Sorption-enhanced Fischer-Tropsch synthesis – Effect of water removal

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ABSTRACT

The Sorption-Enhanced Fischer-Tropsch synthesis (SEFTS), with water removal by means of a solid sorbent, has been demonstrated for the first time experimentally. Commercial water sorbents (Zeolites type 13X and 4 A) were thoroughly characterized to determine water sorption capacity at relevant temperatures (100–250°C) as well as multicycle stability after 100 cycles at 210°C. The adsorption capacity of both zeolties decreased with increasing temperature. The adsorption capacity of 4 A remained almost constant after 100 adsorption/desorption cycles, while 13X lost almost 50% of its capacity. Post characterization of the 13X sample showed distorted crystallinity after 100 cycles which explains the drop in stability. The SEFTS experiments were performed as a cyclic operation, first FT reaction and then water sorbent regeneration, at 210 °C and 5 bar. The system with zeolites showed 10% higher CO conversion after 65 hours on stream compared to the system without any sorbents. The selectivities to C_{5+} was higher for the system with sorbents compared to the system without zeolites. A much steeper deactivation curve was also observed for the system without zeolites at steady state conditions. This might be due to the fact that zeolites adsorbs the water and remove it from the catalyst active centers, thus increase catalyst stability by preventing the catalyst re-oxidation. Overall, this work opens an opportunity for enhancing the catalyst activity in FTS by in situ water sorption.

1. Introduction

Access to sustainable, clean energy is the major challenge of our time. Reducing greenhouse gas emissions from the transport/aviation sector has been prioritized in the EU's climate policy. Technological developments are vital to fulfil the required volumes up to 2050. Rapid implementation of new SAF technologies (e.g., Fischer-Tropsch, Alcohol to Jet, Power-to-Liquid), and related renewable electricity scale-up are all needed to meet demand. Fischer-Tropsch synthesis (FTS) converts synthesis gas, a mixture of H_2 and CO, into a range of hydrocarbons which can be consequently refined into transport fuels [1]. FTS is agnostic to the origin of the syngas produced (natural gas, coal, biomass). The most active catalysts reported in FTS are cobalt, iron, and ruthenium. Ruthenium shows excellent catalytic performance but is too costly and rare for industrial use. Co catalyst is favoured in the industry due to high activity as well as selectivity towards heavier hydrocarbons (C_{5+}) and better stability, relative to Fe. The major difference is in the water gas shift (WGS) activity where cobalt catalysts are reported to have an insignificant activity compared to Fe. However, it is reported that Co catalysts can develop WGS activity at very high CO conversion

levels depending on the H_2O/H_2 ratio [2]. While the Coal to liquid (CTL) and Gas to liquid (GTL) processes are well-known commercial technologies, the Biomass to liquid (BTL) process is still at validation stage mainly due to the challenges regarding the scale and process complexity. The calculated overall chemical energy efficiencies to FT liquid fuels (C_5–C_{20}) from biomass are 25.8–46.5% [3]. It was reported that the maximum overall process efficiency to produce FT fuels via biomass gasification is 51% [4].

To reduce the investment and the operational costs of the potential BTL-FT plant and to efficiently use the syngas in a once-through concept, it is beneficial to operate at high CO conversion levels. However, at excessive conversion, 50% of water is present in the FT reactor, diluting the gas phase [5]. Partial pressures of reactants are substantially reduced which leads to reduce H_2 and CO concentrations i.e., reduced reaction rates. Water has a positive and negative effect on FTS [6]. A positive effect of water on hydrocarbon selectivity was always reported in the literature [7,8]. It has also been suggested that water can increase CO conversion on Co catalysts by increasing the amount of active surface carbon [9]. However, a much stronger negative effect was related to the catalyst deactivation [10–13]. Water is an oxidizing agent, and although

bulk oxidation of metallic cobalt is thermodynamically infeasible under realistic FTS conditions, it has been calculated that very small surface cobalt particles behave differently [14]. Indeed, it has been reported that high water partial pressure negatively influences the Co-based FT catalyst. Bartholomew et al. [15] reported that critical value of water partial pressure ($P_{H2O} > 0.6$ MPa) accelerates catalyst deactivation. This value can be easily exceeded at higher conversion levels ($X_{CO} > 60\%$) and at high operating pressures. High water partial pressure leads to 1) hindering of the reduction of cobalt oxide 2) inducing sintering of the active metal catalyst 3) the formation of inactive cobalt aluminate, and 4) re-oxidation of metallic cobalt to FT inactive cobalt oxides. This results in fewer active Co sites on the catalyst, thus significantly decreasing the catalyst activity [11,16,17]. Parameter which has direct effect on the wax selectivity for a Co-based catalyst, besides H_2/CO ratio and temperature, is the total pressure. The correlation is such that higher pressure will result in higher wax selectivity. However, this also correlates to a higher partial pressure of water which leads, once again, to a higher deactivation rate. Usually, the goal is to operate at high alpha values ($\alpha > 0.9$) which means that conversion needs to be low to avoid water induced catalyst deactivation. However, a low conversion results in high operating and capital investment [18]. It is of interest to maintain a high production of wax and high CO conversion during FTS. Therefore, the process intensification of FTS is necessary.

In-situ removal of the by-product water can lead to substantial conversion improvement of equilibrium-limited reactions, while also protecting catalysts from steam-induced deactivation. FTS has kinetic limitations to further increase its performance. It was reported that lowering the steam partial pressure of 10 bar during FTS would already result in significant conversion enhancement and increase the mol fraction of the product 10 times [19]. This allows a reducing the total volume of catalysts, with a potential lower CAPEX and OPEX of renewable jet fuel production. Typical physisorption adsorbents that can be used for water removal are molecular sieves such as zeolite type materials LTA, LTX, which have well-defined pore sizes and geometries. In addition, they have low Si/Al ratios (<5), thus, making them very hydrophilic [20]. Boddenberg et al. [21] suggested that up to 6 water molecules interact with Na^+ cations when zeolite 13X is saturated with water. To regain the adsorptive capacity of the system the solid adsorbent must be regenerated in a periodic fashion [22]. Typically, a fixed-bed reactor configuration is combined with regeneration cycles. Numerous reactor and regeneration concepts can be found for various adsorption technologies such as: pressure swing, temperature swing, concentration swing, reactive regeneration, displacement regeneration or a combination of these [23]. A robust water adsorbent is essential for the sorption enhanced processes. The requirements for a desired adsorbent are: 1) high water adsorption capacity, 2) high water adsorption selectivity, 3) low water slip, 4) easy regeneration by temperature increase, 5) low activity for side reactions, 6) high hydrothermal stability. The adsorbent must have all these characteristics at the reaction and regeneration conditions (200–300 °C) [24].

First attempts for investigating sorption-enhanced Fischer-Tropsch synthesis (SEFTS) were made by Espinoza et al. [25] who reported a technical feasibility of water vapor removal using ceramic membranes. Rohde et al. [26] reported experimental demonstration of in situ H_2O removal under reactive FT conditions with different membranes, but confirmed the high requirements on membrane selectivity, permeance, and stability. The aim of the present paper is to prove the concept of water removal by means of solid sorbents, and its effect in the FTS. By authors knowledge this approach has never been considered in the experimental context before.

2. Experimental

2.1. Materials

Since the goal of the present paper is proof of concept of the Sorption

Enhanced FTS using solid sorbents, the focus has not been on the synthesis of the catalyst and sorbents. A 20%Co/0.5%Re/γ-alumina catalyst has been selected for this study. This catalyst has been used as a reference catalyst for many years in our lab. A detailed synthesis method and characterization results has been published earlier [1,27]. Commercial zeolites type 13X and 4 A were used as solid sorbents. Zeolites were provided by Zeochem in the shape of beads (1.6 – 2 mm). The sorbents were crushed and sieved ($> 250\mu m$) and used as powders in the and FTS experiments.

2.2. Thermogravimetric analysis

Water adsorption on commercial zeolites 13X and 4 A was investigated using an *in-house* built thermogravimetric analyzer (TGA, ICA electronics). Before TGA experiments, zeolite beads were dried at 140° C for 12 h in a drying oven. About 30–40 mg dried zeolite was placed into an alumina crucible (8 mm ID, 10 mm height) and put in the TGA microbalance under 100 vol% N_2 at the targeted experimental temperature. The TGA crucible is surrounded by a furnace. A thermocouple is inserted from the bottom of the furnace and placed just below the crucible. Temperature and gas flow rates were controlled by Lab-view software. When the weight signal was stabilized, water adsorption was performed at different temperatures (100° C - 250° C) in 40 vol% H_2O/60 vol%N_2 for 20 min. Before each adsorption temperature, fresh zeolite beads were loaded. The change of the sample mass during water adsorption was measured by the TGA microbalance at different temperatures. In addition, the water adsorption on alumina support was investigated at FTS operational temperature of 210 °C. The same TGA set-up was also used to study the competitive adsorption of H_2, CO_2 and water for both zeolites (13X and 4 A). In addition, the stability of the zeolites after 100 water adsorption/desorption cycles was studied at the FT temperature (210 °C). A small amount ($\sim$ 30–35 mg) of zeolite materials was placed in an alumina crucible at 210°C in N_2 flow (F_{total}=500 ml/min). When the base line was found stable, an adsorption experiment was performed in an atmosphere containing 40 vol% H_2O/60 vol% N_2 for 20 min. Subsequently, the gas composition was switched to 100% N_2 at the same temperature and desorption was performed for 30 min. Adsorption/desorption was repeated for 100 cycles. The cyclic water adsorption capacity (g-H_2O/100 g) was calculated from the weight changes during adsorption/desorption as a function of time.

2.3. Sorption enhanced Fischer-Tropsch synthesis (FTS)

The sorption-enhanced FTS has been investigated as dynamically operated FT reactor where the water produced, as a by-product, is systematically removed by solid water adsorbents (Step 1). The H_2O-sorption active site is then regenerated in a separate step (Step 2), allowing for cyclic operation (Fig. 1).
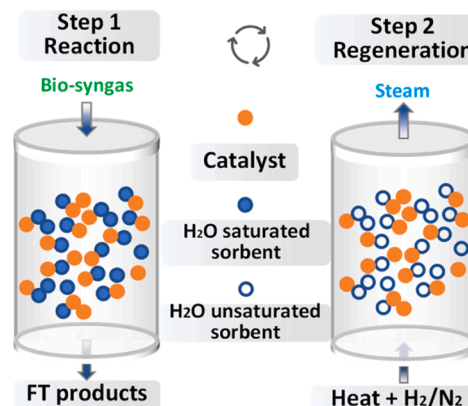

Fig. 1. Dynamically operated fixed bed reactor for the SEFTS.

Fischer-Tropsch kinetic tests were performed in a stainless-steel fixed bed (i. d. 10 mm) reactor using a mixture of catalyst (2.5 g) and sorbent (13.5 g) at 210 °C and 5 bar. First, a reference experiment was defined where only catalyst and inert (silicon carbide, SiC) were present in the reactor. Two more experiments were done with the 13X and 4 A zeolites as dilutants for the catalyst. The goal was to compare the reaction system with and without water sorbents and to observe the effects on conversion and selectivity. The catalyst was sieved to the fraction of 54–90 μm. The inert and adsorption materials were sieved to >250 μm. The mass of SiC and zeolites used were 13,5 g so the weight of the total catalyst bed was kept the same. Before the reaction, the catalyst was reduced at 350 °C for 10 h (125/125 ml/min H_2/He, 1 °C/min). The temperature was reduced to 180 °C and the reactor was pressurized up to 5 bar in He flow. The temperature was increased to 210 °C and syngas was introduced using a flow of 150–170 ml/min syngas (H_2/CO= 2.1). The different flows were used to reach the similar initial conversion level for the system with and without sorbents, but the flow was kept constant throughout the experiment for each system. Regeneration of the sorbents was carried out by ramping the temperature to 300 °C (3 °C/min) for two hours in H_2/He with the same space velocity as the reaction after stabilization of the CO conversion. Three different reaction/regeneration cycles were carried out. After the regeneration, the reactor was cooled down to the reaction temperature in He flow to remove the adsorbed hydrogen and clean the catalyst surface. Liquid Fischer-Tropsch products (wax and water, light hydrocarbons and trace oxygenates) were collected in a hot trap at ~360 K and a cold trap at ambient temperature. The gas phase was analysed on a gas chromatograph (Agilent 6890) equipped with a flame ionization detector (FID) and thermal conductivity detector (TCD). The N_2 was served as an internal standard for quantification of the products for the mass balance. After ~16 h time on stream (TOS) at steady state conditions the activity data is reported based on measurements at constant feed rate (150–170 Nml/min). Selectivity data (C_{5+} and CH_4) are also reported at different conversion levels based on the analysis of C_1–C_4 hydrocarbons in gas phase.

3. Results and discussion

3.1. Effect of temperature on zeolites adsorption capacity

Before testing in any sorption enhanced reaction, it is vital to evaluate the adsorption capacity of the selected water sorbents and its affinity towards the desired compound. The variation in the water adsorption capacity of zeolite, 13X as a function of temperature is shown in Fig. 2a. Given the exothermic nature of any adsorption process, the

adsorption capacity of the zeolite decreased with increasing temperature [28]. Therefore, the highest water adsorption capacity of 17 g_{H2O}/100 $g_{zeolite}$ for zeolite 13X was observed at the lowest temperature of 100 °C. Accordingly, the lowest water adsorption capacity of 7 g_{H2O}/100 $g_{zeolite}$ was observed at the highest temperature of 250 °C. Besides the adsorption capacity at higher temperatures, the kinetics of adsorption and the adsorbate mass transport are vital for the application of the adsorbent in a sorption enhanced reaction process [29]. The adsorption kinetics is faster at higher temperature (curve shifted to the left in Fig. 2b). This means that the zeolite can capture water much faster, thus being also saturated much quicker at higher temperatures. The periodic regeneration is therefore necessary to see the effect of enhancement.

3.2. Effect of co-feeding CO_2 and H_2 on water adsorption on zeolites

All the molecules formed during FTS can potentially be adsorbed by zeolites and this in turn can influence the catalytic performance. Therefore, a competitive adsorption of both CO_2 and H_2 together with H_2O has been investigated. CO_2 adsorption was found to be very low (0.2 gCO_2/100 g) at the relevant FT temperature (210 °C). Adsorption capacity of 13X where H_2O was cofeeding with the different vol% of CO_2 is presented in Fig. 3a. The water sorption capacity of 13X remained almost the same with all vol% of CO_2 fed. This is because water has a much stronger affinity to 13X which dramatically reduces the available adsorption sites for CO_2. CO_2 is a weaker adsorbate, and therefore the adsorbed CO_2 can be pushed out and displaced by stronger adsorbate i. e., H_2O [30]. A slight change in adsorption kinetics is observed (curved shifted to the right, Fig. 3a), meaning that the adsorption process is slower when both molecules are present in the feed. On the other hand the adsorption capacity decreased from 11 g_{H2O+H2}/100 $g_{zeolite}$ to 9 g_{H2O+H2}/100 $g_{zeolite}$ when H_2 was co-fed with the water. H_2 molecules interact with the Na^+ cation of 13X and forms dihydrogen bond (H_2-Na^+). Water tends to form a hydrogen bond network and dislodge Na^+ cations from the zeolite structure and stabilize it in the center of the pore [31]. Since hydrogen bond is much stronger than dihydrogen bond [32] the effect on water capacity is not significant during concurrent feeding of H_2 and H_2O. The slight change in adsorption kinetics is also observed here (curved shifted to the right, Fig. 3b), meaning that the adsorption occurs slower when both H_2O and H_2 are present in the feed.

3.3. Stability of the zeolites

In order to assess the stability of the zeolites at relevant Fischer-Tropsch temperatures, the water sorption capacity has been
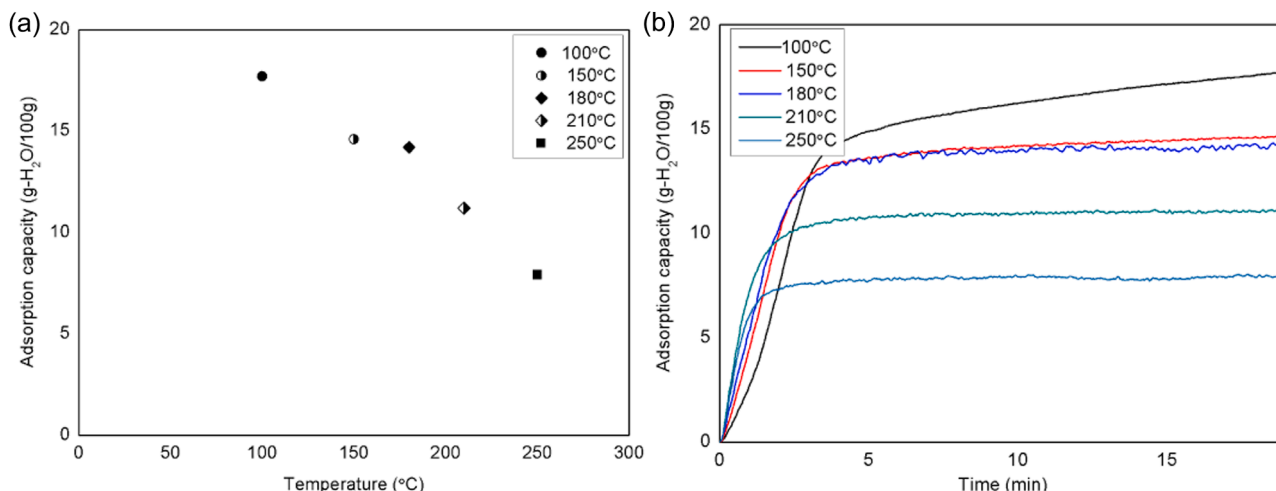

Fig. 2. . Adsorption capacity of 13X zeolite at different temperature in presence of 40/60 vol%H2O/N2 (a); corresponding adsorption kinetics (b).
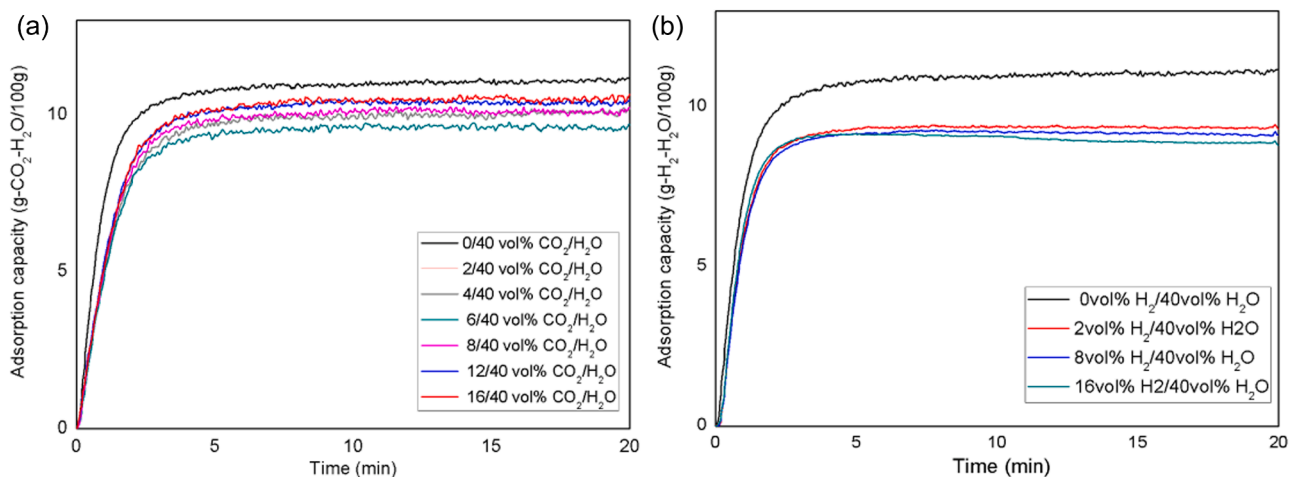
Fig. 3. . Adsorption capacity of 13X during concurrent feeding of H_2O and CO_2 (a); H_2O and H_2 (b).

investigated over 100 adsorption/desorption cycles in TGA. This is very important parameter since SEFTS will be operated in cyclic mode. The 4 A showed very good stability where adsorption capacity remained stable at 9 g_{H2O}/100 $g_{zeolite}$ after 100 cycles. However, 13X zeolite lost almost half of its capacity after 100 cycles, Fig. 4a. The adsorption kinetics of both zeolites remained the same, Fig. 4b. This means that both zeolites are able to capture the water at the same rate after 100 consecutive adsorption/desorption cycles.

The loss of the adsorpton capacity for the 13X zeolite might be due to the degradation of the 13X zeolite structure and crystalllinity. This is confirmed by XRD where spent 13X zeolite showed lower peak intensity compared to the fresh 13X sample, Fig. 5a. The spent 4 A zeolites showed almost the same peak intensities as the fresh 4 A zeolite sample, Fig. 5b.

3.4. Sorption enhanced Fischer-Tropsch experiments

The main goal of the FT tests was to compare the system with and without zeolites. It is important to mention that it was not possible to observe the water concentration or breakthough since the GC is not able to analyze water. Thus, the water was condensed before feeding the gas to the GC. Since water cannot be measured, we have tried to observe the effect of water removal as a change in activity, selectivity and stability. The changes in the CO conversion with the time on stream with reaction and regeneration periods for all 3 systems is presented in Fig. 6. There

are a few phenomena that were observed during these tests. First, for all 3 systems the CO conversion reached the same level as the initial after each regeneration period. This might be explained due to the presence of H_2 in the regeneration conditions, which might re-reduce smaller cobalt crystallites and partially remove some wax and deposits [33,34]. However, for the systems with the zeolites, the CO conversion has even increased to the higher levels for the same gas flow (green and blue lines increasing each time after regeneration period) compared to the system without the zeolites. The system with the 13X zeolite showed the highest CO conversion at the end of the period t5 and t7. At the end of the 65 h the CO conversion for the system with 13X and 4 A has increased from 50% to 60% and 47–57%, respectively. On the contrary, conversion for the system without zeolites remained the same. It is worth to mention here that adsorption capacity for the plain Al_2O_3 support is just 1 g_{H2O}/100 g_{Al2O3} at 210 °C which indicates that there is no water removal for the system without zeolites. The increase in CO conversion with the system with zeolites might be due to the removal of water from the system, and thus favoring CO conversion. The influence of steam inhibition on the reaction rate, and therefore on the conversion is particularly significant for a reaction with large value for equilibrium constant such as FTS. Therefore, removing the water from the system could significantly increase the reaction rate [19]. This has been claimed in a patent [18], however, no experimental verification is reported. Huang *et al.* [35] reported enhanced activity with the addition of 13X zeolite to the Pd catalyst during methane combustion. Another
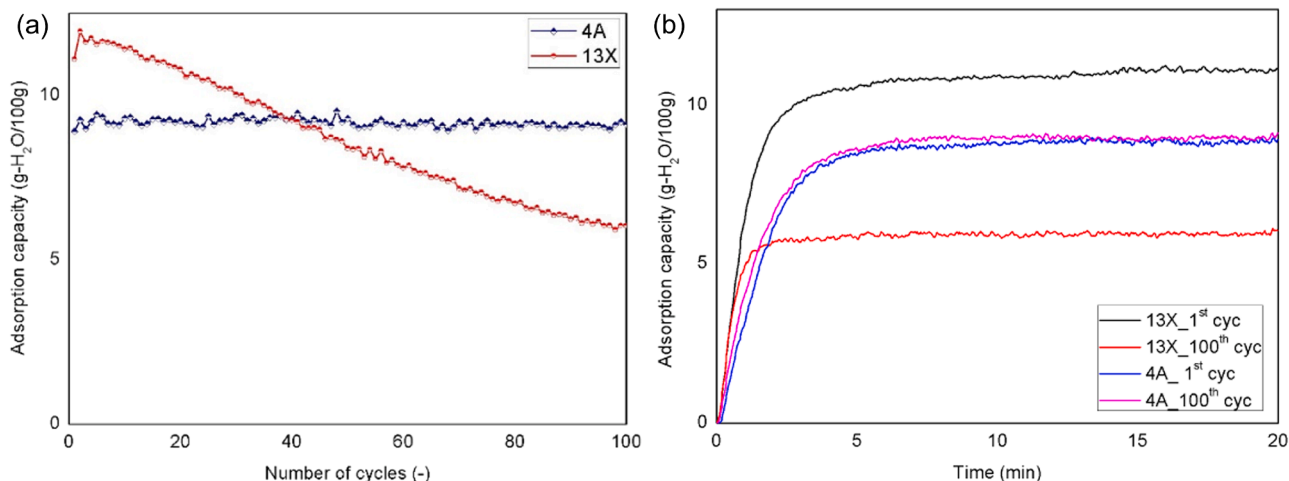

Fig. 4. Water sorption capacity of 13x and 4 A zeolite after 100 cycles (a) adsorption kinetics after 100 cycles (b).
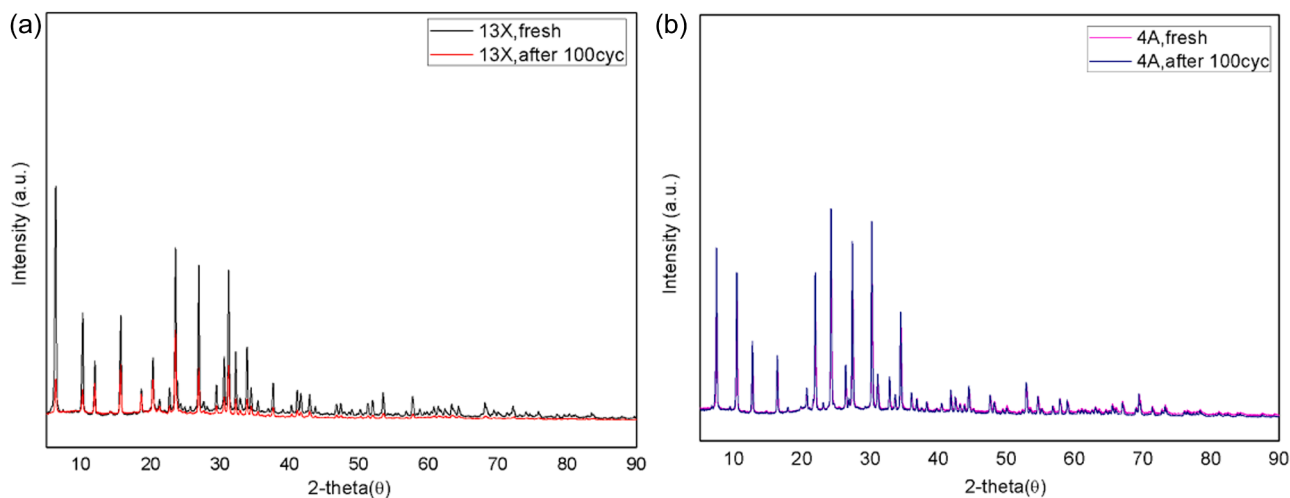
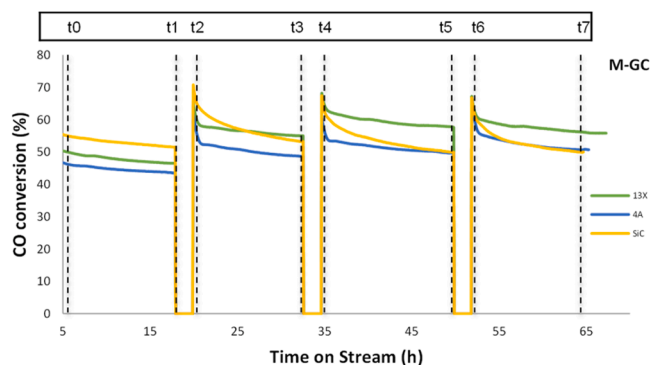**Fig. 5.** XRD of the fresh and spent zeolites (a) 13X zeolite and (b) 4 A zeolite.

Fig. 6. Changes in the CO conversion with the time on stream.

Table 2
Selectivitiy to C_{5+} at different periods for systems with and without sorbents.

C_{5+} (%)	t_0	t_1	t_2	t_3	t_4	t_5	t_6	t_7
SiC	87.9	85.4	87.8	85.3	86.3	84.4	84.4	84.4
4 A	87.6	85.1	85.7	85.9	86.6	86.7	87.8	86.8
13X	84.9	85.6	84.7	86.9	86.9	87.4	87.1	87.5

are worth comparing. It can be seen that the system with zeolites showed higher C_{5+} and lower CH_4 compared to the system without zeolites. Bayat *et al.* [39–42] used mathematical modelling to study SEFTS, and reported increased gasoline yield and decrease in CO_2 yield for a Fe-based catalyst when water was removed by means of membranes.

4. Conclusion

The effect of water removal by means of solid sorbents has been investigated in the Fischer-Tropsch synthesis. The sorption properties and stability of the crystalline structure of the zeolites 13X and 4 A has been characterized at conditions relevant for the FT synthesis operation. The adsorption capcaity of both zeolites decreased with increasing temeprature. The 4 A zeolite showed much better stability compared to 13X. The adsorption capacity remained almost constant after 100 adsorption/desorption cycles, while 4 A lost almost 50% of its capacity. This is due to the structure degradation which is confirmed by XRD. Higher CO conversion and higher selectivity to C_{5+} is observed for the system with zeolites during FTS. A significantly steeper deactivation curve was observed for the system without zeolites. This might be due to the fact that the zeolites absorbs the water and thus remove it from the catalyst surface and active centers, leading to increased catalyst activity and stability. Regarding the investment costs, the application of SEFTS would require a larger reactor volume compared to the conventional fixed bed FTS process. In addition, due to the regeneration step, the FT-reactor would operate in a cyclic mode, with relatively short times on stream before regeneration, thus the production of hydrocarbons per unit total operating time would be reduced. However, with proper selection of water sorbents with high capacity and thermal stability as well as finding the optimal conditions (time, temperature, pressure, conversion level) for reaction/regeneration process, the overall economy of the process could potentially be improved. In addition, the catalyst stability would be prolonged thus the need to change the deactivated catalyst would be also postponed. Operationally, the downtime could be avoided with two reactors in parallel, one for reaction and another for regeneration. Operating the FTS/sorption stage and the desorption stage at the same temperature would avoid heating/cooling in between stages. The

possibility might be related to the higher degree of reduction achieved during the regeneration due to the presence of the zeolites. Paterson *et al.* [36] reported that water, produced during reduction, has a negative impact upon the reduction of the catalyst down a reactor bed and accelerate sintering of the cobalt particles. Second phenomena is stability of the system with the zeolites at the steady state conditions. The system without the zeolites has much steeper decline in CO conversion after each regeneration period. The deactivation curve during each reaction period is much less pronounnced for the systems with zeolites. It is important to notice that water inside the catalyst pores, which is in equilibrium with water in the void space between the catalyst particles, contacts and effects the catalyst surface directly [37]. It has recently been shown that water is present as separate liquid phase in the pores of a suppotred FTS catalyst [38]. It can be speculated that, in the presence of zeolites, the water is removed from the catalyst pores and active centers, thus, reducing the role of the water-rich phase and preventing catalyst deactivation.

The selectivities to C_{5+} and CH_4 are presented in the Tables 1 and 2. It is valuble to compare the selectivities at the same conversion levels. At the end of t5 and t7 the conversion levels of system with 4 A zeolite and the system without zeolites are almost the same and those selectivities

Table 1
Selectivitiy to CH_4 at different periods for systems with and without sorbents.

CH_4 (%)	t_0	t_1	t_2	t_3	t_4	t_5	t_6	t_7
SiC	6.9	8.1	7.1	8.3	7.8	8.7	8.1	8.5
4 A	7.1	8.3	8.0	7.9	8.0	7.8	7.6	7.8
13X	8.0	7.9	7.8	7.5	7.5	7.4	7.7	7.6

findings of the present work are crucial for applying this type of intensified process, which pushes the limits dictated by thermodynamics and kinetics limitations. In addition, it provides information to direct future research on all sorption enhanced processes.

CRediT authorship contribution statement

Saima Sultana Kazi: Conceptualization, Formal analysis, Writing – review & editing, Data curation. **Ljubisa Gavrilovic:** Conceptualization, Funding acquisition, Investigation, Methodology, Project administration, Supervision, Writing – original draft. **Oscar Luis Ivanez Encinas:** Conceptualization, Data curation, Formal analysis, Investigation, Methodology, Writing – review & editing. **Antonio Geraldo de Paula Oliveira:** Conceptualization, Funding acquisition, Methodology, Writing – review & editing. **Edd Anders Blekkan:** Conceptualization, Funding acquisition, Supervision, Writing – review & editing.

Declaration of Competing Interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: Ljubisa Gavrilovic reports financial support was provided by Research Council of Norway.

Data availability

No data was used for the research described in the article.

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