CO cleanup of H_2-rich reformate by preferential CO methanation over nickel-ceria catalysts: from mechanistic studies to catalyst and reactor design

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Abstract: The present report summarizes the results obtained during a systematic study of catalysts, their performances, fundamental principles of the preferential CO methanation reaction and reactor concept design. The most attention is concentrated on Ni/CeO_2 structured catalysts and their operation in the lab, pilot and full scale reactors.

Keywords: Preferential CO methanation, Nickel-ceria washcoat, structured catalysts.

1. Introduction

In the last two decades, CO preferential oxidation (CO PROX) and CO preferential methanation (CO PrMeth) are assumed as the most feasible reactions for CO removal from H_2-rich reformate for low temperature polymer electrolyte membrane fuel cells (LT PEMFC) feeding applications. Despite the existing advantages and disadvantages, both processes provide CO-cleanup to 10 ppm.

This work reports our summarizing results on the development of an effective nickel-ceria structured catalyst for CO-SMET and their performance in the lab, pilot and full scale reactors.

2. Experimental

CO PrMeth was studied over nickel-based catalysts. The properties of catalysts prepared by nitrate (Ni/CeO_2) and chloride ($Ni(Cl)/CeO_2$) precursors were compared. The role of nickel precursor was investigated and the positive effect of chlorine on the catalyst selectivity was demonstrated. The catalysts were characterized by BET, XRD, XPS, HAADF-STEM, EDX-mapping, SEM, TPR, TPD techniques, FTIR *in situ* and CO chemisorption techniques.

Catalytic performance of the prepared systems in a form of grains in the fixed-bed continuous flow reactor was studied. The structured Ni/CeO_2 catalysts supported over corrugated metal wire meshes were studied in CO PrMeth reaction in micro- and milli-channel reactors.

3. Results and discussion

It was shown, that Ni/CeO_2 is active in both CO and CO_2 methanation, exhibiting low selectivity. In contrast to Ni/CeO_2, $Ni(Cl)/CeO_2$ is active in CO and inactive in CO_2 methanation at $T < 300$ °C, providing highly selective operation.

The temperature dependencies of the CO outlet concentration at CO PrMeth, presented in Fig. 1a, illustrate the excellent performance of 10 wt.% Ni/CeO_2 catalyst and its ability to cleanup CO to below 10 ppm in a wide temperature interval.

The kinetic and FTIR in situ study showed that for both Ni/CeO_2 and $Ni(Cl)/CeO_2$ catalysts the CO methanation reaction proceeds similarly over the Ni surface via CO and H_2 chemisorption. The CO_2 methanation kinetics was different for Ni/CeO_2 and $Ni(Cl)/CeO_2$ catalysts. Also the big differences were found in the nature of surface species during CO_2 methanation (Fig. 1b): ceria carbonate and formate species take part in CO_2 methanation over Ni/CeO_2. However, chlorine addition dramatically inhibits the formation of such species due to ceria surface blockage.

The turnover frequencies of Ni surface atoms as well as activation energies in CO methanation were practically similar for all studied catalysts, indicating that Cl did not influence catalyst's activity and CO methanation proceeded by similar ways over Ni surface in both Cl-free and Cl-containing samples. The advanced performance of Cl-containing catalysts was associated with the inhibition of undesirable side reaction of CO_2 methanation. The chlorine doping effect was attributed to the blockage of surface Ce^{3+}-coupled oxygen vacancy sites by CeOCl species that inhibited ceria assisted CO_2 activation and hydrogenation.

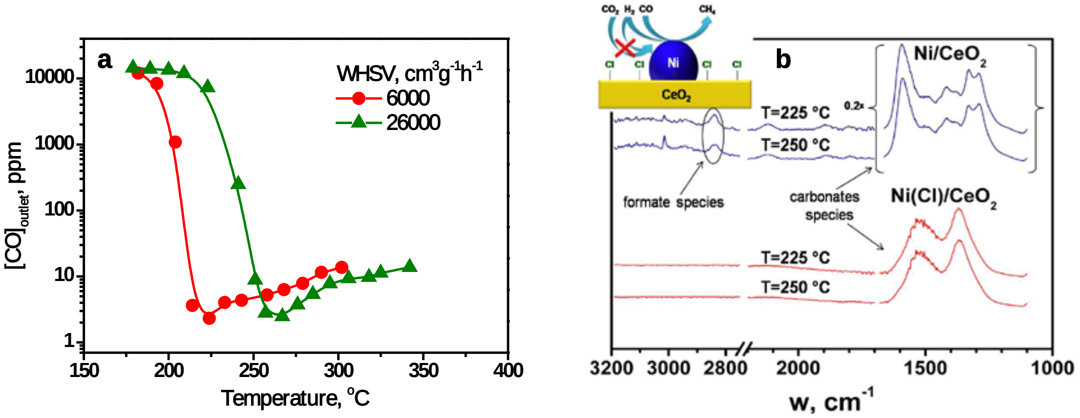

Figure 1. **(a)** The temperature dependencies of the CO outlet concentration at CO PrMeth over 10 wt.% Ni/CeO_2. The inlet gas mixture composition (vol.%): 1.5CO, $20CO_2$, $10H_2O$, H_2 – balance. **(b)** FTIR spectra for CO_2 methanation over Ni/CeO_2 and $Ni(Cl)/CeO_2$ catalysts.

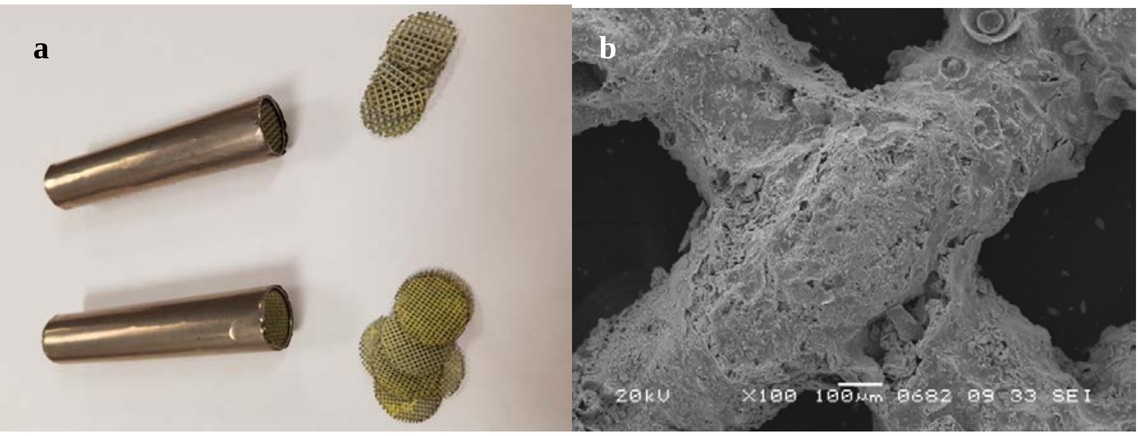

Figure 2. General view (a) and SEM image (b) of the structured 10 wt.% Ni/CeO_2 catalyst washcoated on FeCrAl wire mesh.

The special washcoating procedure was developed and a micro- and milli-channel reactors with structured catalyst was studied (Figure 2). Testing of the lab, pilot and full scale reactors integrated into fuel processor showed that it allowed the decrease of CO concentration to desired level as the outlet temperature was kept below 300 °C.

4. Conclusions

The selected nickel-ceria based catalyst provides efficient CO cleanup and the structured reactors are quite promising for efficient CO removal from hydrogen-rich gas mixtures and therefore attractive for low-temperature PEMFC applications.

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