CO_2 methanation on the Ni-Mn-modified mesoporous silica

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Significance and Relevance

The mesoporous silica was synthesized by a simple procedure from rice husks without template. Incipient wetness impregnation method was used for preparation of Ni-Mn-containing mesoporous silica catalysts. The strong influence of the Ni and Mn content and the peculiar properties of the applied mesoporous carrier on the formation of nickel and manganese oxide species with fine dispersion were demonstrated. Among the prepared catalysts, the 7 wt. % Ni- 3 wt. %Mn supported mesoporous silica catalysts showed the highest catalytic activity in CO_2 hydrogenation to methane. The activity and selectivity of the latter sample was kept for 5 hours reaction time.

Preferred and 2nd choice for the topic: CO_2 utilization and recycling/ Air cleaning and combustion
Preferred presentation: poster/short oral

Introduction and Motivations

The increasing emission of greenhouse gases and their severe effect on the climate has come into the spotlight as a major challenge to sustainable development [1]. The European Green Deal is a new EU strategy aiming to combat climate change by no net emissions of (GHGs) by 2050. CCU is one of the most widely researched approaches, using CO_2 as an alternative, non-petrochemical precursor to chemical feedstocks. There is a broad spectrum of products, but the most valuable intermediates are synthesis gas, that can be used directly to produce fuels, and C1 compounds such as methanol, formic acid and methane [1]. The development of efficient catalysts is of key importance for the processes for CO2 valorization. The application of transition metal-containing (Ni, Co, Cu, Fe) catalysts is a good alternative of noble metals due to their affordable prices and high activity. However, the following order of activity was established. The catalytic support also influences the efficiency of the methanation process. The most promising supports are Al_2O_3, ZrO_2, CeO_2, MCM-41, SBA-15, and zeolites. A disadvantage of these materials is their high cost, which is due to the use of expensive reagents, incl. template, high temperature and longer procedure leading to higher energy consumption. A significantly more economical approach is the use of waste materials, low temperature and absence of expensive templates to obtain mesoporous silicas. Examples of raw materials for obtaining porous materials are most often agricultural waste, such as rice husks, etc.

In the present study, we have developed Ni-Mn- based mesoporous silica (MS) catalysts with high activity and selectivity for CO_2 conversion to methane.

Materials and Methods

The initial and modified materials were characterized by XRD (Bruker AXS Advanced X-ray Solutions GmbH, Karlsruhe, Germany), N_2 physisorption (Quantachrome instruments AUTOSORB iQ-MP-AG, Boynton Beach, FL 33426, USA), thermal analysis (STA449F5 Jupiter of NETZSCH Gerätebau GmbH (Netzsch, Germany), and solid-state NMR (Bruker Avance II+ 600 NMR spectrometer (Karlsruhe, Germany).

Samples were reduced in hydrogen (60 mL/min) up to 400 °C for 1h ex situ before the catalytic experiments. Hydrogenation of methane was performed at atmospheric pressure using a fixed-bed flow reactor. The amount of the catalyst which is used in the catalytic experiment is a 150 mg sample

with particle size 0.2–0.8 mm. The CO_2 reactant was fed in the reactor with a flow rate of 30 ml/min H_2 and CO_2, GHSV= 12 000 $cm^3h^{-1}gcat^{-1}$, (H_2/CO_2 is 4/1) and catalytic experiments were carried out in the interval 250–400 °C. On-line analysis of the reaction products was performed using a NEXIS GC-2030 ATF with a VALCO Plot VPHS-D CFS-PD3053-200 (30 m × 0.53 mm × 20.0 µm) column.

Results and Discussion

The XRD patterns of the reduced catalysts show the formation of finely dispersed nickel nanoparticles. Impregnation with nickel and manganese resulted in a decrease of the surface area but the shape of the isotherms is similar to the parent silica. Therefore, the changes are due to the pore blocking effect of incorporated metal oxides and metal oxide deposition on the outer surface.

Catalytic activity of the obtained catalysts in CO_2 methanation reaction was studied with increasing reaction temperature (Figure 1).

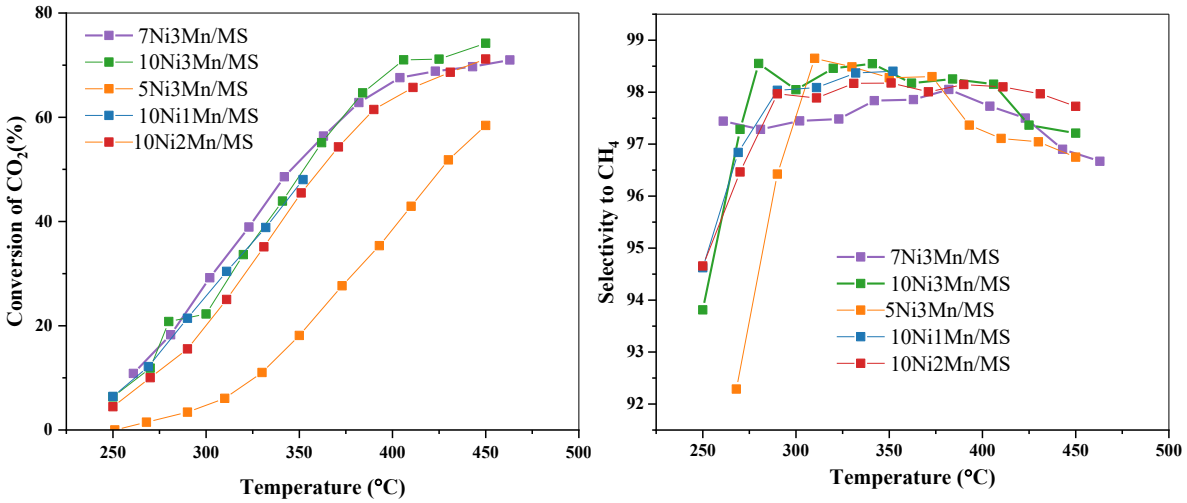

Figure 1. Catalytic activity of the studied catalysts as a function of reaction temperature (H_2:CO_2 = 4:1; GHSV = 12 000 mL $gcat^{-1}$ h^{-1}).

The highest catalytic activity and selectivity to methane were detected for 7Ni3Mn/MS catalyst. The presence of manganese facilitated the reduction of nickel during the reductive pretreatment and improved the nickel dispersion. Formation of Mn_xO_y has a positive effect on the catalytic performance because of the formation of basic sites with moderate strengths, enhancing the adsorption of slightly acidic CO_2. The basic sites promote the formation of monodentate formate species, that can be easily converted to methane. It was found that the presence of nickel nanoparticles and Mn_xO_y with the optimal ratio could result in higher activity and stability of the catalyst. Our results suggest that addition of manganese, a cheap and abundant transition metal, holds significant potential for industrial application in sustainable power to gas technologies.

References

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