THE METAL-SUPPORT SYNERGISTIC EFFECTS FOR CO_2 HYDROGENATION TO METHANOL OVER SUPPORTED NiGa CATALYST

Zhufu Fu[1], Yunian Chen[1], Yuan Xue[*1]
1. China-UK Low Carbon College, Shanghai Jiao Tong University
Shanghai, 200240, China
** E-mail: yuan.xue@sjtu.edu.cn*

ABSTRACT

NiGa catalyst is recognized for its effectiveness in CO_2 hydrogenation into methanol although CH_4 formation remains an unavoidable byproduct. To address the issue, this study comprehensively investigated the catalytic performance and metal-support synergy of supported NiGa catalyst. ZnO outperformed SiO_2, Al_2O_3 and MgO as NiGa supports in terms of methane suppression and methanol formation. Catalyst characterization revealed that NiZnGa formation on ZnO and $ZnGa_2O_4$ identified at the interface between NiZnGa and ZnO played crucial roles in hydrogen activation and CO_2 adsorption. The metal-support interaction changes Ni's electronic structure, affecting the catalyst capability of CO adsorption. Changes of Ni:Ga ratio revealed that NiGa(5:3)/ZnO outpaced other two catalysts (3:1, 1:1) to achieve 46.4% methanol selectivity and 53.8 $g_{MeOH}/kg_{cat.}/h$. The methanol production rate was positively correlated with the medium CO adsorption. *In-situ* DRIFTS analysis revealed the reaction mechanism of NiGa(5:3)/ZnO: CO_2 adsorption and activation occurred on $ZnGa_2O_4$, with methanol formation following the formate and carboxylate pathways.

KEY WORDS

CO_2 hydrogenation; methanol production; NiGa catalyst; metal-support interaction; suppressed methanation.

1. INTRODUCTION

The urgency to reduce anthropogenic Greenhouse Gas emissions has driven research into converting CO_2 into valuable products. Among these, CO_2 hydrogenation to methanol is crucial for sustainable chemistry, enabling both energy and hydrogen storage and fostering a circular carbon economy. While the $Cu/ZnO/Al_2O_3$ catalyst is commonly used industrially, it deactivates quickly under high temperatures and pressures, highlighting a need for improved catalyst designs for high methanol productivity and stability.

Transition metals, particularly Ni and Fe, are prominent in catalysis due to their high activity. Ni, which is effective for CO_2 hydrogenation to CH_4, exhibits strong C–O bond-cleaving abilities. Recent studies suggest tuning Ni's geometric and electronic properties can adjust the CO_2 hydrogenation product distribution. NiGa catalysts, specifically Ni_5Ga_3, show potential for selective methanol production from CO_2, following the formate and reverse water-gas shift pathways[1]. Modifying Ni sites with Ga reduces activation energy and enhances Ni's reactivity[2].

However, NiGa catalysts face challenges with unwanted CH_4 formation, influenced by factors like phase purity, Ni/Ga ratios, and catalyst preparation methods. Surface decomposition of the active Ni_5Ga_3 phase into Ni_3Ga or Ni-Ga_2O_3 leads to decreased methanol selectivity, with excess metallic Ni further increasing CH_4 output[3].

Ni particle size critically affects selectivity, with smaller particles favoring CO and larger ones favoring CH_4[4]. Modifications with ZnO can reduce CO adsorption, curbing methanation, while ZnO's electronic interactions with Ni or Cu-based systems encourage methanol formation[5].

Inspired by these findings, this study modified NiGa with ZnO, achieving effective methanol production with reduced CH_4 output, further exploring the role of different active sites in NiGa/ZnO catalysts.

2. MATERIAL AND METHODS

2.1 Catalyst preparation

A series of Ni-Ga catalysts were synthesized using the impregnation method[1], with commercial supports including ZnO, SiO_2, MgO, and Al_2O_3. NiGa/ZnO catalysts with varying Ni:Ga molar ratios (3:1, 5:3, 1:1) were also synthesized.

2.2 Characterization of the catalysts

Catalysts were characterized using XRD, SEM, and HR-TEM to determine structural properties. Chemical composition and surface properties were analyzed with XPS, and CO-TPD. Additionally, *in-situ* DRIFTS employed to analyze surface species evolution during reaction conditions.

2.3 Catalyst performance evaluation

CO_2 hydrogenation to methanol was carried out in a high-pressure fixed-bed reactor using 0.2 g of catalyst, pre-reduced at 680 °C for 0.5 hours in H_2 (30 mL/min). Reaction conditions included temperatures of 240, 260, and 280 °C under 4 MPa, with a 3:1 $H_2:CO_2$ flow ratio, achieving a WHSV of 6000 mL/g_cat./h. Gas products were analyzed every 15 minutes using a GC with TCD and FID detectors.

3. RESULTS AND DISCUSSION

3.1 Catalytic performance for CO_2 hydrogenation

The CO_2 hydrogenation performance over various NiGa catalysts was evaluated at 240, 260, and 280 °C (Fig.1a). Results showed that NiGa/ZnO catalyst was more effective in suppressing CH_4 formation compared to other catalysts including NiGa/MgO, NiGa/SiO_2 and NiGa/Al_2O_3. Besides, NiGa(5:3)/ZnO also gave a significantly higher methanol selectivity (46.4%) and production rate (53.8 $g_{MeOH}/kg_{cat.}/h$) at 260 °C, with excellent stability over the 20-hour test (Fig.1b).

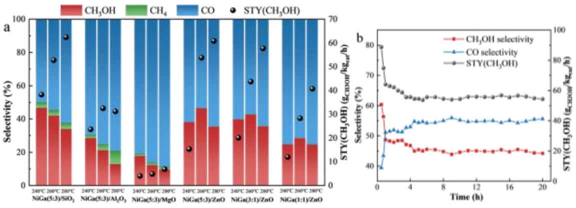

Fig.1: The catalytic properties in CO_2 hydrogenation to methanol over (a) different NiGa catalysts and (b) stability test of NiGa (5:3)/ZnO under 260 °C.
(Reaction conditions: 240-280 °C, 4 MPa, 6000 mL/gcat./h, $CO_2/H_2=1/3$)

3.2 Characterization of Ni-Ga/ZnO catalysts

Comprehensive characterization, using XRD, TEM-EDS and HRTEM, confirmed strong interaction among Ni, Ga, and ZnO, leading to the formation of Ni-based alloy crystals (NiZnGa). Notably, $ZnGa_2O_4$ identified at the interface between the Ni-based alloy and ZnO is crucial for CO_2 adsorption and activation.

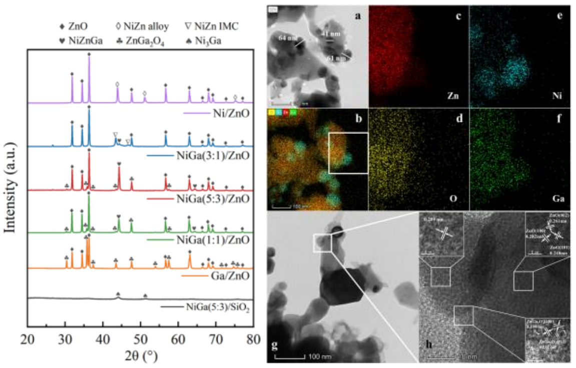

Fig.2: XRD patterns of NiGa catalysts; (a) TEM, (b-f) EDS-Mapping and (g,h) HRTEM images of NiGa(5:3)/ZnO.

A comparative examination of Ni $2p_{3/2}$ binding energies between NiGa(x:y)/ZnO and NiGa(5:3)/SiO_2 (Fig.3a) indicates electron transfer from ZnO to NiGa, which reduced in CO adsorption strength, consequently impeding CH_4 formation. This finding was validated by CO-TPD results (Fig.3b), showing that CO adsorption on NiGa(5:3)/ZnO is almost negligible compared to NiGa(5:3)/SiO_2, which is consistent with CH_4 production.

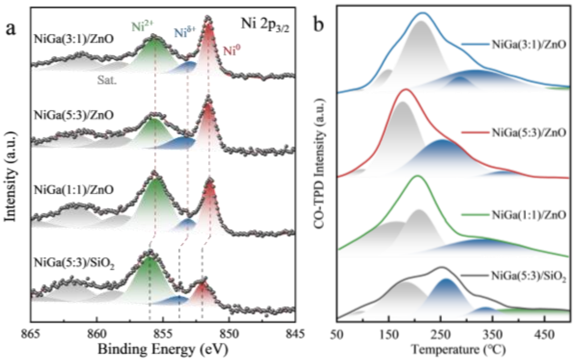

Fig.3: (a) XPS spectra of Ni $2p_{3/2}$ regions and (b) CO-TPD patterns for NiGa catalysts

3.3 Characterization of Ni-Ga/ZnO catalysts

In-situ DRIFTS highlighted the decreased linear adsorption of CO* on Ni-based alloys as a key mechanism in hindering CH_4 formation. The systematic characterization and *in-situ* DRIFTS analysis elucidated the mechanism of CO_2 hydrogenation over NiGa/ZnO (Fig.4): CO_2 adsorption and activation as CO_3* or HCO_3* on the $ZnGa_2O_4$ active site, followed by the formate pathway and carboxylate pathway.

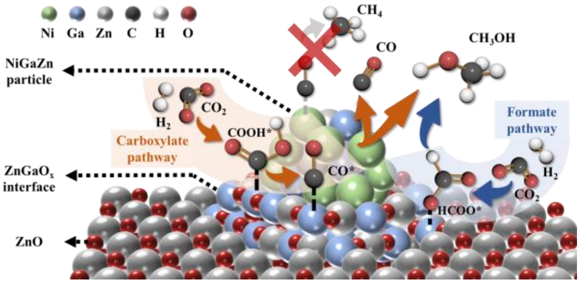

Fig.4: Reaction mechanism of CO_2 hydrogenation over NiGa(5:3)/ZnO.

ACKNOWLEDGEMENTS

This research was financially supported by Natural Science Foundation of Shanghai (22ZR1434200), Natural Science Foundation of China (52306261, 52106174).

REFERENCES

1 F. Studt, *et al.*, Discovery of a Ni-Ga catalyst for carbon dioxide reduction to methanol, *Nat. Chem.* 6 (2014) 320–324.
2 Q. Tang, *et al.*, A new and different insight into the promotion mechanisms of Ga for the hydrogenation of carbon dioxide to methanol over a Ga-doped Ni(211) bimetallic catalyst. *Nanoscale* 11(2019) 9969–9979.
3 R. Goyal, *et al.*, A. Bordoloi, CN_x stabilized Ni-Ga nanoparticles for CO_2 hydrogenation: Role of preparation methods, *Catal. Today* 343 (2020) 48–55.
4 Y. Wang, *et al.*, CO_2 hydrogenation over heterogeneous catalysts at atmospheric pressure: from electronic properties to product selectivity, *Green Chem.* 23 (2021) 249–267.
5 L. Shen, *et al.*, Revealing the promoting effect of Zn on Ni-based CO_2 hydrogenation catalysts, J. Mater. Chem. A 11 (2023) 8248–8255.