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Pure methane from CO_2 hydrogenation using a sorption enhanced process with catalyst/zeolite bifunctional materials

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ABSTRACT

Methanation is a potential large-scale option for CO_2 utilization, and it is one of the solutions for decreasing carbon emission and production of synthetic green fuels. However, the CO_2 conversion is limited by thermodynamics in conventional reaction conditions. However, around 100 % conversion can be obtained using sorption enhanced CO_2 methanation according to Le Chatelier's principle, where water is removed during the reaction using zeolite as a sorbent. In this work 5%Ni5A, 5%Ni13X, 5%NiL and 5%Ni2.5%Ce13X bifunctional materials with both catalytic and water adsorption properties were tested in a fixed bed reactor. The overall performance of the bifunctional materials decreased on going from 5%Ni2.5%Ce13X, 5%Ni13X, 5%Ni5A, to 5% NiL. The CO_2 conversion and CH_4 selectivity were approaching 100 % during prolonged stability testing in a 100 reactive adsorption – desorption cycles test for 5%Ni2.5%Ce13X, and only a slight decrease of the water uptake capacity was observed.

1. Introduction

Converting CO_2 to chemicals and fuels is one of the potential routes for achieving the goal of reducing carbon emission as agreed on in the Paris agreement [1,2]. This makes CO_2 and H_2 from renewable sources, e.g. biomass, wind or solar energy, increasingly important as feedstocks for the chemical industry [3–6]. Methanation via the Sabatier Reaction **(1)** is an exemplary method for CO_2 utilization within the context of large-scale energy storage based on power to gas [7,8], which is aimed at carbon neutrality [9,10]. It is also a promising method for upgrading the biomass thermochemical conversion product gases which contain CO_2 and H_2 [11].

$$CO_2 + 4H_2 \leftrightarrow CH_4 + 2H_2O; \Delta H^0_{298} = -165\ \mathrm{kJ/mol} \quad (1)$$

One important advantage in methanation is that existing infrastructure can be used for the product's transportation and storage, which has great potential for industrial and transport applications. The Sabatier reaction is limited by equilibrium, so, in order to reach high yields, it has to be performed at very high pressures (Fig. 1), or costly separations must be performed to obtain a pure enough product.

The CO_2 methanation reaction equilibrium **(1)** can, however, be shifted towards the products according to Le Chatelier's principle [12] by removing water from the reaction mixture by sorbents like zeolites [13]. The resulting methane-rich product gas can then even easily meet the gas grid feed requirement. There are many publications about CO_2 methanation using zeolite as the catalyst support, but the research on sorption enhanced CO_2 methanation is scarce [14–16]. LTA zeolites (3A, 4A and 5A) and zeolite13X have been used by researchers in the sorption enhanced CO_2 methanation during the past several years [13,17,18]. Borgschulte et al. found that the CH_4 selectivity was greatly enhanced by the zeolite pore size if it is larger than 5 Å [17]. Zeolite 13X is well known for its high water uptake capacity and hence a potential candidate in sorption enhanced CO_2 methanation [19,20]. It was reported by Delmelle et al. that a Ni/13X catalyst allows for a longer operation time compared to Ni/5A catalyst, since zeolite 13X has a significantly higher water sorption capacity [21].

Terreni et al. [22] reported that nano-structured sorption enhanced catalysts with short diffusion pathways are advantageous over physical mixtures of sorbents and catalysts which result in long diffusion path lengths. In other words, bifunctional materials which contain both catalytic and adsorption sites in close proximity are needed. Low temperature promotes high equilibrium CO_2 conversion (Fig. 1), while

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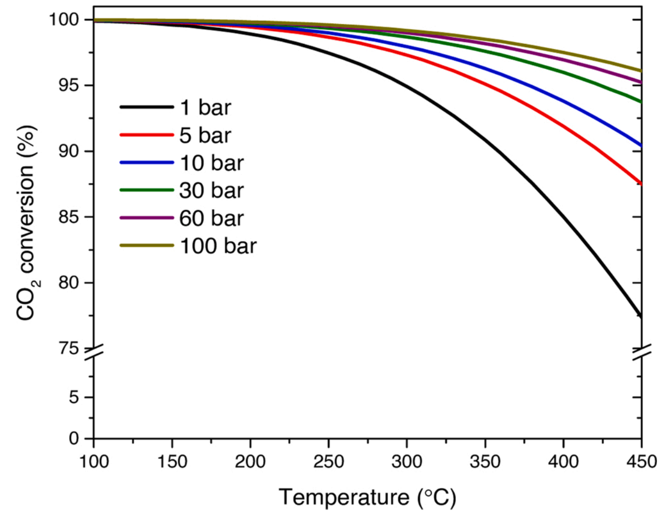

Fig. 1. Thermodynamic equilibrium conversion for the stoichiometric feed gas composition of CO_2 methanation. The equilibrium constant K_{eq} was retrieved from the database of Factsage™ software for the reaction of CO_2 methanation $4H_2+CO_2 \leftrightarrow CH_4+2H_2O$ at different pressures and temperatures. More information concerning the calculation procedure can be found in the supplementary material.

temperatures above 280 °C are typically required to obtain reasonable CO_2 conversion kinetics and resulting in far from 100 % equilibrium conversion values. Bifunctional materials should thus have high activity and selectivity below 280 °C, as well as high water adsorption capacity for obtaining high CO_2 conversion, which can also prevent carbon formation and lead to efficient operation of the CO_2 methanation in a fluidized-bed reactor [23]. Bifunctional materials prepared by loading catalytically active metal directly into the zeolite have therefore been identified as a promising solution. A schematic of such bifunctional materials is shown in (Fig. 2).

Recently, three papers were published by the current authors on the aforementioned bifunctional materials, detailing synthesis options, catalyst material, catalyst metal concentration and promoters in conjunction with their performance and material characterization details [19,20,24].

The current work focuses on the combined sorption enhancement and catalytic properties of the following impregnated zeolite bifunctional materials: 5%Ni5A, 5%Ni13X, 5%NiL and 5%Ni2.5%Ce13X. The previous publications focused only on preparation, characterization, conversion and selectivity of the non-enhanced process. The bifunctional material 5%NiL, though, has not been described in the earlier mentioned publications. It was included to provide a second larger pore zeolite in addition to zeolite 13X.

2. Experimental

2.1. Catalyst preparation and characterization

The 5%Ni5A, 5%Ni13X, 5%NiL and 5%Ni2.5%Ce13X were prepared by evaporation impregnation and characterized thoroughly by e.g. STEM-EDX, TEM, N_2 physisorption, XRD, XPS and chemisorption as described in our previous work [19,20]. The zeolite L was prepared as the references [25,26], the zeolite L based bifunctional material was synthesized by evaporation impregnation according to the description in references [19,20] and the characterization details can be found in the Supplementary Material.

2.2. Sorption enhanced CO_2 methanation in a fixed-bed reactor

The catalyst activity, selectivity, and sorption enhancement capacity,

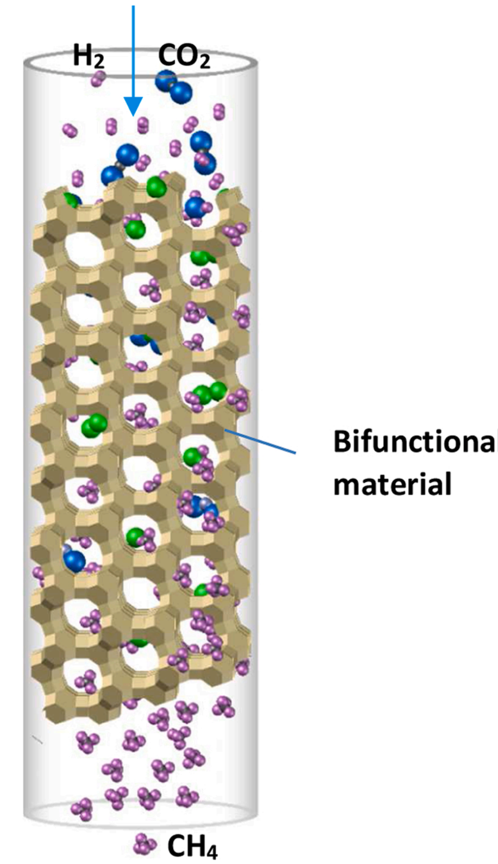

Fig. 2. Schematic of sorption enhanced CO_2 methanation.

as well as prolonged stability experiments were performed in a quartz fixed-bed reactor described in our previous work [24]. The input gases in experiments were controlled by mass flow controllers, which had output pressure of 1–1.3 bar. All flow rate unit refers to under normal condition (20 °C, 1 bar).

Before the experiment, 6.5 g of calcined catalyst 5%Ni2.5%Ce13X was loaded in the reactor and reduced under 100 mL/min H_2 at 500 °C for 2 h. The 5%Ni13X, 5%Ni5A and 5%NiL samples were tested in the same reactor system with a 8.4 g loading. The catalyst activity determination experiments were carried out between 180 °C–360 °C with a gas hourly space velocity (GHSV) of 923 mL/$g_{cat.}$/h, in a reaction mixture of H_2, CO_2, CH_4 and N_2, where N_2 was used as balance gas. The total input volumetric gas flow rate was 100 mL/min. Additionally, different GHSV values were applied. The gas produced from the reactor flowed through a cooling condenser and was analyzed by GC (Varian, CP-4900 Micro-GC) equipped with HayeSep A, molecular sieve columns (Molsieve 5 Å PLOT) and a thermal conductivity detector. Helium was used as the carrier gas.

The CO_2 conversion (2) and catalyst selectivity (3) for CH_4 are defined as [27,28]:

$$X_{CO_2} = \frac{n_{CO_2,\,in} - n_{CO_2,\,out}}{n_{CO_2,\,in}} \tag{2}$$

$$S_{CH_4} = \frac{n_{CH_4,\,out}}{n_{CO_2,\,in} - n_{CO_2,\,out}} \tag{3}$$

Where $n_{CO_2,\,in}$ is the input molar flow rate of CO_2 in the experiment, $n_{CO_2,\,out}$ and $n_{CH_4,\,out}$ are the molar flow rates of CO_2 and CH_4 calculated from GC results, respectively (a selectivity lower than 100 % means that CO is formed).

The water breakthrough capacity of bifunctional materials was calculated using equation:

$$C_{wb} = t_{wb} \cdot S_{wp} \quad (4)$$

where, C_{wb} is the water breakthrough capacity of the bifunctional material, having the unit mmol/g (per gram bifunctional material), t_{wb} (min) is the time it takes to for the bifunctional material to be saturated with water, it starts from the beginning of the reaction to water exiting the catalyst bed and being detected by the humidity detector, and S_{wp} is the rate of water production in the catalyst bed (mmol/min/g). The conversion was calculated based on the GC analysis results.

3. Results and discussion

3.1. Sorption enhanced and non-sorption enhanced experiments using a fixed-bed reactor

Sorption enhanced and non-sorption enhanced CO_2 methanation experiments using 5%Ni2.5%Ce13X were carried out at the same experimental conditions for comparison.

Before the non-sorption enhanced CO_2 methanation was performed, the bifunctional material was utilized in an experiment at 180 °C to saturate it with water, then the furnace temperature was increased to investigate the catalyst performance. The sorption enhanced experiments were carried out with a completely dry sorbent.

The bifunctional material was regenerated at 300 °C under 90 mL/min N_2 and 10 mL/min H_2 for 1 h before each sorption enhanced CO_2 methanation. Each sorption enhanced CO_2 methanation experiment was carried out for 55 min until water exited the system i.e. the breakthrough capacity was reached. The experimental results are shown in Figs. 3 and 4.

For the non-sorption enhanced CO_2 methanation, displayed in Fig. 3 the catalyst activity seems to be severely diffusion limited by the presence of water at lower temperatures [19]. The CO_2 conversion reached equilibrium (82 %) at 270 °C and it decreased to 52 % at 360 °C as conversion was limited by thermodynamics [18]. It can be clearly seen, that the CO_2 conversion reaches practically thermodynamic equilibrium at the high temperature. However, a close to complete CO_2 conversion can be obtained at temperatures between 180–320 °C with the sorption enhanced CO_2 methanation conditions. A slight decrease in CO_2 conversion was observed when the temperature was increased to 320 °C, which results from the thermodynamics of the methanation equilibrium as well as the water uptake capacity of the zeolite: both are reduced at high temperature. Slightly lower CO_2 conversion (98.6 %) was obtained at 180 °C, which is due to decreased Sabatier reaction rates at low temperature. The sorption enhanced CO_2 methanation resulted in a significant increase in the conversion % (up to 84 %) which shows the very high impact of water removal by the bifunctional material 5% Ni2.5%Ce13X.

Around 100 % CH_4 selectivity was obtained from both non-sorption and sorption enhanced CO_2 methanation using 5%Ni2.5%Ce13X within the temperature range of 180–330 °C, although a slight decrease at 360 °C can be observed. This shows that the sorption enhancement has no significant effect on the CH_4 selectivity. Our previous article showed that a proper acid-base balance is beneficial for non-sorption enhanced CO_2 methanation of 5%Ni2.5%Ce13X [24] concerning zeolite material acidity as Lewis acidity is not as influential as Brønsted acidity and the basic sites should clearly not be too strong [29]. The evidence is lacking for a changing reaction path of CO_2 methanation in this work, even though the presence of CeO_2 often leads to a carbide pathway to produce *CO [30]. The strong water removal by the bifunctional material would be beneficial for cutting short reaction steps in the carbide pathway [31], since it enables water removal in time. The CO_2 conversion is still around 100 % under sorption enhanced condition at 180 °C, even though the catalyst catalytic activity is low at 180 °C. This can also be ascribed to the strong water removal effect by the bifunctional material. Additionally, the CO_2 conversion and CH_4 selectivity clearly results from the highly dispersed subnanometer Ni particles of the bifunctional material [24].

A high CH_4 selectivity around 100 % was also obtained from all bifunctional materials without Ce promotion (Fig. 4), while the CO_2 conversions are different especially in non-sorption enhanced CO_2 methanation [32]. The dispersion of Ni on 13X was higher than on 5A zeolite due to the fact that 13X zeolite has a larger pore size, which resulted in a higher activity of 5%Ni13X [19]. The zeolite L also has larger pores compared to 5A zeolite. Around 100 % CO_2 conversion could be obtained with 5%Ni5A and 5%Ni13X bifunctional materials even without Ce promotion which has been shown to increase activity, while the water vapor breakthrough time of 5%Ni13X was longer compared to 5%Ni5A (Fig. 5). The higher water uptake capacity of zeolite 13X [33] promoted the sorption enhanced methanation. The influence of sorption enhancement could also be seen when using 5%NiL in CO_2 methanation, but the water vapor breakthrough time was only some minutes when using 8.4 g of catalyst indicating considerably lower water uptake capacity compared to zeolite 13X [32].

The water breakthrough capacities of all the catalysts investigated are displayed in Fig. 5.

Table 1 summarizes the performance of representative bifunctional materials for sorption enhanced CO_2 methanation found in literature. The comparison reveals that the 5%Ni2.5%Ce13X has an excellent

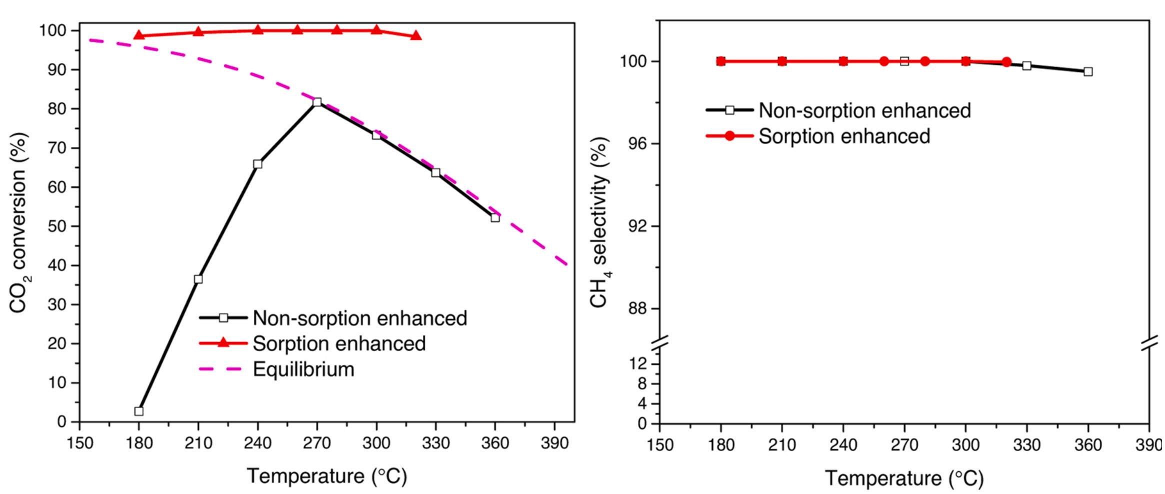

Fig. 3. CO_2 conversion and CH_4 selectivity of 5%Ni2.5 %Ce13X at non-sorption enhanced and sorption enhanced CO_2 methanation. Inlet gas composition (volumetric basis): 6 % N_2, 10 % H_2, 2.5 % CO_2, 81.5 % CH_4, 100 mL/min in total (GHSV = 923 mL/g_{cat}/h). 6.5 g catalyst was reduced at 500 °C under 100 mL/min H_2 for 2 h.

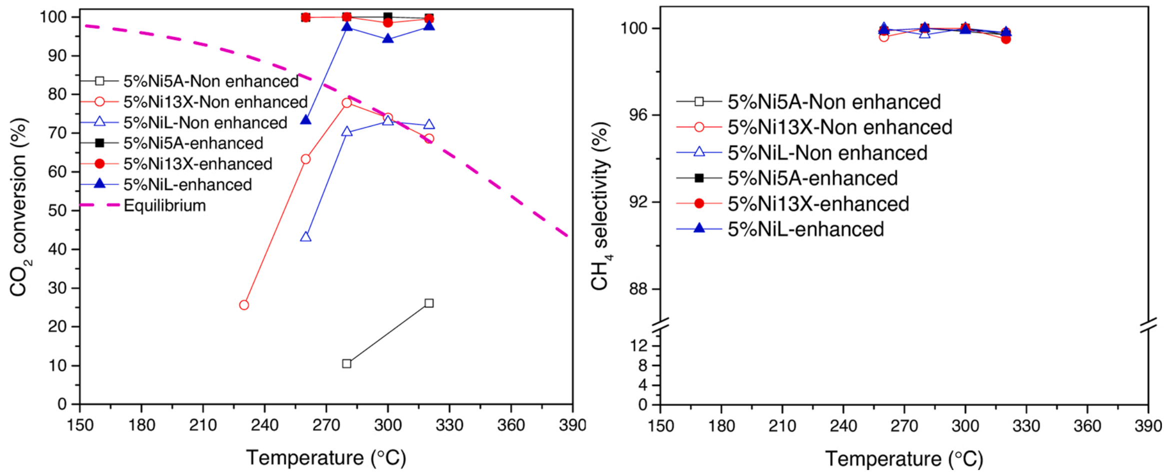

Fig. 4. CO_2 conversion and CH_4 selectivity of 3 different bifunctional materials at non-sorption enhanced and sorption enhanced CO_2 methanation. Inlet gas composition (volumetric basis): 9.9 % H_2, 2.5 % CO_2, 81.6 % CH_4, 6.0 % N_2, 100 mL/min in total (GHSV = 714 mL/g_{cat}/h). The bifunctional material of 8.4 g was reduced by a 100 mL/min H_2 for 2 h at 450 °C before testing.

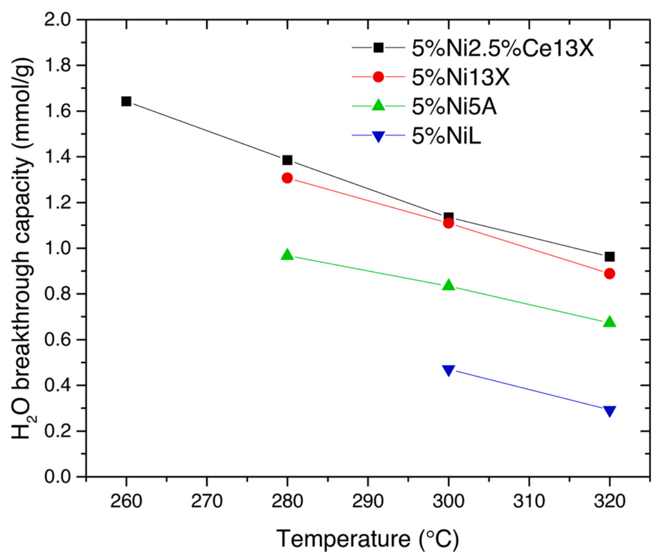

Fig. 5. H_2O breakthrough capacities of 5%Ni2.5%Ce13X, 5%Ni13X, 5%Ni5A and 5%NiL calculated from sorption enhanced CO_2 methanation experiments (GHSV = 923 mL/$g_{cat.}$/h).

activity and performance in the sorption enhanced CO_2 methanation at 1 bar total pressure and that both 5%Ni13X and 5%Ni5A are promising bifunctional materials.

3.2. Effect of CH_4 partial pressure

In a practical large-scale two step CO_2 methanation, a considerable amount of CH_4 will be fed to the sorption enhanced second step for maximizing the CH_4 content in the final product [18]. In an industrial methanation plant, the process will be divided into at least two different consecutive reactors, in which the first one(s) operate at higher temperature bringing the conversion to equilibrium, which would be at around 80 % [18]. In order to avoid the costly separation of H_2 from CO_2 and CH_4, a sorption enhanced reactor is required to bring the conversion close to 100 %. Thus, in the current study, methane corresponding to practical operational conditions was co-fed into the reactor to investigate and demonstrate operation.

The effect of the CH_4 partial pressure on sorption enhanced CO_2 methanation was investigated in a lab scale fixed bed reactor system. The bifunctional material was regenerated at 300 °C under 90 mL/min N_2 and 10 mL/min H_2 for 1 h before each sorption enhanced CO_2 methanation experiment.

Different CH_4 partial pressures were employed for sorption enhanced CO_2 methanation at 210–300 °C. The water breakthrough capacities of the bifunctional material are shown in Fig. 6. A 100 % CO_2 conversion was observed in the experiments with varying CH_4 partial pressures. The water breakthrough time was observed to occur around 21.4 min during experiments at 300 °C and extended to 47 min during experiments at 210 °C (Table S. 1). The water breakthrough capacities (Fig. 6) were calculated from sorption enhanced CO_2 methanation experiments. Inlet gas composition: y % N_2, 10 % H_2, 2.5 % CO_2, x % CH_4, 100 mL/min in total, x from 0 to 81.5, y from 87.5–6.0. An amount of 6.5 g catalyst was reduced at 500 °C under 100 mL/min H_2 for 2 h. It is shown that there is no significant difference for different CH_4 partial pressures (Fig. 6)

Table 1
Performance of representative bifunctional materials for sorption enhanced CO_2 methanation.

Bifunctional Catalyst	Metal loading (wt.%)	Feed gases H_2: CO_2: N_2: CH_4	GHSV	Bifunctional catalyst mass (g)	Pressure (bar)	Temp. (°C)	X_{CO_2} (%)	S_{CH_4} (%)	T_{reg} [a] (°C)	Ref.
Ni/5A	6	400: 50: 0: 0	1000 /h	13	1.2	170	100	100	N.A.	[13]
Ni/Al_2O_3 mix 4A	N.A.	9.9: 2.5: 6: 81.6	2500 mL/g_{cat}/h	3.6	1	250–350	100	100	350–450	[18]
Ni/5A	5	4.05: 1: 0: 0	92 /h	250	1	300	100	100	300	[21]
Ni/13X	5	4.05: 1: 0: 0	92 /h	250	1	300	100	100	300	[21]
5%Ni2.5%Ce13X	5	10: 2.5: 6: 81.5	923 mL/$g_{cat.}$/h	6.5	1	180–320	100	100	300	This work
5%Ni13X	5	9.9: 2.5: 6: 81.6	714 mL/g_{cat}/h	8.4	1	260–320	100	100	450	This work
5%Ni5A	5	9.9: 2.5: 6: 81.6	714 mL/g_{cat}/h	8.4	1	260–320	100	100	450	This work
5%NiL	5	9.9: 2.5: 6: 81.6	714 mL/g_{cat}/h	8.4	1	260–320	98	100	450	This work

[a] $T_{reg.}$-regeneration temperature of bifunctional material.

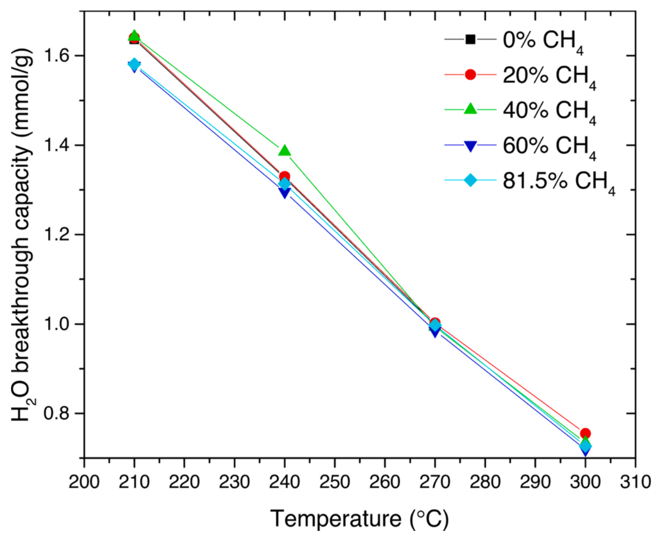

Fig. 6. H_2O breakthrough capacities of 5%Ni2.5%Ce13X under different CH_4 partial pressures (GHSV= 923 mL/g_{cat}/h).

especially at temperatures in the range of 270–300 °C. It can therefore be concluded that the CH_4 partial pressure has no significant effect on sorption enhanced CO_2 methanation with 5%Ni2.5%Ce13X bifunctional material (i.e. zeroth order in methane partial pressure), which may result from the low competitive adsorption of CH_4 (CH_4 capacity) on the bifunctional 5%Ni2.5%Ce13X.

3.3. Effect of regeneration temperature

The regeneration is performed to retain the water uptake capacity of the bifunctional material. The effect of the regeneration temperature on sorption enhanced CO_2 methanation was investigated in a lab scale fixed bed reactor system.

It was found, that the regeneration temperature has a significant effect on restoring the water uptake capacity i.e. desorbing water, which was also visible in the water breakthrough experiments (Fig. 7). When comparing the different regeneration temperatures it can be noticed that, in general, the water uptake capacities are larger at low temperatures, which should be reflected in a practical operation. The water breakthrough time can be found in the supplementary material (Table S. 2). Even though a higher water breakthrough capacity can be obtained through more efficient desorption of water at higher regeneration temperature, the associated heat loss and higher operation costs should be taken into account in practical sorption enhanced CO_2 methanation. A too high regeneration temperature could also lead to a collapse of the structure of the bifunctional material, which is not beneficial for a long-term operation.

3.4. Effect of gas hourly space velocity (GHSV)

Gas hourly space velocity (GHSV) determines the reactants residence time in the catalyst bed and influences the reactants conversion. The effect of GHSV on sorption enhanced CO_2 methanation was investigated using bifunctional material 5%Ni2.5%Ce13X in a lab scale fixed bed reactor system. The results are displayed in Fig. 8 and Table S. 3 (supplementary material). The bifunctional material was regenerated at 300 °C under 90 mL/min N_2 and 10 mL/min H_2 for 1 h before each sorption enhanced CO_2 methanation.

It can be seen in Fig. 8, that the H_2O breakthrough capacity at different GHSV values show a similar trend and magnitude, decreasing with an increase of the reaction temperature due to the lower temperature being advantageous for water adsorption on zeolite. The differences between the H_2O breakthrough capacities are different at different temperatures; the lower the reaction temperature the larger the H_2O breakthrough capacity. This is due to the rapid increase of water capacity of zeolite 13X with a decreasing temperature.

3.5. Performance stability

To investigate the catalyst stability and the regenerability of water breakthrough capacity of the bifunctional 5%Ni2.5%Ce13X, sorption enhanced CO_2 methanation was performed until the water breakthrough point and regeneration was performed during 100 cycles. The results are shown in Fig. 9 and a typical water breakthrough capacity and duration of an absorption cycle of bifunctional catalyst 5%Ni2.5%Ce13X is shown in Fig. 10.

Overall, the 5%Ni2.5%Ce13X shows very good stability for the long-

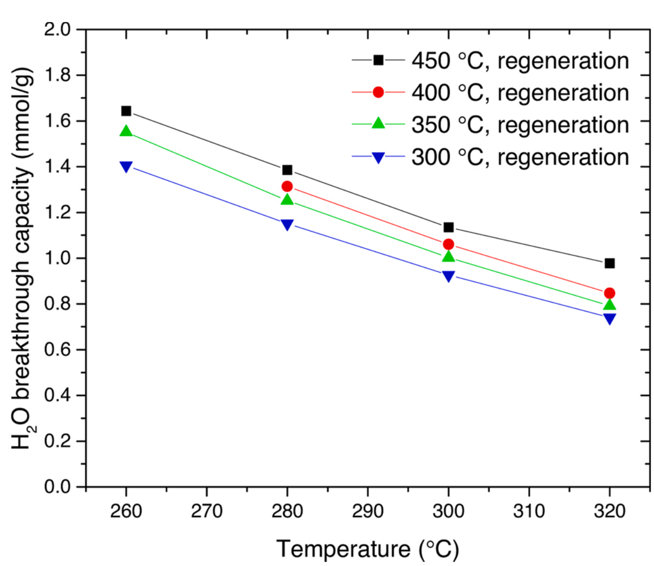

Fig. 7. Water breakthrough capacities of 5%Ni2.5%Ce13X at different regeneration temperatures (1 h regeneration), calculated from sorption enhanced CO_2 methanation experiments. Inlet gas composition (volumetric basis): 6 % N_2, 10 % H_2, 2.5 % CO_2, 81.5 % CH_4, total flow rate 100 mL/min (GHSV = 923 mL/g_{cat}/h). 6.5 g catalyst was reduced at 500 °C under 100 mL/min H_2 for 2 h.

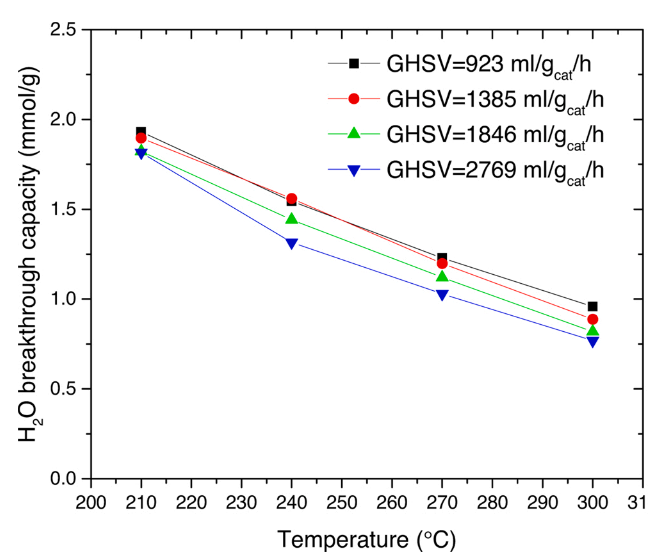

Fig. 8. H_2O adsorption capacities of 5%Ni2.5%Ce13X at different GHSV values (ml/g_{cat}/h), calculated from sorption enhanced CO_2 methanation experiments. Inlet gas composition (volumetric basis): 6 % N_2, 10 % H_2, 2.5 % CO_2, 81.5 % CH_4, total flow rate 100, 150, 200 and 300 mL/min. 6.5 g catalyst was reduced at 500 °C under 100 mL/min H_2 for 2 h.

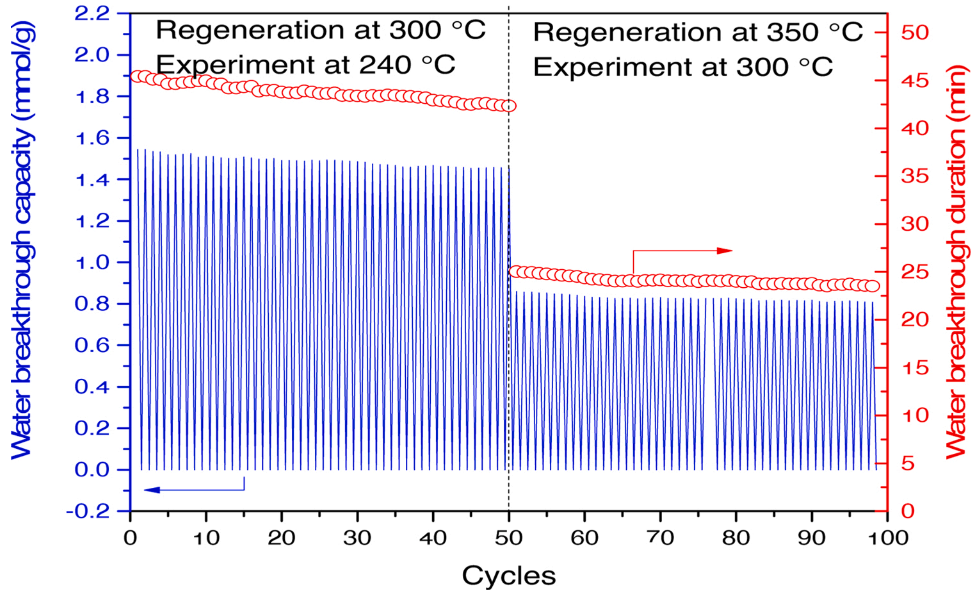

Fig. 9. Water breakthrough capacity and stability of bifunctional catalyst 5%Ni2.5%Ce13X. Cycles 1-50: regeneration at 300 °C, experiment at 240 °C; 51-100 cycles: regeneration at 300 °C, experiment at 240 °C. Regeneration under 90 mL/min N_2 and 10 mL/min H_2 for 1 h, each sorption enhanced experiment was run around 52 min with input gases 10 mL/min H_2, 2.5 mL/min CO_2, 81.5 mL/min CH_4 and 6 mL/min N_2; GHSV = 923 mL/g_{cat}/h. Total time was around 223 h for 100 cycles.

term sorption enhanced CO_2 methanation (Fig. 9). The CO_2 conversion and CH_4 selectivity were around 100 % during the 100 cycles test, and only a slight decreasing of the water uptake capacity was observed. Both the experiments performed at 240 and 300 °C show a similar behavior during the methanation. No significant change of the crystal structure (Fig. S. 6, supplementary material) and surface properties (Table S. 5, supplementary material) was observed during the experiment. No carbon deposition was either detected in the thermo-gravimetric analysis (TGA) results (Fig. S. 7, supplementary material), which were performed on the spent 5%Ni2.5%Ce13X in an air atmosphere. This was compared to the mass loss behavior to fresh 13X zeolite and reduced 5%Ni2.5% Ce13X. The low reaction temperature enabled by the active catalyst and removing H_2O by sorbent in the sorption enhanced CO_2 methanation most probably contributed to avoiding carbon deposition on the catalysts [23]. In addition, the TEM result shows that the spent 5%Ni2.5% Ce13X maintained very good metal dispersion (Fig. S. 8, supplementary material). However, an observation of some particles formation (TEM, Fig. S. 8) in the prolonged 100 cycle experiments caused possibly by limited sintering of Ni or the formation of some carbonaceous deposits on the surface of the particles could be a possible reason for the slight deactivation observed for the bifunctional materials. Another possible reason for the slight decrease of the micropore surface area and the water uptake capacity is the CO_2 and H_2O co-adsorption on the zeolite 13X [34,35].

It can be concluded that the bifunctional material had a high catalytic performance for CO_2 methanation; the extremely low water partial pressure which resulted from the sorption effect of the zeolite 13X did not lead to a rapid degradation of the bifunctional material in 100 cycles test (over 223 h on stream).

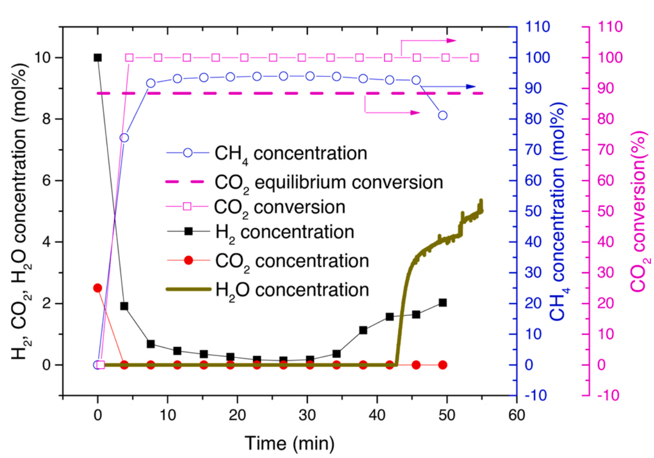

Fig. 10. Typical water breakthrough capacity and duration of bifunctional catalyst-sorbent 5%Ni2.5%Ce13X. Regeneration at 300 °C, experiment at 240 °C; Regeneration under 90 mL/min N_2 and 10 mL/min H_2 for 1 h, each sorption enhanced experiment was run with input gases 10 mL/min H_2, 2.5 mL/min CO_2, 81.5 mL/min CH_4 and 6 mL/min N_2 (GHSV = 923 mL/g_{cat}/h). No CO was detected by the GC. A CH_4 concentration of 94 % means full conversion of CO_2 (N_2 dilution).

4. Conclusions

In this work, four different bifunctional catalyst-sorbent materials (5%Ni2.5%Ce13X, 5%Ni13X, 5%Ni5A and 5%NiL) were tested in atmospheric CO_2 methanation with a stoichiometric feed ratio of $4H_2$: $1CO_2$. All the materials showed high water capacity and very high selectivity towards methanation. Their high catalytic activity and sorption enhancement significantly increased the low temperature yields, which was observed during non-sorption enhancement experiments with the same materials. The best performing material appeared to be 5%Ni2.5%Ce13X, which was further subjected to long term testing with 100 adsorption-desorption cycles where also the catalyst stability was examined. The conversion was shown to be independent of the methane partial pressure under the reaction conditions. The material shows 100 % CO_2 conversion and practically 100 % selectivity for CH_4 formation at temperatures as low as 180 °C.

CRediT authorship contribution statement

Liangyuan Wei: Conceptualization; Software; Investigation; Formal Analysis; Data Curation; Visualization; Writing - Original Draft. **Hamza Azad**: Investigation; Formal Analysis; Data Curation; Visualization; Writing. **Wim Haije**: Conceptualization; Investigation; Methodology; Supervision; Writing - Reviewing and Editing. **Henrik Grenman**:

Conceptualization; Methodology; Resources; Supervision; Project administration; Funding acquisition; Writing - Reviewing and Editing. **Wiebren de Jong**: Resources, Supervision, Writing - Reviewing and Editing

Declaration of Competing Interest

The authors report no declarations of interest.

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Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:https://doi.org/10.1016/j.apcatb.2021.120399.

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