Effect of catalyst composition on the activity and stability of Pt-Ni/ $MgAlO_x$ methane steam reforming catalysts

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Significance and Relevance

A series of mono- and bimetallic Ni/ and NiPt/$MgAlO_x$-based catalysts with different support compositions were prepared and tested for methane steam reforming during simulated daily startup and shutdown operation (DSS). The results obtained show a direct impact of the Ni:Pt and Ni:Mg/Al ratios on the catalyst activation/reactivation under methane steam reforming conditions. For certain catalyst compositions, formation of hardly reducible species was unraveled by *in situ* XRD and XAS investigations. Based on the knowledge gained, possible catalysts candidates for DSS were identified.

Preferred and 2nd choice for the topic: *1) H_2 storage and transportation, green H_2 production, hydrogen vectors, 2) Fundamental advances in understanding catalysis*
Preferred presentation: Short oral or poster

Introduction and Motivations

Steam reforming (SR) of methane is a well-established commercial process for generating approximatively 90% of the worldwide hydrogen production[1]. Ni-based catalysts are widely employed to produce H_2 in large-scale methane steam reformers under stationary conditions due to good price/performance ratio. Most of the applied catalysts are based on Ni/Al_2O_3, with high active metal loading (15-30%). To increase the stability against sintering and maintain Ni species dispersed, mixed oxides with tailored compositions can be exploited[2]. For domestic applications such as *in situ* H_2 production for fuel cells, where the power demand is varying on a daily basis, the SR reaction is conducted in a daily start-up/shut-down (DSS) operation mode. This approach exposes the catalysts to dynamic conditions, making Ni-based systems susceptible to oxidation and deactivation. Recent studies have shown that Ni oxidation to hardly reducible species can be prevented by adding small amounts of noble metals like Pt, Pd, Rh as catalyst dopants.[2,3] An alternative path is the tuning of the active metal-support interaction by adjusting the catalyst composition, which is systematically investigated in our study.

Materials and Methods

A series of samples with different Ni:Pt and Ni:Mg/Al ratios were synthesized and characterized by electron microscopy, XRD, H_2-TPR, and N_2-physisorption. Additionally, selected samples were studied by *in situ/operando* XAS and XRD measurements. Systematic CH_4 steam reforming tests were conducted in a plug-flow reactor. Besides performing several consecutive light-off/light-out activity tests, various atmospheres were applied to study the catalyst stability. An on-line FTIR spectrometer (Multigas FTIR, MKS) and mass spectrometer (Omnistar 320, Pfeiffer) were used for the analysis of the gas mixture at the reactor outlet.

Results and Discussion

The durability of the Ni-based mono and bimetallic catalysts was systematically investigated under dynamic reaction conditions. Various catalyst deactivation processes were induced by dynamic temperature and gas atmospheres variations (e.g. inert, steam-saturated inert, reaction mixture). Catalyst reactivation under reaction conditions was subsequently studied. For selected samples and conditions, the deactivation and reactivation processes were followed during *in situ/operando* XRD and XAS experiments. Pronounced changes in Ni state (oxidation state, particle size) were identified in the deactivated catalysts, which could be correlated to the observed catalytic activity trends. As illustrated in Fig. 1, to withstand DSS operation, catalyst self-reactivation could be facilitated by the noble metal presence. Moreover, a careful adjustment of the support properties, e.g. metal-support interaction with Ni and/or the noble metal, prevents a fast drop in the catalyst activity under dynamic reaction conditions.

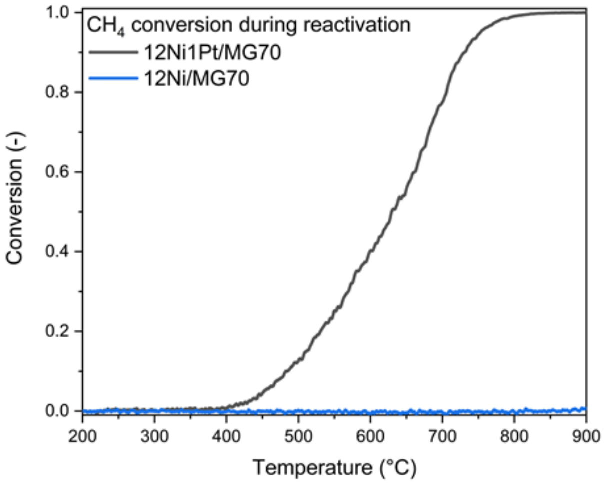

Figure 1: CH_4 conversion profile during reactivation of various catalysts following harsh deactivation.

References

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Acknowledgements

This project has received funding from the European Union's Horizon 2020 Research and Innovation programme under the Marie Skłodowska-Curie Action – International Training Network (MSCA-ITN), grant agreement 813748.