On the structure reactivity and synthesis strategy of mixed-oxides prepared by microwave-assisted solution combustion synthesis – XAS and XRD operando study

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Significance and Relevance

One of the most optimal regarding the economic perspective and catalytic performance, compositions of CO_2 methanation catalyst consists of Ni as an active phase and mixed Al_2O_3-MgO support. Typically, to obtain strong metal-support interaction and form well-dispersed surface nickel nano-crystallites, such catalyst was produced via thermal decomposition of hydrotalcites.[1] To optimize the synthesis protocol, and eliminate energy consuming steps such as precipitation, drying and calcination, thermal solution combustion synthesis (T-SCS) has been successfully applied. It was reported that T-SCS derived catalysts resulted in enhanced catalytic performance compared to the hydrotalcite-derived counterpart.[2] Another improvement, to limit the time and energy delivered to the synthesis was application of microwave reactor as a heat source (M-SCS). With this approach, it was possible to obtain the Ni-Mg-Al catalyst with excellent properties in a preparation protocol shorter than 10 minutes.

Preferred and 2nd choice for the topic: Oral preferred or Short Oral

Introduction and Motivations

CO_2 hydrogenation to methane brings a promising perspective for conversion of carbon dioxide into the desired synthetic natural gas (SNG), due to the simplicity of the process (ambient pressure of the reaction, relatively low temperature range 250-450 °C) allowing simplified scalability, finding its confirmation in the increasing number of plants introduced worldwide. Nickel catalyst is the best compromise between the good catalytic performance and costs of production. Presence of alumina in the support enhances specific surface area, and inhibits Ni sintering, MgO delivers surface basicity necessary for adsorption and activation of carbon dioxide.[1,2]

Materials and Methods

Initially, solution containing nitrate precursors $Ni(NO_3)_2 \cdot 6H_2O$ (Chempur, p.a.), $Mg(NO_3)_2 \cdot 6H_2O$ (Sigma Aldrich, p.a.), $Al(NO_3)_3 \cdot 9H_2O$ (Chempur, p.a.) with desired amount of urea (100 or 175%) was complexed for 40 minutes on the magnetic stirrer, at 50 °C. Later, solution in the Pyrex beaker was placed inside the microwave reactor set for 800 or 1000 W, and heated till the combustion was completed.

Table 1. List of the studied samples in regard to the synthesis conditions

Catalyst	Urea content [%]	Microwave power [W]
SCS_100_800	100	800
SCS_175_800	175	800
SCS_100_1000	100	1000
SCS_175_1000	175	1000

CO_2 methanation reaction tests were performed with the use of a tubular fixed-bed quartz U-type reactor under the following conditions: $CO_2/H_2/Ar$ of 1.5/6/2.5, with a total flow of 100 ml/min, GHSV of 12 000 h^{-1}, 1 bar, t from 250 to 450 °C.

The catalysts were characterized using the following methods: ICP-MS, low-temperature N_2 sorption, H_2-TPR, CO_2-TPD, TEM, XPS. In-situ XRD, XAS and EXAFS were performed at the Swiss-Norwegian beamline (SNBL, BM31) at the European Synchrotron Radiation Facility (ESRF) in Grenoble (France).

Results and Discussion

Results of temperature-programmed surface reaction measured at steady-state (TPSR) are compared in Fig. 1. It is visible that both catalysts synthesized with the above-stoichiometric urea content resulted in superior catalytic performance. CO_2 conversion of SCS_175_800 and SCS_175_1000 is almost identical, which suggests that in this case, the increase of the microwave power output did not bring any beneficial effect. On the other hand, for the catalysts prepared with stoichiometric urea amount (SCS_100_800, SCS_100_1000), the observed catalytic conversions are lower, than in the case of counterparts obtained at above-stoichiometric urea contribution. The CO_2 conversion is visibly improved, in the SCS_100_1000 sample at 300 °C, compared to the SCS_100_800, suggesting that the certain dynamics of the combustion (provided either from the heat energy delivered to the system (1000 W) or fuel decomposition) is essential to form a reactive interface with an enhanced activity. The synthesis conditions, in particular the urea/(Ni+Mg) ratio has an impact on the physico-chemical properties. The use of stoichiometric urea amount resulted in better development of surface basicity confirmed with CO_2-TPD.

On the contrary, the above stoichiometric fuel content resulted in an improvement development of nano pores at the surface, while higher used power (1000 W) contributed to increase in S_{BET} of ca 30%. Furthermore, with an increase of energy delivered to the synthesis (fuel+power) the shift towards higher 2θ in XRD reflection corresponding to MgO (200) at 42.9 deg was registered, suggesting a deficit of oxygen in the lattice. During the operando XAS-XRD measurement, it was observed that among all the studied samples, SCS_175_800 is remaining the least reduced after the reaction. It suggests that surface reactivity of this catalyst is more effective than for other materials – incomplete reduction of nickel preserved the oxygen at the surface, allowing formation of additional basic sites and activation of CO_2.

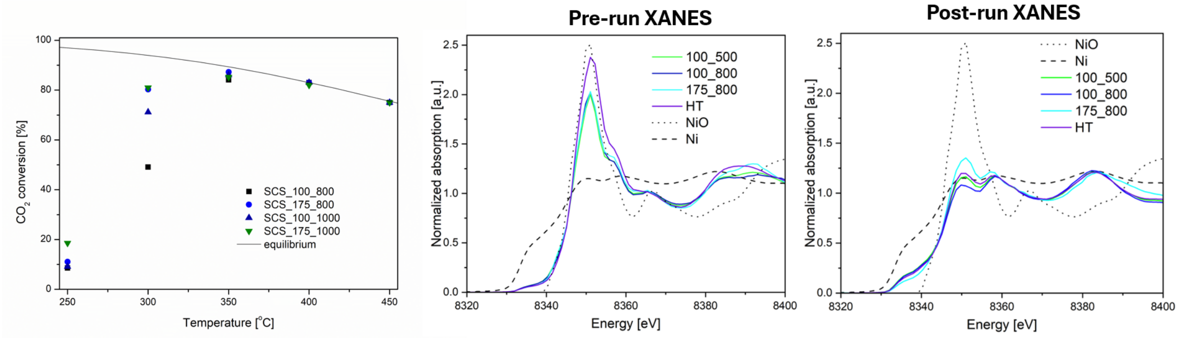

Figure 1. CO_2 conversion of the M-SCS catalysts (left), XANES spectra comparing the M-SCS (100_800, 175_800) samples with hydrotalcite-derived (HT) and T-SCS (100_500), before the in-situ catalytic reaction (middle), after in-situ catalytic reaction (right).

References

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