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Short Communication

Development of improved nickel catalysts for sorption enhanced CO₂ methanationR. Delmelle^{a,*}, R.B. Duarte^a, T. Franken^a, D. Burnat^a, L. Holzer^b,
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ABSTRACT

Sorption enhanced CO₂ methanation is a complex process in which the key challenge lies in the combined optimization of the catalyst activity and water adsorption properties of the zeolite support. In the present work, improved nickel-based catalysts with an enhanced water uptake capacity were designed and catalytically investigated. Two different zeolite frameworks were considered as supports for nanostructured Ni, and studied with defined operation parameters. 5Ni/13X shows significantly increased, nearly three-fold higher, operation time in the sorption enhanced CO₂ methanation mode compared to the reference 5Ni/5A, likely due to its higher water sorption capacity. Both catalysts yield comparable CO₂ conversion in conventional CO₂ methanation (without water uptake). Regeneration of the catalysts performance is possible via a drying step between methanation cycles under both reducing and oxidizing atmospheres; however, operation time of 5Ni/13X increases further after drying under air.

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Introduction

Methane production from waste carbon dioxide with renewable hydrogen can become of crucial significance for future energy turnaround strategy in countries like Switzerland or Germany, because it contributes to the reduction of CO₂ emissions. Such CO₂ emissions can be reused and even valorized by its chemical conversion with hydrogen produced

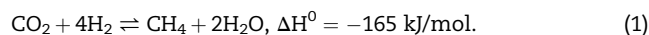
from renewable excess energy [1]. Conventional methanation processes involve nanostructured active metals on various supports (e.g. SiO₂ [2], ZrO₂ [3], Al₂O₃ [4], carbon nanotubes [5]). Despite the existence of other elements at the research level, Ni remains the best choice for the active metal when considering activity, selectivity and price [6]. The efficiency of CO₂ methanation, also known as Sabatier reaction (1), is increased by the application of Le Châtelier's principle, via the in-situ removal of water from the reaction sites, causing an

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equilibrium shift: the so called sorption enhanced methanation process [7,8] (see Fig. 1). Additionally, high selectivity to CH₄ is desired, and therefore uptake of water already at the reaction centre is optimal.



Zeolites are materials commonly used as adsorber material in industrial processes such as dehydration of ethanol and flue gas cleaning of exhaust air, but can also be used as catalyst support [9,10]. Zeolite LTX (13X) provides 9 Å pores, which allow an easy diffusion of molecules inside the zeolite channels, and high water sorption capacity (26 g_{water}/kg_{zeolite} at 21 °C and 53% relative humidity (RH)) [11,12]. Zeolite LTA (5A) was previously tested by the authors [7,13,14] and proved itself efficient in the sorption enhanced CO₂ methanation, due to its relatively good water uptake capability (23 g_{water}/kg_{zeolite} at 21 °C and 53% RH) and adequate pore size (5 Å), that allows accessibility of the molecules involved in the Sabatier reaction to the internal zeolite surfaces [7,14]. It is essential to understand how the properties of the zeolite support affect the catalytic reaction in order to design catalysts with an improved yield, extended operation time or fast kinetics for the sorption enhanced CO₂ methanation. For example, the role played by the heat of water sorption by the zeolite is omitted in Eq. (1). As water sorption is vital in this application, 13X was subjected as support for sorption catalyst and compared to the 5A reference.

Zeolites have limited water sorption capacity; consequently a regeneration step, i.e. drying of the catalyst bed with a dry gas is required, preferably at the same temperature level

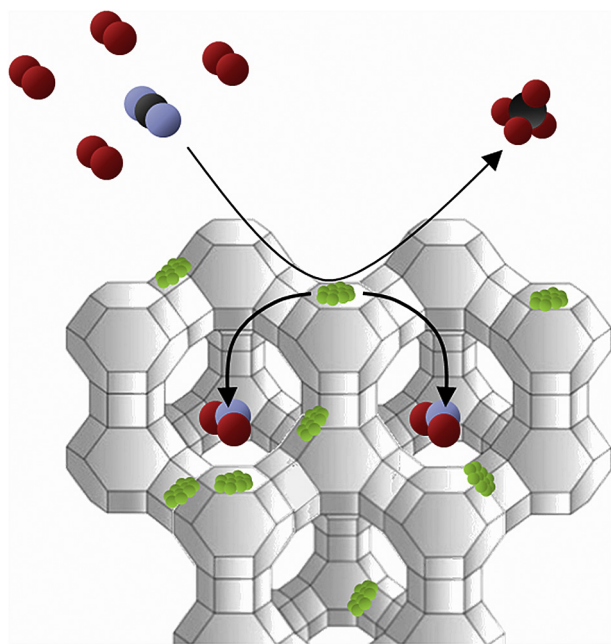


Fig. 1 – Molecular structure model of sorption enhanced CO₂ methanation over a nickel catalyst on zeolite. Red, blue, black and green spheres represent hydrogen, oxygen, carbon and nickel atoms, respectively. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

to avoid time consuming cooling and heating periods without operation [15]. Proper choice of the drying gas is a strategic key parameter: reducing environment yields higher reduction degree of the metallic active phase, which might result in higher catalytic activity [16]; however, a higher oxygen partial pressure obtained by an air stream allows cleaning of the catalyst surface from poisons present in CO₂ sources [17,18] or from coke, an intermediate species of the methanation reaction [19]. We elucidate the influence of the atmosphere used for the regeneration of the water saturated zeolite and of the zeolite support on the performance of nickel catalysts for sorption enhanced CO₂ methanation.

Experimental

Nickel catalysts were supported on commercial zeolites LTA and LTX (beads, 2 mm, Zeochem) by a wet impregnation process from a solution of nickel nitrate hexahydrate (Ni(NO₃)₂·6H₂O, Sigma Aldrich) in water. Zeolites were dried at 140 °C for 12 h before synthesis. The mixture of zeolite beads and Ni solution was stirred for 1 h at room temperature (RT) and subsequently the solvent was removed at 70 °C in a rotary evaporator. The samples were dried again for additional 12 h at 140 °C and then calcined at 500 °C in a muffle for 4 h to remove residual nitrate salts. Inductively Coupled Plasma Optical Emission Spectrometry (ICP–OES) measurements of the catalysts revealed that all samples contain about 4 wt.% nickel before calcination and 5 wt.% nickel after calcination, in agreement with the values calculated for the Ni supported zeolite with and without adsorbed solvent, respectively. The resulting samples are named 5Ni/5A and 5Ni/13X if prepared on LTA and LTX, respectively.

Catalytic screening of material systems for CO₂ methanation was performed in a tubular fixed-bed reactor with volume of 340 mL and an internal diameter of 32.8 mm coupled to a mass spectrometer (MS), model Pfeiffer OmniStar GSD 320 O1. The reactor contains a catalyst mass of 250 g. The reactions were carried out under atmospheric pressure. Samples were initially reduced for 1 h at 500 °C in 800 mL/min of a 1:1 molar ratio of H₂/Ar before reaction. After cooling to 300 °C under this reducing atmosphere, CO₂ methanation was performed with a GHSV (gas hourly space velocity = reactant gas flow rate per reactor volume) of 92 h⁻¹ and reactant feed composition of CO₂ and H₂ with total flow of 520 mL/min and molar ratio 1:4.05 (5% excess of hydrogen to avoid coking). Argon was added at the reactor outlet as tracer prior to the MS for normalization of the MS signal. The activity and stability of the catalysts were tested at a reactor temperature of 300 °C according to the following sequence: (i) initially, the samples were subjected to CO₂ methanation up to the saturation of the zeolite support with water, identified by the breakthrough of water; (ii) the samples were then dried for 20 min with a flow of 800 mL/min of air or 1:1 molar ratio of H₂/Ar (zeolite drying time was prolonged to 40 min at specific tests to determine the influence of drying time in the subsequent test under sorption enhanced CO₂ methanation mode); (iii) the whole cycle procedure was then repeated six times. The amounts of H₂, CO, CO₂ and CH₄ were recorded by the MS as function of time. The flow rate was controlled by mass flow controllers (Bronkhorst,

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