Enhancing Low-Temperature CO_2 Methanation: The Role of Praseodymium Oxide in Ni-Based Catalysts

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Significance and Relevance

The Ni/PrO_x (Nickel/Praseodymium oxide) catalyst developed in this study effectively achieve crucial challenge of thermodynamic limitation in CO_2 methanation by enhancing CH_4 selectivity and CO_2 conversion rates at low temperature ranges (250 to 350 °C). Through the unique oxygen mobility and formation oxygen vacancies property of PrO_x, CO_2 activation pathway are significantly improved. This approach overcomes the high kinetic barrier for low temperature CO_2 activation. Our findings demonstrate the potential of PrO_x utilization for development enhanced low temperature performance catalyst by experimental validation.

Preferred and 2nd choice for the topic: 1st CO_2 utilization and recycling, 2nd H_2 storage and transportation, green H_2 production, hydrogen vectors
Preferred presentation: Oral preferred or Short Oral

Introduction and Motivations

Research on nickel-based CO_2 methanation catalyst has been actively studied due to their relative advantage of cost-effectiveness rather than noble metals. However, the nickel catalysts require high temperature (above 300 °C) for achieving significant CO_2 methanation activity.[1] This limitation is due to the high kinetic barrier of CO_2 activation step, which require suitable catalyst surface properties for enhancing CO_2 activation.[2] Based on the theoretical background, we aimed to enhance low temperature activity by PrO_x based nickel catalyst which could provide electron donor sties suitable for improved CO_2 activation.

Results and Discussion

In Fig. 1 activity test comparing with conventional support based catalysts, Ni/PrO_x shows exceptional low temperature activity. The trend in T_{50} (the temperature at which 50% of CO_2 is converted) was observed as follows: Ni/PrO_x (253 °C) < Ni/Al_2O_3 (322 °C) < Ni/SiO_2 (379 °C). Also, the highest CH_4 selectivity on entire temperature range was observed. This result indicates that PrO_x support enhance low temperature activity and CO_2 hydrogenation pathway compared to other conventional supports in same nickel loading condition. The exceptional activity of Ni/PrO_x is closely associated with Its superior CO_2 activation ability in low temperature range, as observerd in Fig. 1 (c). The peak observed on 211 °C indicates that Ni/PrO_x surface was appropriate for the direct CO_2 decomposition to CO at low temperatures ($CO_2 \rightarrow CO + O^*$). The direct CO route for CO_2 methanation on Ni/PrO_x support present appropriate reaction pathway of CO_2 hydrogenation to CH_4.This enhancement of CO_2 activation behavior is clearly associated to surface chemical property, specifically electron donor properties.

To elucidate the correlation between improvement of CO_2 activation and PrO_x support properties, we focused on structural oxygen mobility and vacancies formation behavior of PrO_x. The structural oxygen mobility induces evacuation of structural oxygen and provide abundant oxygen vacancies for electron donor for activating CO_2 to CO and O*. Fig. 2 presents our analytic characterizations for elucidating PrO_x oxygen mobility property. In Fig. 2 (a), the structural oxygen evacuation profile result suggests high oxygen mobility of Ni/PrO_x and evacuation behavior in reduction condition. The oxygen mobility, as a property that induce superior oxygen vacancies formation, was investigated through Raman spectroscopy and Pr 3d XPS results. Through quantitative analysis of results in Fig. 2 (b), I_D/I_{F2g}

ratio (intensity ratio of the Defects band to the F_{2g} band), from 0.28 to 0.33 respectively, was observed. This result indicates that PrO_x was transformed oxygen deficiency oxide phase which has abundant electron donor sites. In Fig. 2 (c), Pr 3d XPS clearly supported the electron properties of Ni/PrO_x. The $Pr3^+/Pr^{4+}$ ratio of Ni/PrO_x increase from 0.85 to 0.96 respectively according to H_2 treatment. This results indicates that Ni/PrO_x surface has superior oxygen vacancies formation and high electron donating properties induced by oxide phase transformation.

Through characterization and activity test, we clearly observed exceptional low temperature activity and abundant oxygen vacancies formation induced by PrO_x support effects on surface of catalyst. This combined results suggests that the PrO_x provides suitable chemical properties to reduce the kinetic barrier of CO_2 activation at low temperature by formation oxygen vacancies which serve as electron donor sites for CO_2 adsorption and activation. This advantage in the reaction mechanism directly influenced on enhancement of low temperature catalytic activity of Ni/PrO_x. In conclusion, our study demonstrates the potential of PrO_x in enhancing low-temperature CO_2 methanation by comprehensive experimental analysis.

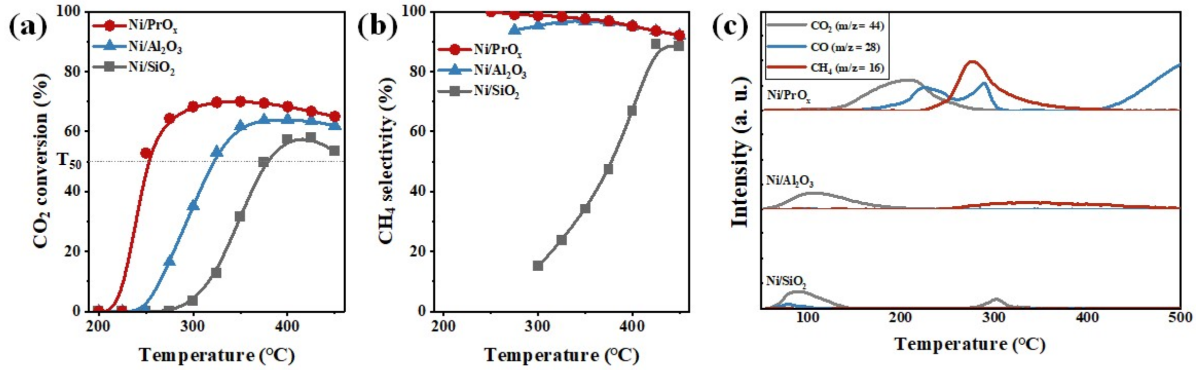

Fig. 1. (a) CO_2 conversion, (b) CH_4 selectivity and (c) CO_2-TPSR profile of Ni/PrO_x, Ni/Al_2O_3 and Ni/SiO_2 catalysts.

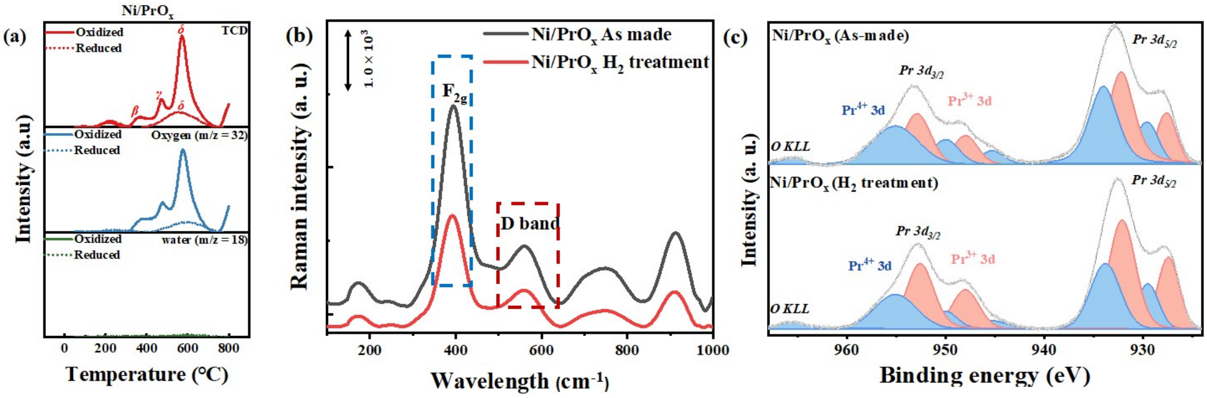

Fig. 2. (a) Structural oxygen evacuation, (b) Raman spectroscopy and (c) Pr 3d XPS profiles of Ni/PrO_x catalyst.

References

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2. T. Zhang, W. Wang, F. Gu, W. Xu, J. Zhang, Z. Li, T. Zhu, G. Xu, Z. Zhong, F. Su, *Appl. Catal. B: Environ.* **2022,** *312*, 121385-121400.

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