ZrO₂ catalyst by Tan, J. J., et al [3].

In this research, acidified carbon nanotube supported Ni_{core}@Pd_{shell} nanoparticles via surface decoration with Tetramethoxysilan (denoted Ni_c@Pd_s-TMOS/A-CNT) synthesized by wet chemical reduction method demonstrated a promising potential on a low temperature and high-performance CO₂ thermocatalytic reduction. Catalyst characteristic was performed by ambient-pressure X-ray photoemission spectroscopy (APXPS) and products were collected by gas chromatography (GC).

Experiments

The Ni_c@Pd_s-TMOS/A-CNT was synthesized by using a wet chemical reduction method with sequential control. The first step, the A-CNT (Cnano Technology Ltd.) solution was stirred with the nickel(II) chloride hexahydrate (NiCl₂·6H₂O, 99%, Sigma-Aldrich Co.) at 200 rpm, 25 °C for 4 h after that quickly injected over stoichiometric NaBH₄ (99%, Sigma-Aldrich Co.) solution into it to reduce Ni²⁺ to Ni. In the second step, the Pd²⁺ solution mixed with the previous solution and reduced by NaBH₄ remained at the first step. The final step, after waiting for the bubbles in the solution missing, added TMOS (>98%, Fluka Chemie Ag) liquid into the sample prepared at the second step and centrifuged it at 9000 rpm. After that, wash it with acetone, centrifuge again and dry at the end.

Results

For investigating thermal catalytic CO₂ reduction reaction resulting in variation of surface configuration, in-situ ambient pressure x-ray photoemission spectroscopy (APXPS) has been applied. According to the fitting result of the in-situ APXPS measurement shown in Fig. 1, Pd oxide will be reduced by CO₂ previous to Ni oxide in 100% CO₂ atmosphere, but surface restructuring occurs simultaneously, which leads to surface concentration of Ni increasing. At 200 °C, the concentration of Ni increases, meanwhile, this temperature is a critical temperature to catalyze CO₂ reduction reaction. Moreover, H₂ is the major product and 2.5% CH₄ generates. As temperature rises, CO will dominate the CO₂ reduction reaction with superior selectivity and near 85.7% at 300 °C. However, compared to the 100% CO₂ atmosphere, the CH₄ appears at 50 °C when the inlet gas replaced by CO₂ and H₂ mixing gas. That is, the H₂ arises from TMOS decomposing at 200 °C and H₂ is capable of promoting CO₂ methanation at low temperature. Another

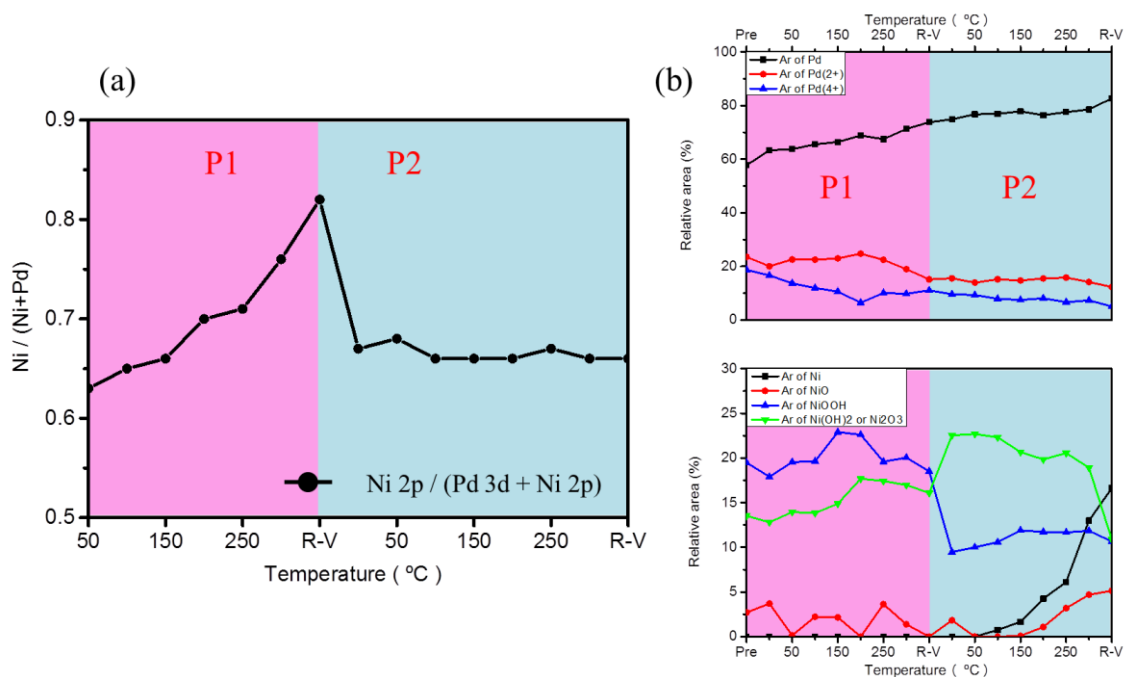


Fig. 1 The in-situ APXPS fitting results of $\text{Ni}_c\text{@Pd}_3\text{-TMOS/A-CNT}$ (a) Ratio of relative area between Ni 2p and sum of Ni 2p and Pd 3d. (b) Chemical configuration of Pd 3d (upper), and Ni 2p (lower).

observation is that CO may desorb at a temperature higher than 200 °C and H_2 also can enhance CO_2 to CO reduction reaction by an order from 10.4 ppm to 147.1 ppm in 100% CO_2 and mixing gas at 200 °C, respectively. Furthermore, a different trend is generated in mixing gas, CH_4 production gradually raises with temperature increases. It should be related to the reaction kinetic, CO_2 methanation can occupy some active sites only if there are enough H_2 supply. At last, a few of high C product appears at 300 °C, we suggest that there is a critical amount of Ni metal to be capable of facilitating the bond formation of C-C.

Discussion

In this research, thermocatalyst of $\text{Ni}_c\text{@Pd}_3\text{-TMOS/A-CNT}$ shows a promising catalyst design to promote CO_2 methanation at low temperature with a high yield in CO_2 and H_2 mixing gas, although the selectivity is still an urgent problem to deal with.

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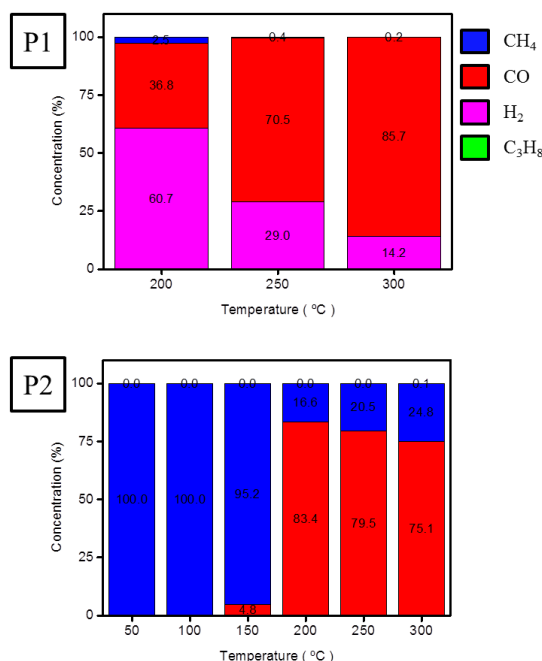


Fig. 2 The GC product distribution of $\text{Ni}_c\text{@Pd}_3\text{-TMOS/A-CNT}$ at P1 and P2 atmosphere