In situ study of the carbon dioxide reforming of methane reaction using ZSM-5 zeolite as catalyst

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The methane reforming reaction is an important strategy to convert two greenhouse gases into value-added products such as syngas, a key feedstock for the Fischer-Tropsch process [1]. However, most of the used catalysts suffer from rapid deactivation due to carbon deposition and the sintering of the metal sites that act as active sites for the reaction [2]. In this context, zeolite, microporous aluminosilicates with channels and cavities in their structure, can be used as support for active metal sites, and have shown promising efficiency towards the DRM reaction. Nickel-exchange ZSM-5 zeolite catalysts are of particular interest, with the choice of nickel driven by its abundance and sustainability, combined with its well-established activity [3]. In addition, an adopted strategy to enhance the catalytic activity of bifunctional catalysts for DRM has involved combining nickel with a second metal; cerium (Ce) in particular facilitates the reduction of NiO to metallic Ni, increasing the availability of active sites for DRM reaction, and contributes to the gasification of the amorphous carbon [4]. The present project aims to investigate *in situ* the DRM process, to follow the structural evolution of the chosen zeolite catalyst, the molecule-zeolite interactions, and the reaction progression using high-resolution powder X-ray diffraction and mass spectrometry. The experimental process is carried out at the high-resolution powder diffraction beamline ID22 of the ESRF (Grenoble, France).

To identify the most suitable Si/Al ratio in the zeolite framework, the adsorption behavior of three ZSM-5 zeolites towards CO_2 and CH_4 was first investigated by loading the powder into a quartz capillary connected to the beamline gas handling system. Gas adsorption experiments were performed by introducing the gases at increasing pressures (0-20 bar) at room temperature, while powder diffraction patterns were collected at each pressure step. Based on the results from this adsorption experiment, the selected ZSM-5 zeolite (MFI type), with a Si/Al ratio of 25, was then doped with nickel via wet impregnation to introduce the active metal sites. *In-situ* DRM tests were performed at ID22 on both pristine and Ni-doped zeolites under a CO_2/CH_4 (1:1) gas flow. Despite significant gas uptake at room temperature, no syngas formation was observed at 700 °C, nor phase transition or other structural change in the pristine zeolite structure, confirming the high thermal stability of ZSM-5 under reaction conditions.

Then, the DRM experiment was carried out using the Ni-doped zeolite. The Ni-exchange samples were calcined first *in-situ* at 550 °C under air, leading to the sintering of a small amount of an additional metallic nickel phase as observed in the powder pattern. In contrast with the behavior of the non-exchange sample, the calcined Ni-doped zeolite exhibited clear catalytic activity at 700 °C, with the production of both H_2 and CO detected by mass spectrometry. No major zeolite framework modifications were observed, although a broad diffraction feature attributed to amorphous carbon was detected. These results indicate that, as expected, pristine ZSM-5 is catalytically inactive for DRM. Nickel incorporation enables efficient syngas production while preserving the structural integrity of the zeolite support, which suggests that, in this specific system, the primary role of ZSM-5 is to provide a thermally stable and structurally robust support for the active metal sites; therefore, further experiments are required to investigate catalyst deactivation over longer reaction times, and the use of additional promoters, such as rare earth elements, to enhance catalytic performance.

These results highlight the value of combining *in-situ* high-resolution powder X-ray diffraction with mass spectrometry to track phase evolution, the formation of additional phases and the evolution of the gas composition during the reaction, providing key insights into the role of each component in the catalytic process of this complex reaction.

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