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Modifying spinel precursors for highly active and stable CO_2 methanation catalysts

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PURPOSE OF THE ABSTRACT

Energy transition from fossil to renewable energy sources is necessary to keep the temperature increase below critical levels. A promising technology to achieve this goal is the hydrogenation of CO_2 with renewable hydrogen towards methane. Although much research is being done, a highly active, selective, stable and inexpensive catalyst is needed to make the process economical.

Nickel is widely used as catalytic active metal for the CO_2 methanation due to its high selectivity and low cost. For the commonly used Ni/Al_2O_3 catalysts, the formation of the more stable $NiAl_2O_4$ spinel phase on the surface leads to a decrease in catalytic activity and selectivity. In our approach we modify this undesired phase by introducing manganese into the spinel to form $M_yMn_xAl_{2-x}O_4$ species as new catalyst precursors. By the individual use of two different metals Ni and Co as active elements in the Mn based spinels, we demonstrate the more general feasibility of this concept. The CO_2 methanation is used as model reaction to evaluate the influence of the catalyst composition on the catalytic activity and selectivity.

Carbon dioxide conversion up to 82% and methane selectivity up to 90% at 450°C are achieved with the optimized catalyst composition and are thus much higher in comparison with the $NiAl_2O_4$ species (c.f. Figure 1). The manganese content influences the activity and selectivity significantly, whereas the highest yields are produced with low manganese content ($0{,}25 < x < 0{,}5$). Characterization with XRD, TPR and CO_2-TPD shows that the integration of manganese into the spinel was successful and that it leads to an easier reduction at much lower temperatures of 450°C than the undesired spinel phase (>700°C). The large change in activity can be attributed on the hand to the improved reducibility of the spinel precursor and on the other hand to the change in surface basicity of the modified spinel. Furthermore, we demonstrate with chemisorption techniques in combination of operando DRIFTS analysis how manganese changes the surface properties and how this alters the reaction mechanism from the classic CO based one towards a formate mechanism that contributes additionally to the observed high activity.

In conclusion it is shown that even small modifications of an undesired secondary phase can lead to a new class of active catalysts with enhanced activity, selectivity and stability compared to the standard supported catalysts. This approach can be tailored to different catalytic systems where the formation of a second unwanted phase is a main deactivation factor.

FIGURES

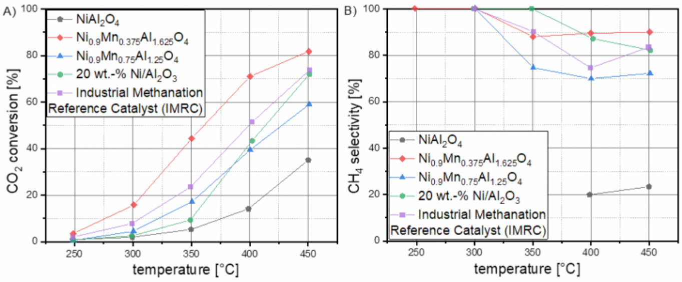

FIGURE 1

Figure 1

Performance of activated Ni based catalyst precursor in the methanation of CO2 towards methane. A) CO2 conversion & B) CH4 selectivity. Activation conditions: 10% H2 in Ar 450 °C 60 min, methanation conditions: CO2/H2 = 1/4 diluted in Ar , GHSV = 20000 h-

FIGURE 2

KEYWORDS

CO2 Methanation | Spinel Catalysts | Stability | Metal Mixed Oxides

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BIBLIOGRAPHY