Forced dynamic (operando) reactors to understand the structure and deactivation of CO_2 dry reforming over the NiZn alloy catalyst

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Highlights

- Forced dynamic (operando) reactors was applied to study the DRM catalysts
- Operando DRIFTS-MS was used to elucidate the reaction mechanism for DRM over the NiZn alloy catalysts
- The structure and deactivation of NiZn alloy were induced with the forced dynamic reactor.

1. Introduction

Dry reforming of methane (DRM), which converts both CO_2 and CH_4 into industrially high-valued syngas (CO and H_2), has been considered a promising and vital route to relieve the high CO_2 concentration in the atmosphere [1]. Ni-based catalysts are typically used for DRM. Given the high reaction temperature (typically above 600 °C) and the complex reacting environment as well as the side reactions [1,2], the dynamic change of the active phase, the kinetics and deactivation of the catalysts are uncertain and vital to deep the understanding to design more stable DRM catalysts.

From the 1960s, the forced dynamic reactors, which mainly study the response of the catalysts when the inputs are controlled in step changes, pulse, and periodical operation, have been used to study the structure-function and improve the catalytic performance [3]. Recently, the operando methodologies, the most common of which is DRIFTS technology, are a popular method to study the catalyst structure and surface species on the catalysts [1,4].

Herein, we propose the forced dynamic (operando) method, a refinement of the forced dynamic and operando methods. The catalyst structure, mechanism, and deactivation of DRM over the NiZn alloy catalyst were presented.

2. Methods

The DRM catalysts were NiZn alloy over $ZrZnO_x$ solid solution (noted as Ni/ZZ and Ni/Z, respectively), which was reported in our previous work[2].

The forced operando DRM over the catalysts was performed on a Nicolet iS50 FT-IR spectrometer (Thermo Scientific) equipped with a Harrick Praying Mantis DRIFTS gas cell and connected to a Transpector CPM100 mass spectrometer (INFICON). The forced dynamic DRM was performed on the low-pressure pulse reactor (stainless steel, I.D.=4.5 mm, Length =280 mm, Demede Engineering & Research) connected to a micro-GC (Varian GC 490) and a mass spectrometer (Thermostar, Pfeiffer Vacuum). The concentration and temperature were the two main modulators, and the response of the catalysts was analyzed.

3. Results and discussion

Figure 1a shows the scheme of the forced dynamic (operando) reactors. Multiple techniques and an advanced analytical workflow are used to study the response of the catalysts with different modulators to obtain essential parameters. Figure 1b shows the in situ XRD results of the Ni/ZZ catalysts[2]. The formation of NiZn alloy was formed by high-temperature reduction (above 750 °C). Figures 1c and 1d show the results of a series of programmed DRM tests by altering the CH_4/CO_2 concentration. The NiZn alloy, as well as the mono Ni catalysts, show different tolerance to CH_4 or CO_2. The NiZn alloy is sensitive to high concentration CO_2, and can lead to the deactivation (Figure 1d), while the mono Ni is more susceptible to high concentration CH_4 in the feed (Figure 1c). Figures 1e and 1f show the operando DRIFTS-MS results over the Ni/ZZ catalyst. By monitoring the dynamic change of the surface intermediates and the products, it was proposed that the Ni/ZZ might follow the formate route and have a balanced coke formation by CH_4 decomposition and coke removal. Thus, the NiZn alloy leads to less coke deposition than Ni/Z [2]. In summary, the forced dynamic operando experiments provide a new strategy to understand the catalyst structure, the function of the NiZn alloy, and the reaction mechanism as well as the deactivation under DRM conditions.

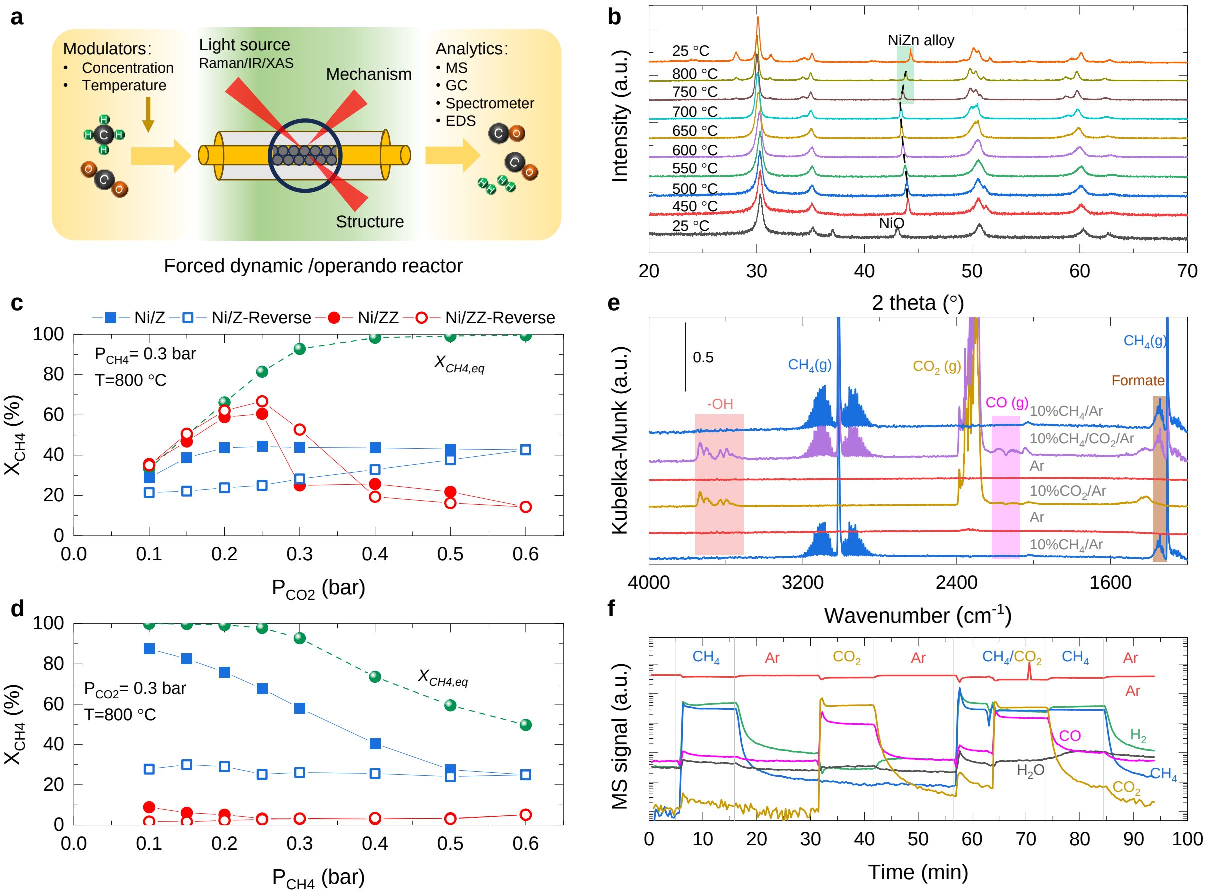

Figure 1. a) Scheme of the forced dynamic (operando) reactors, b) in situ XRD results of the Ni/ZZ catalyst, c-d) the performance of the NiZn alloy with forced dynamic reactors by varying the CH_4 and/or CO_2 concentration, e-f) the operando DRIFTS-MS results of the Ni/ZZ catalyst

4. Conclusions

Using the forced dynamic operando reactors, the dynamic change of the NiZn alloy structure, function, deactivation, and reaction pathways are resolved. Applying the forced dynamic operando reactors will accelerate the study of DRM catalysts.

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Keywords

Dynamic/operando reactors, forced controlled inputs, dry reforming of methane, catalysts