

Novel $\text{Nd}_{2-y}\text{Ca}_y\text{Co}_{1-x}\text{Ni}_x\text{O}_4$ -driven nanocomposite POM catalysts: synthesis, catalytic performance and chemical transformations

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At present, the problem of catalytic methane conversion into syngas - the mixture of CO and H_2 - is very acute. Catalytic partial methane oxidation ($\text{CH}_4 + 0.5\text{O}_2 = \text{CO} + \text{H}_2$) seems to be one of the most perspective methods which allows obtaining syngas under milder conditions. However, its practical application is complicated by the lack of systematic structural investigations of existing and newly discovered POM catalysts and different reaction pathways on their surface [1]. According to our considerations, metal-oxide nanocomposites produced by the reductive decomposition of perovskite-like oxides can be regarded as the perspective precursors for the POM catalysts [2].

Our studies deal with the synthesis of POM catalysts using the reductive decomposition of newly obtained complex oxides $\text{Nd}_{2-y}\text{Ca}_y\text{Co}_{1-x}\text{Ni}_x\text{O}_4$ with perovskite-like K_2NiF_4 structure. For these compounds the crystal structure and compositional boundaries are determined for the first time. According to the Rietveld refinement of the XRD data, the gradual distortion of the K_2NiF_4 structure was indicated with increasing Ni content. H_2 -TPR measurement showed that all $\text{Nd}_{2-y}\text{Ca}_y\text{Co}_{1-x}\text{Ni}_x\text{O}_4$ solid solutions were reduced completely at 700 °C producing fine Ni^0 and Co^0 metal nanoparticles incorporated into Nd_2O_3 and CaO oxide matrix. $\text{Nd}_{1.5}\text{Ca}_{0.5}\text{NiO}_4$ -derived catalyst demonstrated the highest POM conversion and selectivity among all the $\text{Nd}_{2-y}\text{Ca}_y\text{Co}_{1-x}\text{Ni}_x\text{O}_4$ derivatives (Figure 1). However, metal nanoparticles were found to reoxidize in the course of POM reaction. Such oxide particles participated in the solid state reaction regenerating the initial perovskites-like structure which was indicated by the ex situ XRD measurements.

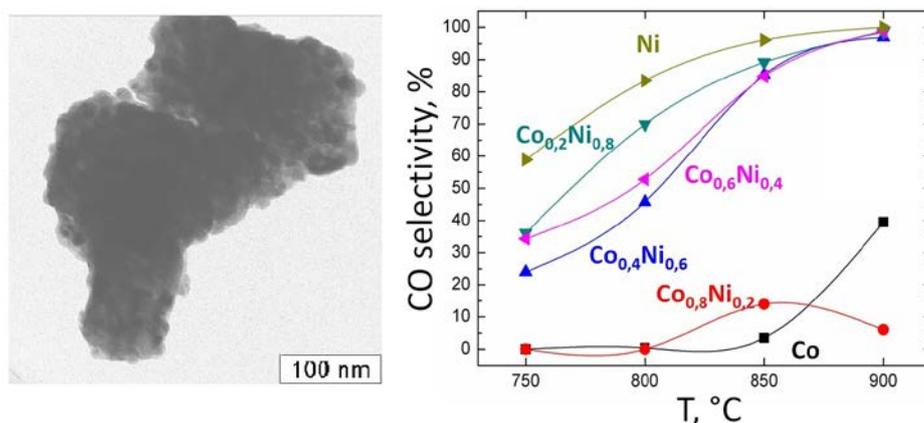


Figure 1: TEM image of the $\text{Nd}_{1.3}\text{Ca}_{0.7}\text{Co}_{0.4}\text{Ni}_{0.6}\text{O}_4$ reduction product after POM test (left) and the dependence of CO selectivity vs temperature for $\text{Nd}_{2-y}\text{Ca}_y\text{Co}_{1-x}\text{Ni}_x\text{O}_4$ -based catalysts with various Co/Ni ratio (right).

References

- [1] - B.C. Enger, R. Lødeng, A. Holmen, Appl. Catal. A **346**, 1-27 (2008).
- [2] - A.G. Dedov, A.S. Loktev, D.A. Komissarenko et al, Fuel Proc. Technol. **148**, 128-137 (2016).