Screening of Ni-alloyed catalysts (NiM/Al_2O_3:M=Zn, In, Ga_3, Cu) by *in situ* IR spectroscopy: DBD-induced CO_2 reduction

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Abstract: The study investigated the activation of CO_2 by different nickel-alloyed catalysts in a plasma environment using *in situ* FTIR. The results showed that the DBD environment led to rapid consumption of carbonates and increased formic acid production. The behaviour of formic acid growth differed among the alloyed metal with a depletion of carbonates observed on Ni-Ga and a reduction in bi-carbonate on Ni-Zn. The study highlights the importance of plasma in enhancing the dissociation of CO_2 and the reduction of carbonates.

Keywords: Plasma environment, Reaction mechanism, *in situ* FTIR.

1. Introduction

Nonthermal plasma (NTP) technology has made a significant contribution in different applications of sustainable chemistry and engineering, where NTP exhibits non-equilibrium properties and high energy density and induces unconventional chemical behaviour and different mechanisms [1]· The well-known thermal catalyst such as metallic nickel was found to be active for methanation under plasma discharge at low temperatures and exhibited high conversion and selectivity comparable to thermal systems. The application of plasma nickel-based catalysts in CO_2 methanation has been the subject of extensive research in recent years. Recent research has also focused on the development of new nickel-based catalysts, including the use of novel materials and the optimization of plasma treatment conditions.

For example, a study by Z. Li et al. [2] investigated the use of nickel-cobalt (Ni-Co) alloys as catalysts for the methanation of CO_2. The authors found that the Ni-Co alloys showed improved performance compared to nickel (Ni) alone, and attributed this to the synergistic effect of the Ni and Co components. Another study by J. Zhang et al. [3] examined the effect of plasma treatment time on the performance of nickel (Ni) as a plasma catalyst for methanation. The authors found that longer plasma treatment times led to improved performance in terms of CO_2 conversion and CH_4 selectivity, and suggested that this was due to the formation of more active sites on the surface of the Ni catalyst. However, the underlying mechanism, plasma-nickel interactions, and possible synergistic effects are not yet well explained [4]. In this work, Differences in the activation of carbon dioxide by different nickel alloys in a plasma environment was investigated by *in situ* fourier transform infrared (FTIR) in the methanation of CO_2 in an DBD environment

2. Experiment

The DBD -activated methanation was investigated by *in situ* FTIR in Ni-Cu/Al_2O_3, Ni-Zn/Al_2O_3, Ni-Ga/Al_2O_3, Ni-In/Al_2O_3 and Ni/Al_2O_3 catalysts and compared to thermal conditions. FTIR spectra were recorded with a JASCO 6600 spectrometer. The experiments were carried out by the means of an IR cell as shown in Figure 1. This cell setup allows treatments under static conditions up to pressures of 75 kPa and the temperature is controlled by a thermocouple placed close to the pellet. Prior to the measurements, the reduced sample was again treated *in situ* in 10% hydrogen at 500 °C for 1.5 h. Then, CO_2 hydrogenation was performed by flowing CO_2 (10 mL min^{-1}) and H_2 (40 mL min^{-1}) diluted in Ar (100 mL min^{-1}). Furthermore, to gain insights into the evolution of surface species adsorbed on the catalysts during thermal and DBD conditions, transient experiments were performed by alternatingly flowing H_2/Ar and CO_2/Ar. Ar was used as a balance gas to dilute the reaction gas and avoid signal saturation of IR spectra. Also, blank measurements were performed under the same conditions

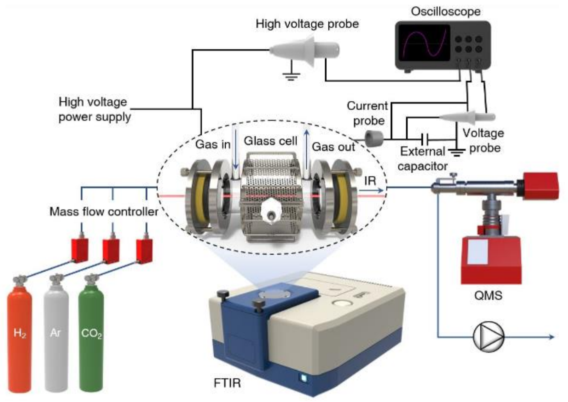

Fig. 1. Schematic diagram of the *in situ* FTIR reactor

3. Results and discussion

In the current study, *in situ* Fourier Transform Infrared (FTIR) spectroscopy was utilized to analyse the products resulting from the catalytic process and to evaluate the differences in the behaviour of the dielectric barrier discharge (DBD) plasma. The results revealed that water peaks were present in the DBD environment for all samples, which aligns with the findings of the control group without the use of a catalyst. However, the presence of a clear carbon monoxide peak, which was present in the control group, was only observed in the group utilizing Ni-Ga alloy catalysts.

The thermal catalysis process was observed to have a significant impact on the presence of carbonate and formate on the surface of Ni-Ga, Ni-Zn and Ni catalysts, as depicted in Figure 2. At the outset of the reaction, the surface was characterized by a substantial concentration of carbonate and a minimal concentration of formate. As the reaction progressed, a slow growth in carbonate was observed while formate rapidly increased. The addition of a plasma environment led to a rapid consumption of carbonate, resulting in a corresponding rise in formic acid.

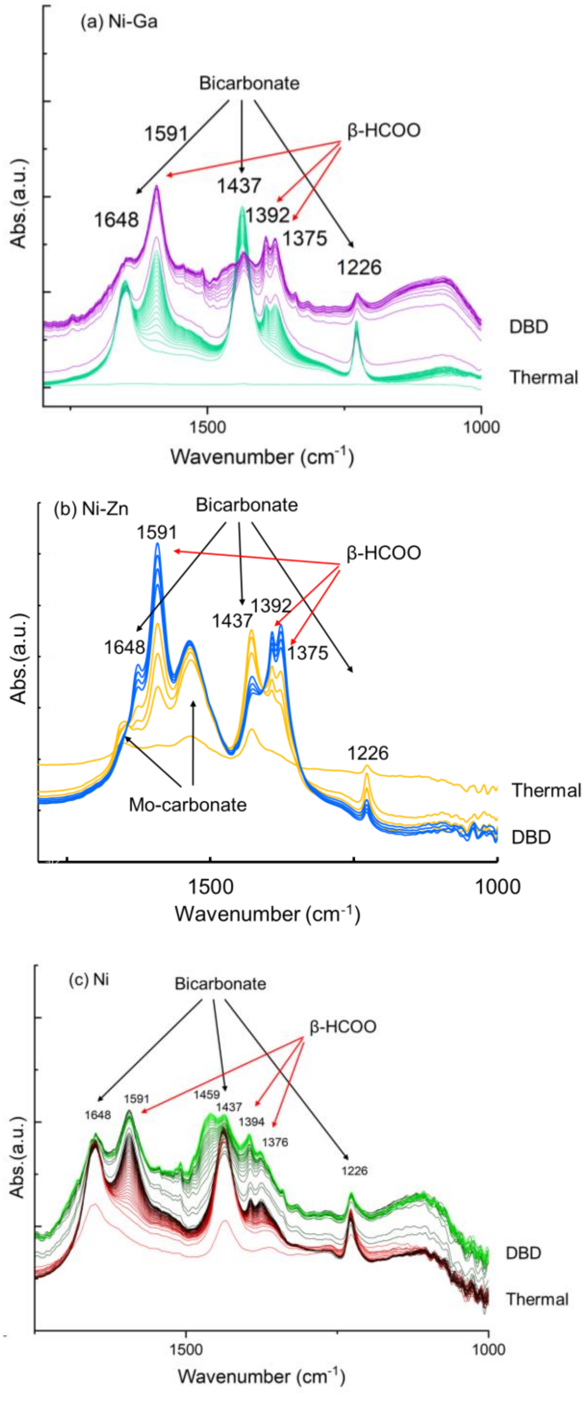

Fig. 2. *In situ* FTIR spectra during thermal and DBD environments reaction of a gas mixture CO_2 (10 mL min^{-1}) and H_2 (40 mL min^{-1}) diluted in Ar (100 mL min^{-1}) over (a) Ni-Ga/Al_2O_3, (b) Ni-Zn/Al_2O_3, (c) Ni/Al_2O_3 at 75 kPa and 300 °C

This outcome suggests that the plasma environment enhances the dissociation of carbon dioxide and the reduction of carbonate species. Furthermore, the behaviour of formic acid growth differed among the Ni-Ga, Ni-Zn, and Ni catalysts. Following exposure to the DBD plasma, a significant depletion of carbonates was observed on the surface of the Ni-Ga catalysts, whereas a significant reduction in the bi-carbonate was observed on the Ni-Zn catalysts, while the monocarbonate remained stable. The growth of formic acid on the surface of the Ni catalyst was less prominent compared to the Ni-Ga and Ni-Zn catalysts, which may be attributed to the stability of the carbonates on the Ni surface and the low consumption rate of the carbonates. [5]

However, this effect was not clearly observed on Ni-Cu and Ni-In catalysts. This discrepancy could be attributed to the negligible amount of carbonate remaining on the surface of Ni-Cu and Ni-In during the thermocatalytic process. The plasma environment had no significant impact on the reduction of formic acid on these catalysts. It can be concluded that the plasma promotes the formation of formic acid from carbon dioxide during the reduction process, but a catalyst with specific properties is required for the further reduction of formic acid [6].

4. Conclusions

The study used FTIR spectroscopy to analyse the products of a catalytic process with a DBD plasma environment. The presence of water peaks was observed in all samples, but a clear carbon monoxide peak was only seen in the group with Ni-Ga alloy catalysts. The thermal catalysis process had a significant effect on the presence of carbonate and formate on Ni-Ga, Ni-Zn, and Ni catalysts, resulting in an increase in formic acid in the plasma environment. The behaviour of formic acid growth differed among the catalysts, with the Ni-Ga catalysts showing a significant depletion of carbonates and the Ni-Cu and Ni-In catalysts showing no significant impact on formic acid reduction. The plasma promotes formic acid formation but a specific catalyst is required for further reduction.

Acknowledgments

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