

Selective CO methanation in the reformat gas over Ni-, Co- and Fe/CeO₂ catalysts: tuning catalyst activity and selectivity

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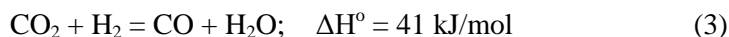
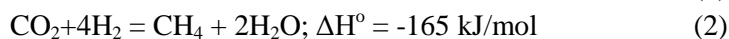
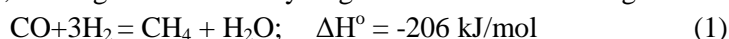
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Abstract: Selective CO methanation (CO-SMET) in the reformat gas, containing (vol.%): 1.0 CO, 65 H₂, 10 H₂O, 20 CO₂ with He as balance, was investigated over Ni-, Co- and Fe/CeO₂ catalysts with various halogen additives. The catalytic activity of ceria-based catalysts in CO-SMET strongly depend on the nature of the metal and the selectivity is regulated by the addition of halogens. Among the catalysts studied, the Ni/CeO₂ catalyst with chlorine addition showed the good performance and was the most selective. This phenomenon could be explained by ceria surface blocking by chlorine species and appropriate inhibition of CO₂ hydrogenation activity.

Keywords: Selective or Preferential CO methanation, CO cleanup, Nickel ceria catalysts.

1. Introduction

The process of selective CO methanation in reformat gas is a promising way for deep CO removal designed for low-temperature proton-exchanged membrane fuel cell feeding applications, as well as a challenging fundamental problem of substrate-selective hydrogenation. In addition to the target CO methanation reaction (1), undesirable CO₂ methanation (2) and reverse water-gas shift (3) reactions may occur, causing considerable hydrogen losses and increasing CO outlet concentration:



This work reports our summarizing results on the development of an effective ceria-based catalyst for CO-SMET¹⁻⁴.

2. Experimental

To investigate the effect of nature of metals were obtained Ni-, Co- and Fe/CeO₂ catalysts. Catalysts with metal loading of 10 wt.% were prepared by incipient wetness impregnation of CeO₂ by the water solutions of metal's nitrate and chloride salts. The effect of halogen additives was studied on Ni/CeO₂ catalyst prepared from a nitrate precursor. Halogen-promoted Ni(F^{*})/CeO₂, Ni(Cl^{*})/CeO₂ and Ni(Br^{*})/CeO₂ catalysts were prepared by treatment of Ni/CeO₂ by the aqueous solutions of NH₄F, NH₄Cl and NH₄Br, respectively. The Ni/CeO₂(Cl^{*}) catalyst was prepared by impregnating the Cl-containing CeO₂ (CeO₂(Cl^{*})) with an aqueous solution of Ni (II) nitrate. The CeO₂(Cl^{*}) was prepared by impregnating CeO₂ with an aqueous solution of ammonium chloride. All catalysts were characterized by BET, XRD, HAADF-STEM, EDX-mapping, XPS and CO chemisorption techniques. The reaction kinetics was studied in a flow reactor at atmospheric pressure in the temperature interval 180 – 360 °C, at WHSV = 29 L·g⁻¹·h⁻¹ and feed gas composition (vol.%): 1.0 CO, 65 H₂, 10 H₂O, 20 CO₂ with He as balance. The nature of adsorbed species was studied by the FTIR in situ technique.

3. Results and discussion

Fe-based and Co(Cl)/CeO₂ catalysts were inactive in CO and CO₂ methanation reactions. Ni/CeO₂ and Co/CeO₂ catalysts were active in both CO and CO₂ methanation, but showed low selectivity. Ni(Cl)/CeO₂

catalyst showed the best performance in selective CO methanation, being less active than Ni/CeO₂ and Co/CeO₂, but considerably more selective¹.

The additives of fluorine reduce the depth of CO purification and have a little effect on the activity and selectivity of Ni/CeO₂ catalyst; the chlorine additives inhibit the CO₂ methanation, that provides high selectivity towards CO methanation in the presence of CO₂; the bromine additives totally inhibit both CO and CO₂ methanation activity³.

Fig. 1 represents the temperature dependencies of the CO outlet concentration and CO selectivity in CO-SMET for all Ni/CeO₂ catalysts. It is seen, that Ni/CeO₂ was active, but unselective. The minimal CO outlet concentration over the Ni/CeO₂ was 130 ppm at 250 °C.

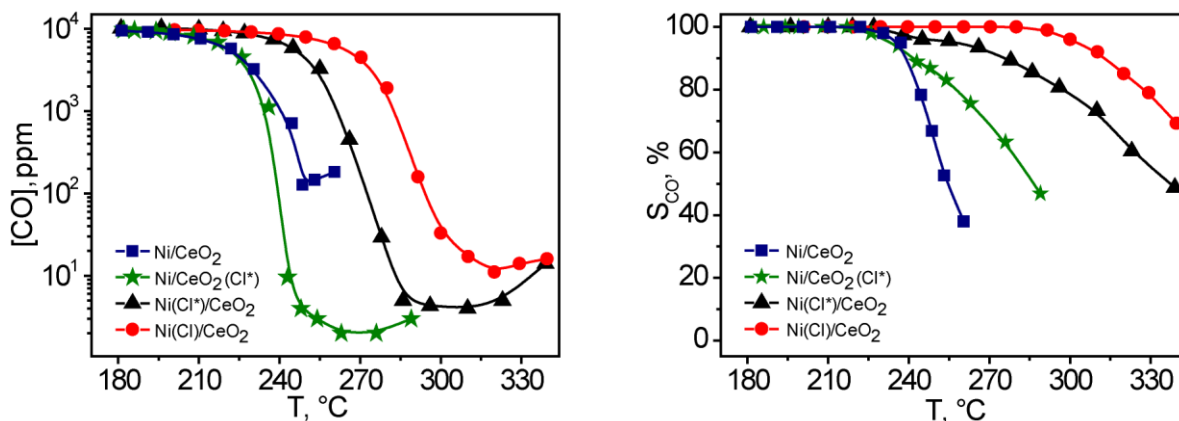


Figure 1. The temperature dependencies of the CO outlet concentration and CO selectivity for CO-SMET over the studied catalysts. Feed gas composition (vol. %): 1.0 CO, 65 H₂, 10 H₂O, 20 CO₂ with He as balance. WHSV: 29 L·g⁻¹·h⁻¹.

All Cl-containing Ni/CeO₂ catalysts showed much higher CO cleanup efficiency and provided CO removal from reformat gas to the level of ≤10 ppm with high selectivity.

XRD, HAADF-STEM and EDX-mapping analysis showed the presence of chlorine on the surface of all Cl-containing Ni/CeO₂ catalysts. The kinetic and FTIR in situ study showed that for all catalysts the CO methanation reaction proceeds similarly over the Ni surface via CO and H₂ chemisorption. The CO₂ methanation reaction over Ni/CeO₂ proceeds via CO₂ adsorption over ceria surface and stepwise hydrogenation to hydrocarbonates and formates by the hydrogen spilled over from Ni. While for all Cl-containing catalysts this reaction pathway is locked by chlorine, providing inactivity in CO₂ methanation and therefore high efficiency in CO-SMET^{2,4}.

4. Conclusions

Only Cl-containing Ni/CeO₂ catalysts can be considered as effective catalysts for the CO-SMET. All Cl-containing Ni/CeO₂ catalysts no matter by which method they were doped with chlorine, showed sufficient performance in CO-SMET. The chlorine doping effect was attributed to the blockage of ceria surface by CeOCl species that inhibited ceria-assisted CO₂ activation and hydrogenation.

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