

2 Chapitre 2 : Méthodologie

2.1 Appareil pour l'étude d'adsorption

L'étude de l'adsorption consiste à mettre l'adsorbant en contact avec un flux saturé d'eau pour évaluer sa variation de masse au cours du temps et déterminer sa capacité d'adsorption à l'équilibre. Ces expériences ont été réalisées en utilisant l'analyseur gravimétrique intelligent (IGA, Intelligent Gravimetric Analyser, Hiden Isochema, Royaume-Uni) muni d'une microbalance très sensible avec une résolution de 0,1 μg et une stabilité à long terme de $\pm 1 \mu\text{g}$. Il permet l'acquisition de données de tous les états transitoires et à l'équilibre pendant les expériences d'adsorption afin de déterminer, respectivement, la cinétique et la capacité d'adsorption (points isotherme) d'un échantillon donné. Le dispositif comprend un système de contrôle de débit utilisé pour régler la pression et la composition du débit d'entrée qui peut être composé à la fois de vapeurs et de gaz. Des échantillons sont chargés sur la microbalance dont la température est contrôlée soit avec une enveloppe d'eau (0-80 °C) soit avec un four (80-1000 °C) avec une précision de 0,2 °C. Les connexions entre le générateur de vapeur et la microbalance contenant l'échantillon sont chauffées à 50 °C pour éviter la condensation.

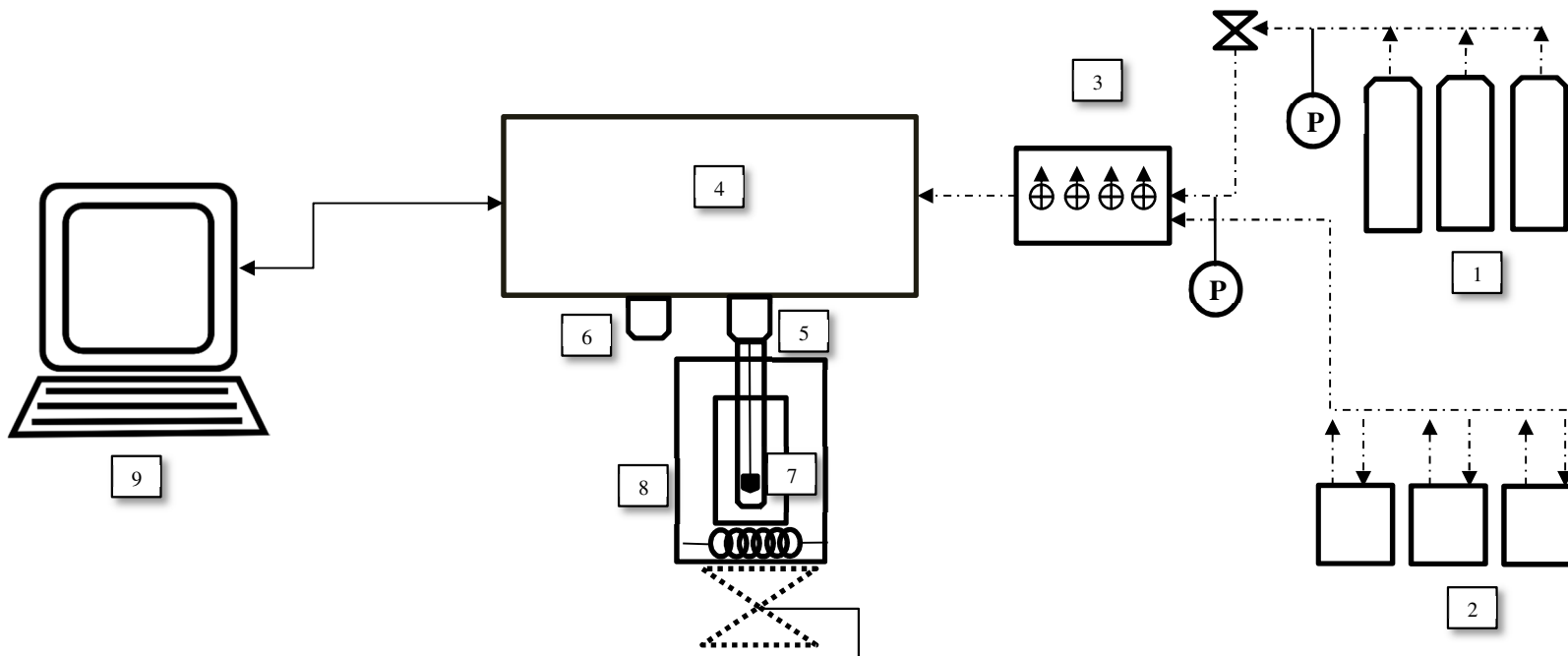


Figure 2.1. Schéma de l'appareil (IGA). 1- Cylindres de gaz 2- Générateurs de vapeurs 3- Contrôleur de flux 4- Microbalance
5- Réacteur 6- Contrepoids 7- Échantillon 8- Contrôleur de température 9- Ordinateur

2.2 Adsorbants

Différentes zéolithes hydrophiles ont été testées en tant qu'adsorbants potentiels pour l'eau à hautes températures. Les zéolithes LTA- (3A, 4A et 5A) et FAU-13X en perles ont été fournies par Zeochem (Louisville, USA). La poudre de zéolithe LTA-4A et FAU-13X a été fournie par Advanced Specialty Gas Equipment (ASGE, Middlesex, USA).

L'hydroxysodalite (SOD) a été synthétisée directement à partir d'aluminate de sodium (NaAlO_2 , Anachemia, Montréal, Canada, CAS n°1302-42-7, qualité technique), de métasilicate de sodium nonahydraté ($\text{Na}_2\text{SiO}_3 \cdot 9\text{H}_2\text{O}$, Acros organics, NJ, USA, CAS N°13517-24-3, 44-47,5% en poids de solides totaux) et d'hydroxyde de sodium (NaOH , VWR, Westchester, USA, CAS n° 1310-37-2, qualité ACS). Ces réactifs ont été mélangés avec de l'eau distillée pour former une solution de précurseur ayant une composition molaire de $50\text{Na}_2\text{O} : \text{Al}_2\text{O}_3 : 5\text{SiO}_2 : 1005\text{H}_2\text{O}$ selon le mode opératoire proposé par Lafleur et al.^[64] La poudre de SOD a été obtenue après la synthèse hydrothermale effectuée dans des autoclaves en acier inoxydable avec inserts en Teflon à 140 °C (four Isotemp, Fisher Scientific) pendant 3h30. La poudre a été lavée avec de l'eau distillée jusqu'à pH neutre, puis séchée pendant une nuit à 90 °C.

Les caractéristiques de toutes les zéolithes utilisées sont présentées dans le Tableau 2.1.

Tableau 2.1. Caractéristiques des zéolithes

| Type de zéolithe | Forme | Taille des pores (Å) | Si/Al ratio | Taille des particules | |
|------------------|--------|----------------------|-------------|-----------------------|-------------|
| | | | | Perles (mm) | Poudre (µm) |
| 3A | K-LTA | 3,2 | 1 | 1,5-2,5 | - |
| 4A | Na-LTA | 3,8 | 1 | 1,5-2,5 | 53-250 |
| 5A | Ca-LTA | 4,8 | 1 | 1,5-2,5 | - |
| 13X | Na-FAU | 7,4 | 1-1,5 | 1,5-2,5 | 53-250 |
| SOD | Na-SOD | 2,7 | 1 | - | 53-250 |

2.3 Déroulement des expériences

Toutes les expériences d'adsorption ont été réalisées selon la même procédure. Chaque échantillon d'environ 30 mg a été chargé sur la microbalance et régénéré à 300 °C sous un débit d'azote de 100 ml/min (Praxair Canada, 99,998%) jusqu'à ce qu'aucune variation de masse ne soit enregistrée. La température de l'échantillon a ensuite été réduite à celle choisie, entre 25 et 250 °C, et lorsque la stabilité de la température a été obtenue, le flux d'azote a été envoyé au générateur de vapeur pour le saturer avant d'atteindre l'échantillon. La pression partielle d'eau souhaitée a été réglée en changeant la température du générateur de vapeur préchauffé dans la plage de 5-45 °C. La pression totale a toujours été fixée à 100 kPa et la variation de la masse a été enregistrée jusqu'à ce qu'un plateau soit atteint. Les données ont finalement été utilisées pour déterminer la cinétique du processus d'adsorption et obtenir les isothermes.

2.3.1 Étude de la capacité d'adsorption en fonction de la température et en fonction de la granulométrie

Le but de ces expériences est d'étudier la variation de la capacité d'adsorption des zéolithes LTA-(3A, 4A, 5A), FAU-13X et SOD sur une plage de température de 25 à 250 °C, pour analyser l'effet de la température, sous un flux de N₂ saturé en eau à 20 °C et une pression totale de 100 kPa. Dans une première série d'expériences, les zéolithes LTA-(3A, 4A, 5A) et FAU-13X ont été testées sous forme de perles pour démontrer l'effet de l'augmentation de la température. Par la suite, les zéolithes LTA-4A, FAU-13X et SOD ont aussi été étudiées sous forme de poudre pour analyser l'influence de la granulométrie sur la capacité d'adsorption. La pression partielle de l'eau a été maintenue à 2,33 kPa.

2.3.2 Étude de la capacité d'adsorption en fonction de la pression partielle de l'eau : isothermes d'adsorption

Pour l'étude de l'effet de la pression partielle, des expériences ont également été réalisées à des températures constantes et à différentes pressions partielles d'eau pour les zéolithes 13X et 4A. Dans le but de démontrer l'efficacité des zéolithes à hautes températures, quatre isothermes ont été étudiées à hautes températures à savoir 100, 150, 200 et 250 °C. La

variation de la pression partielle de l'eau de 1,09 à 9,1 kPa se fait en changeant la température de génération de la vapeur.

2.3.3 Étude de la cinétique d'adsorption

Les données d'adsorption transitoire ont été utilisées pour caractériser la cinétique d'adsorption de la FAU-13X et de la LTA- (3A, 4A et 5A).

Le modèle choisi est le modèle double exponentielle étirée DSE (double stretched exponential) défini comme suit (Équation (8))^[65] :

$$M_t / M_e = A_1 * (1 - e^{-(k_1 t)^{\beta_1}}) + (1 - A_1) * (1 - e^{-(k_2 t)^{\beta_2}}) \quad (8)$$

Avec :

- A_1 et $(1-A_1)$: les contributions fractionnelles des mécanismes d'adsorption correspondant aux constantes de vitesse d'adsorption k_1 et k_2 ;
- k_1 et k_2 : les constantes de vitesse (min^{-1}) ;
- M_t : gain en masse au temps t (g) ;
- M_e : gain en masse à l'équilibre (g) ;
- t : temps d'adsorption (min).

Le modèle DSE peut être simplifié pour donner 3 autres modèles selon les cas suivants :

- Si $\beta_1 = \beta_2 = 1$: on obtient le modèle double exponentielle (DE, Équation 9)

$$M_t / M_e = A_1 * (1 - e^{-k_1 t}) + (1 - A_1) * (1 - e^{-k_2 t}) \quad (9)$$

- Si $k_1 = k_2 = k$ et $\beta_1 = \beta_2 = \beta$: on obtient le modèle exponentielle étirée (SE, Equation 10)

$$M_t / M_e = 1 - e^{-(kt)^\beta} \quad (10)$$

- Si $k_1 = k_2 = k$ et $\beta_1 = \beta_2 = 1$: on obtient le modèle linear driving force (LDF, Equation 11)

$$M_t / M_e = 1 - e^{-kt} \quad (11)$$

Nos données expérimentales ont été corrélées avec ces quatre équations par régression non linéaire pour tous les adsorbants mentionnés ci-dessus et à toutes les températures en utilisant le logiciel Excel. Deux critères ont été appliqués pour sélectionner l'équation offrant la meilleure corrélation :

- 99% des résidus devaient être à $\pm 0,02$;
- Si plusieurs équations remplissaient le premier critère, l'équation avec le plus petit nombre de variable est choisie pour souci de simplicité.

3 Chapitre 3: Hydrophilic Zeolite Sorbents for In-Situ Water Removal in High Temperature Processes

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Résumé

Une approche intéressante pour réduire les émissions anthropiques de dioxyde de carbone (CO₂) serait de le valoriser en produits à valeur ajoutée (par exemple des alcools ou du diméthyléther) par recyclage chimique. Cependant, dans la plupart de ces réactions importantes, l'eau est produite comme un sous-produit qui limite thermodynamiquement la conversion du CO₂ et peut conduire à la désactivation des catalyseurs. L'élimination de l'eau par adsorption (SERP) permettrait de surmonter ces inconvénients et plusieurs zéolithes (SOD, LTA et FAU) ont été sélectionnées pour évaluer leur potentiel d'adsorption d'eau in-situ à hautes températures. Ce travail vise à étudier la capacité et la cinétique d'adsorption de l'eau dans une large plage de température de 25-250 °C et à évaluer le potentiel des adsorbants sélectionnés pour l'élimination in-situ de l'eau dans la réaction RWGS (reverse water gas shift, « réaction du gaz à l'eau inverse »). Pour toutes les zéolithes, la capacité d'adsorption de l'eau a montré une diminution importante à des températures plus élevées, mais la capacité à 250 °C était encore significative. Alors que la faible cinétique d'adsorption de la SOD limite son utilisation, la poudre FAU-13X donne de meilleurs résultats que le LTA-4A, ce qui est confirmé par une augmentation plus importante de la concentration en CO à la sortie du réacteur pour la réaction RWGS. Les données d'adsorption transitoire obtenues dans cette étude ont été corrélées par une équation double exponentielle étirée et les constantes cinétiques ont été déterminées. Ces résultats sont essentiels pour modéliser et concevoir un processus SERP efficace et déterminer les conditions de réaction optimales.

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Abstract

An attractive approach to reduce anthropogenic emission of carbon dioxide (CO₂) would be to valorize it into added-value products (e.g. alcohols or dimethylether) by chemical recycling. However, in most of these important reactions, water is produced as a by-product that limits CO₂ conversion thermodynamically and can lead to the deactivation of catalysts. Water removal in sorption-enhanced reaction process (SERP) would allow the overcoming of these drawbacks and several zeolites (SOD, LTA, and FAU) have been selected to assess their potential to adsorb water in-situ at high temperature. This work aims to study the water adsorption capacity and kinetics in a large temperature range of 25–250 °C and evaluate the potential of the selected adsorbents for in-situ water removal in the reverse water gas shift (RWGS) reaction. For all zeolites, the water uptake showed an important decrease at higher temperatures but the capacity at 250 °C was still significant. While the poor adsorption kinetics of SOD limit its use, FAU-13X powder gave better results than LTA-4A, which were confirmed by a more important increase of CO concentration at the exit of the reactor for the RWGS reaction. Transient adsorption data obtained in this study were fitted by a double stretched equation and the kinetic constants were determined. These results are essential to model and design an efficient SERP process and determine the optimal reaction conditions.

Keywords:

In-situ water separation; Sorption-enhanced reaction process; Zeolites; Adsorption.

3.1 Introduction

Atmospheric pollution and climatic changes are among the most important environmental, social, and economic issues nowadays. They are mainly caused by numerous pollutants such as particulate matter, volatile organic compounds (VOC), sulphur dioxide (SO₂), carbon oxide (CO), and greenhouse gases (GHG). It is well known that one of the most important GHG is carbon dioxide (CO₂) and most of its emission come from human activities. The CO₂ atmospheric concentration was 280×10^{-6} L/L before the industrial revolution and it is expected to reach 570×10^{-6} L/L by the end of the century.^[1] CO₂ valorization by chemical recycling represents an interesting way to reduce CO₂ emissions and allows simultaneously its conversion into high value-added products. Several processes involving CO₂ as a reagent are of industrial importance, like the synthesis of methanol^[2] (Equation (4)), ethanol^[9] (Equation (5)) or dimethylether (DME)^[10] (Equation (6)).

An important reaction that also occurs simultaneously in the above-mentioned examples is the reverse water gas shift reaction (RWGS, Equation (2)).

By converting CO₂ into CO, the RWGS reaction also allows the synthesis of hydrocarbons^[12] following the Fischer-Tropsch (FT) process (Equation (7)).

In all these reversible reactions, water is produced in large amounts as a by-product, which limits CO₂ conversion and can lead to the deactivation of the catalysts. Combining equilibrium-limited reactions with selective in-situ water removal by a sorption-enhanced reaction process (SERP) would be an effective way to by-pass thermodynamic limitations following Le Chatelier's principle and allow industrially the increase of CO₂ conversion, product yield and selectivity of all above-mentioned reactions.^[11]

Knowledge of the reaction conditions is essential for the selection of an appropriate adsorbent and the reaction temperature is one of the key parameters to consider. All synthesis reactions mentioned above occur around 250 °C, which is a high temperature for an adsorption processes. The adsorbent should therefore have a good adsorption capacity and selectivity at this temperature, requires appropriate kinetics and the material should offer good structural stability during the cyclic adsorption/desorption steps.

In the open literature, the removal of water has been studied using various adsorbents like hygroscopic salts, silica gel (SG), activated carbon (AC), polymeric desiccants, clays, mesoporous materials, aluminophosphates, and zeolites. It is often mentioned that the dissolution under highly humid conditions and the agglomeration tendency of hygroscopic salts generally limits their use.^[19] They are also unstable and decompose at high temperature (e.g. MgCl_2 releasing HCl above $190\text{ }^\circ\text{C}$ ^[21] and $\text{Ca}(\text{NO}_3)_2$ releasing oxygen and carcinogenic nitrites above $132\text{ }^\circ\text{C}$ ^[22]). SG is a very hydrophilic material, but water is totally desorbed at $150\text{ }^\circ\text{C}$ and it starts to decompose above $200\text{ }^\circ\text{C}$.^[22] Concerning AC, clays, and mesoporous materials, they are typically already regenerated at low temperatures of $150\text{ }^\circ\text{C}$, $120\text{ }^\circ\text{C}$, and less than $100\text{ }^\circ\text{C}$, respectively, and have usually more affinity to organic sorbates.^[19; 24] On their side, polymeric desiccants and aluminophosphates are very unstable, degradable and are regenerated around $100\text{ }^\circ\text{C}$.^[24] Among the identified water adsorbents, only zeolites seem therefore to be potential candidates for high temperature applications.

Hydrophilic zeolites have a good adsorption capacity for water, high thermal stability and regeneration temperature higher than $220\text{ }^\circ\text{C}$.^[19] Zeolites Linde Type A (LTA) and Faujasite (FAU) were widely used for water adsorption, and especially for water-alcohol mixtures separation at temperatures lower than $100\text{ }^\circ\text{C}$.^[34; 36; 40; 45; 48-51; 66] Only very few experimental studies were found including adsorption data at high temperatures (up to $200\text{ }^\circ\text{C}$) but most of them focused on membrane permeation for gases separation or molecular sieving^[38; 40; 51-53] and were not oriented toward adsorption studies. Works at higher temperatures (up to $310\text{ }^\circ\text{C}$) concern modelling and simulation only.^[11; 18]

As water removal is essential to assess the efficiency of the SERP processes, different studies including adsorption capacity, kinetics, and tests under reaction conditions were performed in this work using selected hydrophilic zeolites (SOD, LTA, and FAU) to determine their potential to be used as water adsorbents in high temperature applications. These data are also essential for modelling purposes, in the design and optimisation of the SERP processes. To the best of our knowledge, a similar experimental work has not been reported in the open literature.

3.2 Experimental

3.2.1 Materials

Different hydrophilic zeolites were tested as potential high temperature water adsorbents. Zeolite beads LTA-(3A, 4A, and 5A) and FAU-13X with particle size of 1.5–2.5 mm were supplied by Zeochem, Louisville, USA. Zeolite powder (53–250 μm) LTA-4A and FAU-13X were supplied by Advanced Speciality Gas Equipment (ASGE), Middlesex, USA. Hydroxy-sodalite (SOD) was directly synthesized from sodium aluminate (NaAlO_2 , Anachemia, Montreal, Canada, CAS no.1302-42-7, technical grade), sodium metasilicate nonahydrate ($\text{Na}_2\text{SiO}_3 \cdot 9\text{H}_2\text{O}$, Acros organics, NJ, USA, CAS no.13517-24-3, 0.44–0.475 g/g total solids) and sodium hydroxide (NaOH , VWR, Westchester, USA, CAS no.1310-37-2, ACS grade). These reagents were mixed with distilled water to form an initial precursor solution with the molar composition of $50\text{Na}_2\text{O}:\text{Al}_2\text{O}_3:5\text{SiO}_2:1005\text{H}_2\text{O}$ following the procedure given in Lafleur et al.^[64] SOD powder was obtained after hydrothermal synthesis performed in Teflon-lined stainless-steel autoclaves at 140 °C (isotemp oven, Fisher Scientific) for 3 h and 30 min. The powder was washed with distilled water until neutral pH than dried overnight at 90 °C.

3.2.2 Adsorption Setup and Procedure

All adsorption studies were performed using the intelligent gravimetric analyzer IGA-003 (Hiden Isochema, United Kingdom), a highly sensitive microbalance with a resolution of 0.1 μg and long-term stability of $\pm 1 \mu\text{g}$. It allows data acquisition of all transient and equilibrium stages of adsorption experiments to determine, respectively, the kinetics and the adsorption capacity (isotherm points) of a given sample. The device includes a flow control system used to set the pressure and the composition of the inlet flowrate which can be composed by both vapours and gases. Samples are loaded on the microbalance whose temperature is controlled either with a water jacket (0–80 °C) or a furnace (80–1000 °C) with a precision of 0.2 °C. Connections between the vapour generator and the microbalance holding the sample are heated to 50 °C to avoid condensation.

All adsorption experiments were carried out following the same procedure. Each sample of around 30 mg was loaded on the microbalance and regenerated at 300 °C under a 100

mL/min flowrate of nitrogen (Praxair Canada, 99.998 %) until no weight variations was registered. The sample temperature was then reduced to the selected one, between 25 and 250 °C, and when temperature stability was achieved, the nitrogen flow was sent to the vapour generator to get saturated before reaching the sample. The IGA was designed to ensure that, when required, the gas phase was saturated in water in the conditions of the work. The desired water partial pressure was set by changing the temperature of the pre-heated vapour generator in the range of 5–45 °C. The total pressure was always set to 100 kPa and the weight uptake was recorded until a plateau was reached. Data were finally used to determine the kinetics of the adsorption process and obtain the isotherms.

3.2.3 Experiments under Reaction Conditions

Zeolites (SOD, LTA-4A, and FAU-13X) in powder form were tested under reaction conditions to evaluate their potential to adsorb water in-situ and improve conversions and yields. The RWGS reaction was selected as a case study for its simplicity, low number of reactants and its importance in several syntheses (e.g. alcohols, DME, or FT). The reaction was carried out in a vertically-positioned SS cylindrical reactor (10.2 cm length and 0.635 cm inner diameter) filled with a mixture of 0.4 g of adsorbent, 0.4 g of catalyst (Cu-ZnO-Al₂O₃, 50–90 µm, Alfa Aesar) and 4.1 g of SiC as inert diluent to complete the volume to 3.2 mL. Before reaction, the catalyst was reduced in-situ at 250 °C and 500 kPa under a 25 mL/min (20/80 % H₂/Ar) flowrate and then the adsorbent was regenerated under 100 % Ar flowrate. When H₂ was totally flushed (checked by GC analysis and referenced as time zero), a 10/10/5 mL/min H₂/CO₂/Ar flowrate was sent to the reactor to perform the RWGS reaction. Argon was used as internal standard for gas analysis. Exit gas composition was determined by GC using a Carboxen-1010 PLOT column (30 m x 0.53 mm I.D.) and a TCD detector (250 °C).

3.3 Results and discussion

To evaluate the efficiency of the selected SOD, LTA and FAU zeolites as high temperature water adsorbents, adsorption experiments were performed to investigate the effect of different parameters like temperature, particle size and water partial pressure. The potential

of the studied adsorbents for in-situ water removal was then evaluated in the RWGS reaction.

3.3.1 Effect of Experimental Conditions on the Adsorption Capacity

The adsorption capacity was investigated in the temperature range of 25-250 °C. Figure 3.1 shows the water weight uptake of zeolite beads as a function of temperature under a 20 °C-saturated nitrogen flow (2.33 kPa water partial pressure). As expected, the adsorption capacity decreased with the increase of temperature for all zeolites, the adsorption of water on zeolites being a physical process. As showed in Figure 3.1, zeolite 13X has the best water adsorption capacity, even though its capacity drops from 0.281 g/g at 25 °C to 0.038 g/g at 250 °C. Zeolites 3A, 4A, and 5A have approximately the same capacities (0.209 g/g, 0.207 g/g, and 0.202 g/g, respectively) at 25 °C and 0.011 g/g, 0.022 g/g, and 0.019 g/g, respectively, at 250 °C. Some of our data can be compared to the available literature ones and a good agreement can be seen in Table 3.1.

The higher adsorption capacity of FAU over LTA zeolites may be explained by the difference in their pore size. Zeolite 13X has a larger pore size (0.74 nm) than zeolites 3A, 4A and 5A (0.32, 0.38, and 0.48 nm, respectively) and as water molecule size is 0.26 nm, a larger pore can rooms more water molecules. Actually, the pore size of LTA zeolites allows only one water molecule to be present in the cross-section of each pore while the pore size of zeolite 13X may let two water molecules ($2 \times 0.26 < 0.74$ nm). At 250 °C, FAU-13X and LTA-(3A, 4A, 5A) zeolites still have a significant water uptake, demonstrating that in terms of adsorption capacity, these zeolites have a good potential to be used in the SERP processes.

Table 3.1. Values of water adsorption capacity for zeolites LTA-(3A, 4A and 5A) and FAU-13X obtained in this work and in the literature

| Zeolite | Form | Temperature (°C) | Capacity (g/g) | P _{water} (kPa) | Reference |
|---------|--------|------------------|----------------|--------------------------|-----------------------------------|
| LTA-3A | Pellet | 20 | 0.242 | 2.211 | Kim et al. ^[39] |
| | Pellet | 30 | 0.182 | 2.224 | Kim et al. ^[39] |
| | Pellet | 40 | 0.170 | 2.320 | Kim et al. ^[39] |
| | Pellet | 100 | 0.145 | 2.337 | Simo et al. ^[40] |
| | Pellet | 200 | 0.0162 | 2.337 | Simo et al. ^[40] |
| | - | 25 | 0.20 | 2.33 | Wei et al. ^[41] |
| | Bead | 25 | 0.209 | 2.337 | This work |
| | Bead | 50 | 0.184 | 2.337 | This work |
| | Bead | 100 | 0.147 | 2.337 | This work |
| | Bead | 200 | 0.026 | 2.337 | This work |
| LTA-4A | Powder | 25 | 0.265 | 2.33 | Bonaccorsi et al. ^[42] |
| | Powder | 25 | 0.27 | 2.33 | Wu et al. ^[43] |
| | Powder | 25 | 0.255 | 2.33 | This work |
| LTA-5A | Pellet | 25 | 0.20 | 2.33 | Zheng et al. ^[24] |
| | Bead | 25 | 0.248 | 1.58 | Wang et al. ^[45] |
| | Bead | 50 | 0.196 | 1.23 | Wang et al. ^[45] |
| | Bead | 100 | 0.133 | 1.27 | Wang et al. ^[45] |
| | Bead | 25 | 0.2016 | 2.33 | This work |
| | Bead | 50 | 0.1641 | 2.33 | This work |
| | Bead | 100 | 0.1396 | 2.33 | This work |
| FAU-13X | Bead | 20 | 0.339 | 2.208 | Kim et al. ^[39] |
| | Bead | 30 | 0.29 | 2.329 | Kim et al. ^[39] |
| | Bead | 40 | 0.2703 | 2.252 | Kim et al. ^[39] |
| | Bead | 25 | 0.255 | 1.83 | Wang et al. ^[45] |
| | Bead | 50 | 0.218 | 1.68 | Wang et al. ^[45] |
| | Bead | 100 | 0.153 | 1.52 | Wang et al. ^[45] |
| | Powder | 25 | 0.325 | 2.33 | Bonaccorsi et al. ^[42] |
| | Bead | 25 | 0.2802 | 2.33 | This work |
| | Powder | 25 | 0.3176 | 2.33 | This work |
| | Bead | 50 | 0.2446 | 2.33 | This work |
| | Bead | 100 | 0.1897 | 2.33 | This work |

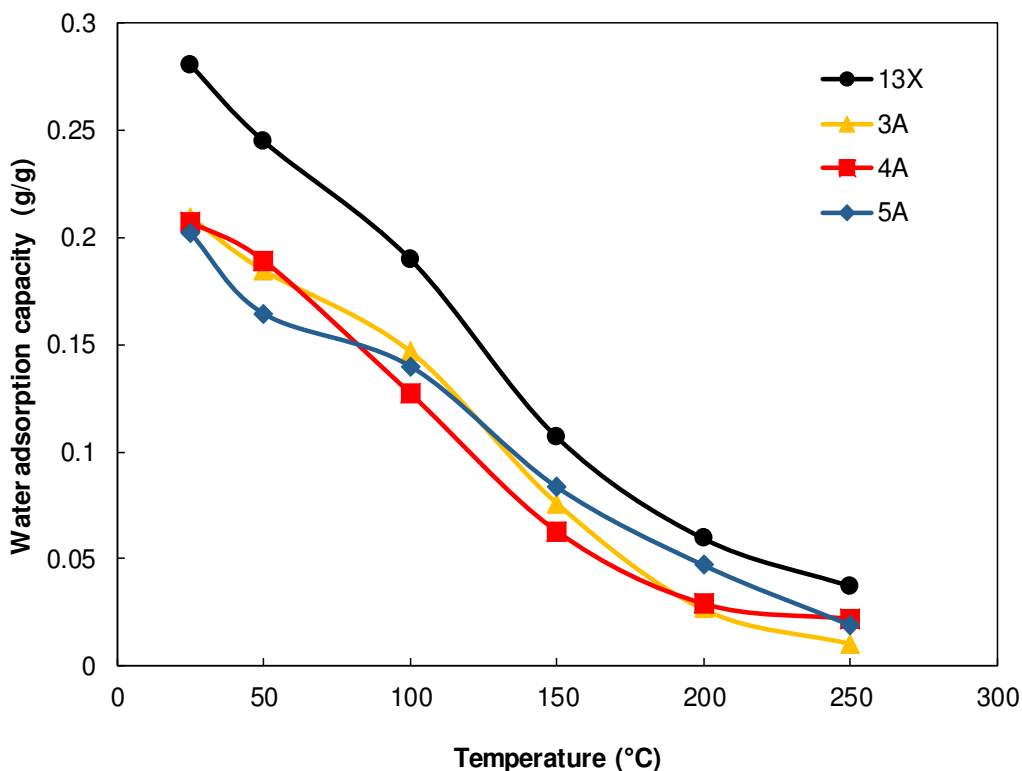


Figure 3.1. Water weight uptake under a 20 °C-saturated N₂ flow at different temperatures and 100 kPa total pressure for bead-shaped zeolites FAU-13X and LTA-(3A, 4A, and 5A). Lines were inserted for trend illustration.

Compared to FAU and LTA, SOD powder has half the capacity of zeolite 4A and one third of the 13X capacity at 250 °C. As SOD adsorption kinetics was found to be significantly slower than the other zeolites investigated, its equilibrium adsorption capacity could hardly be determined accurately. The same phenomenon also occurred at lower temperatures when SOD powder has not reached its maximum capacities even after a very long time. Figure 3.2 is an example of the adsorption capacity as function of time for SOD, 4A, and 13X zeolites at 25 and 250 °C.

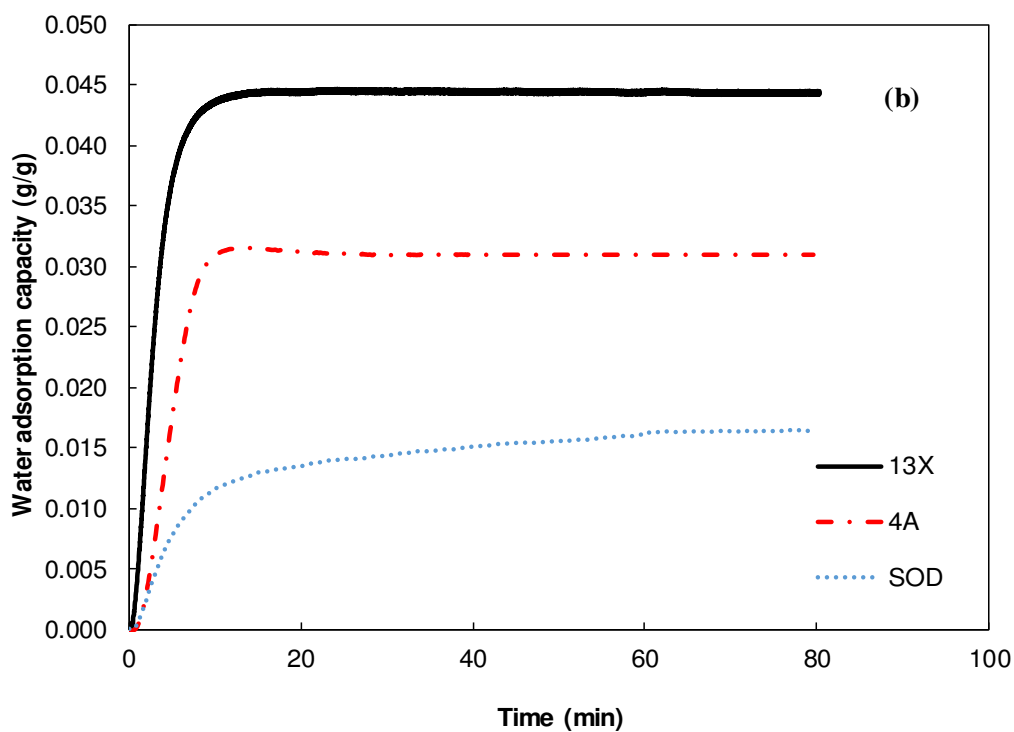
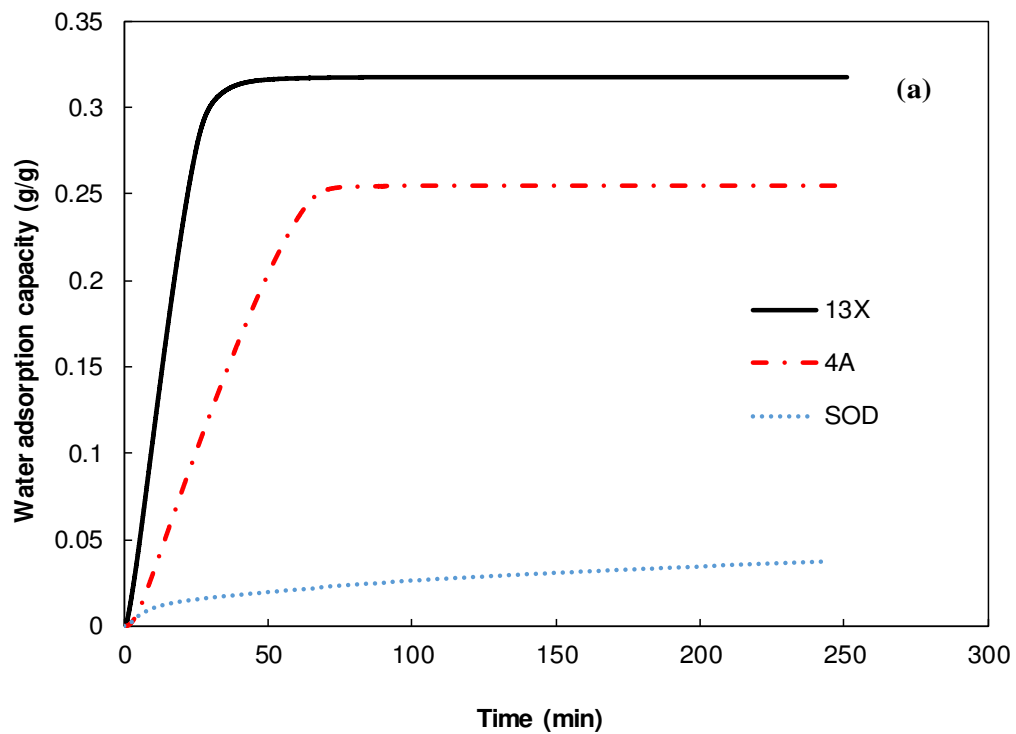


Figure 3.2. Water adsorption capacity as a function of time for zeolite powders FAU-13X, LTA-4A, and SOD under a 20 °C-saturated N₂ flow, 100 kPa total pressure, at 25 °C (a), and 250 °C (b).

The maximum capacity at 25 °C was reached in 45 min for zeolite 13X and in 1 h for zeolite 4A. In comparison, 4 h was not enough for SOD to reach approximately only 12 and 15 % of the capacity of zeolites 13X and 4A, respectively. This behaviour can be explained by the pore size of SOD (0.27 nm) which is very close to the water molecule size (0.26 nm). In consequence, the water diffusion which is directly related to the adsorption kinetics is very slow. Because the rate of adsorption is a key characteristic of an appropriate adsorbent, SOD was not further investigated.

A comparison of water adsorption capacities between beads and powders for zeolites 13X and 4A was also performed. As it can be seen in Figure 3.3, the powders have higher adsorption capacities due to their larger specific area compared to beads. The increase of adsorption capacity for powders over beads was found to be 4.8 and 3.7 % at 25 °C and 0.9 and 0.7 % at 250 °C, for zeolite 4A and 13X, respectively.

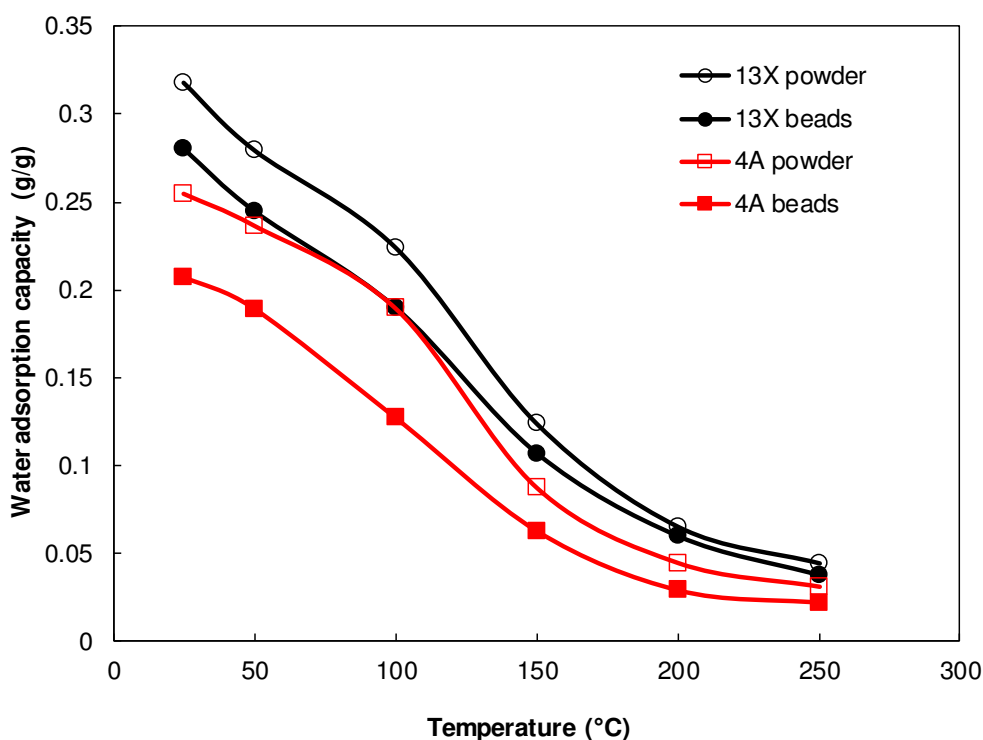


Figure 3.3. Comparison of water weight uptake between beads and powders for zeolites FAU-13X and LTA-4A under a 20 °C-saturated N₂ flow at 100 kPa total pressure. Lines were inserted for trend illustration.

Beside the effect of temperature at given water partial pressures (Figures 3.1–3.3), experiments were also performed at constant temperatures and different water partial pressures. Figure 3.4 shows different isotherms for 13X and 4A zeolites between 100 and 250 °C, when water vapour pressure was varying from 1.09 to 9.1 kPa. It can be observed that according to IUPAC, the isotherms are type I, which confirms that the investigated zeolites contained only micropores and that these materials have a high water sorption capacity even at low water partial pressure. Here again, the best results were obtained for FAU-13X. It possesses a higher adsorption capacity than zeolite 4A on the entire range of temperature and water partial pressure considered in this study. The difference between the uptake capacity of 13X and 4A is about 0.05 g/g at 100 °C and around 0.03 g/g at the other temperatures. At the temperature of interest for the SERP processes (250 °C), FAU still has around 0.05 g/g water uptake capacity compared to 0.02 g/g for 4A, for water partial pressures above 2 kPa.

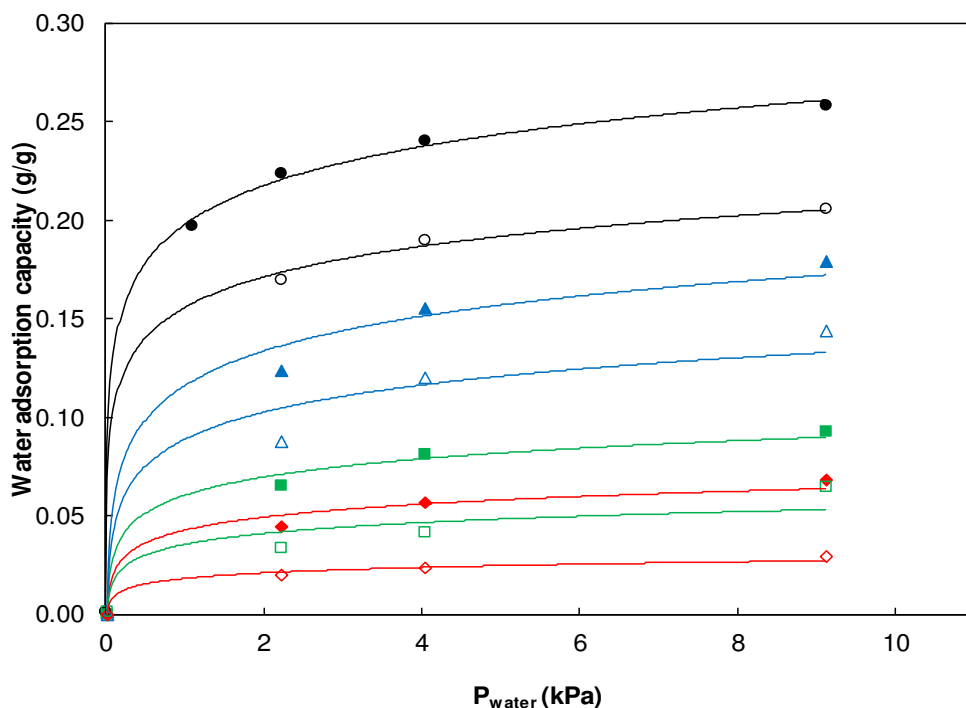


Figure 3.4. Isotherms of water weight uptake for zeolites FAU-13X (filled symbols) and LTA-4A (empty symbols) powders at different temperatures (● 100 °C, ▲ 150 °C, ■ 200 °C, and ◆ 250 °C) and 100 kPa total pressure. Lines were inserted for trend illustration.

3.3.2 Kinetics Study

In addition to a good adsorption capacity at high temperature, the optimal water adsorbent should also possess good adsorption kinetics. Knowledge of the kinetic constants is primordial to model and design an efficient SERP process. In this work, the transient adsorption data obtained before reaching equilibrium (e.g. Figure 3.2) were used for characterizing the adsorption kinetics of FAU-13X and LTA-(3A, 4A and 5A) using a double stretched exponential (DSE) model (Equation (8)).^[65] In Equation (8), M_t is the weight uptake at a given time (t) and M_e is the equilibrium weight uptake at the same temperature whereas A_1 is the fractional contributions of an adsorption process defined by its adsorption rate constants k_1 and its exponent β_1 .

The DSE equation can be simplified, thus offering 3 related equations: a double exponential equation (DE) for $\beta_1 = \beta_2 = 1$ (Equation (9)); a stretched exponential equation (SE) for $k_1 = k_2 = k$ and $\beta_1 = \beta_2 = \beta$ (Equation (10)); and a linear driving force equation (LDF) for $k_1 = k_2 = k$ and $\beta_1 = \beta_2 = 1$ (Equation (11)).

These four equations were fitted to our experimental data by non-linear regression for all above-mentioned adsorbents and all temperatures. Two criteria were applied to select the equation offering the best correlation: (i) 99 % of residuals had to be within ± 0.02 and (ii) if several equations fulfilled the first criteria, the equation with the lower number of variables was selected for the sake of simplicity.

The best correlation was achieved with the DSE equation for all zeolite types and on the whole temperature range investigated. Figure 3.5 shows an example for FAU-13X powder at 25 °C. Is it possible to see that all DSE residuals were within ± 0.02 , thus making this equation the only one suitable according to the above mentioned first criteria. For the DSE equation, five constants (A_1 , β_1 , β_2 , k_1 , and k_2) were determined at each temperature and for each zeolite type (Table 3.2).

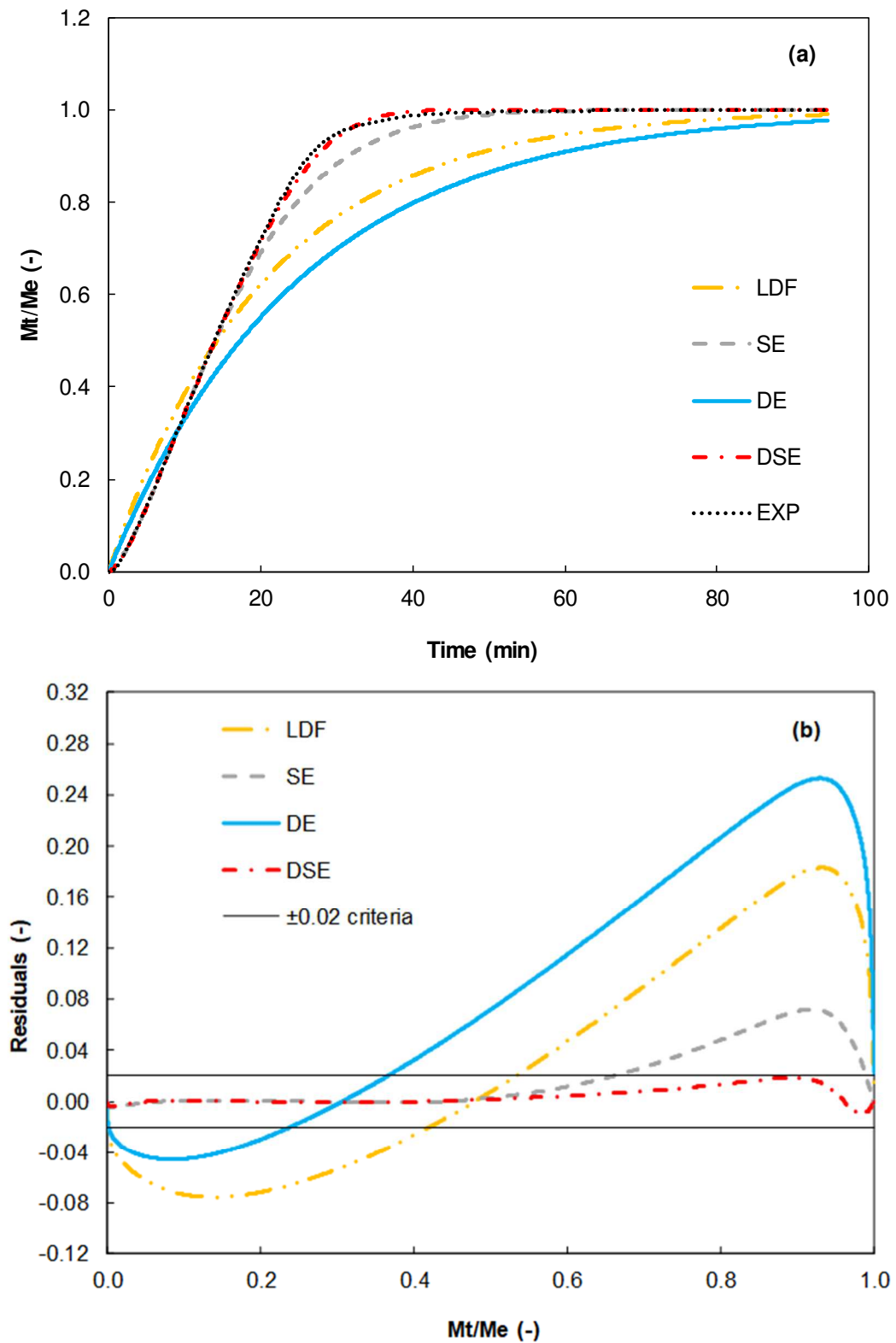


Figure 3.5. Fit (a) and residuals (b) of DSE, DE, SE, and LDF kinetics equations for zeolite FAU-13X powder at 25 °C under a 20 °C-saturated N₂ flow and 100 kPa total pressure.

Table 3.2. Values of the DSE model parameters for zeolites LTA-(3A, 4A, and 5A) and FAU-13X

| Zeolite | Temperature (°C) | A_1 | k_1 | k_2 | β_1 | β_2 |
|---------------|------------------|-------|-------|-------|-----------|-----------|
| LTA-3A bead | | | | | | |
| | 25 | 0.48 | 0.01 | 0.04 | 2.51 | 1.35 |
| | 50 | 0.37 | 0.02 | 0.04 | 3.16 | 1.51 |
| | 100 | 0.45 | 0.02 | 0.06 | 2.61 | 1.51 |
| | 150 | 0.83 | 0.04 | 0.11 | 1.26 | 1.95 |
| | 200 | 0.56 | 0.08 | 0.17 | 1.66 | 1.94 |
| | 250 | 0.68 | 0.17 | 0.33 | 2.11 | 2.39 |
| LTA-4A bead | | | | | | |
| | 25 | 0.82 | 0.02 | 0.07 | 1.86 | 1.74 |
| | 50 | 0.77 | 0.02 | 0.08 | 2.15 | 2.02 |
| | 100 | 0.82 | 0.03 | 0.12 | 1.84 | 2.10 |
| | 150 | 0.85 | 0.05 | 0.13 | 1.37 | 2.77 |
| | 200 | 0.83 | 0.11 | 0.22 | 1.76 | 2.47 |
| | 250 | 0.71 | 0.13 | 0.28 | 2.22 | 2.40 |
| LTA-4A powder | | | | | | |
| | 25 | 0.34 | 0.01 | 0.03 | 4.55 | 1.67 |
| | 50 | 0.36 | 0.02 | 0.04 | 4.42 | 1.68 |
| | 100 | 0.61 | 0.03 | 0.08 | 2.70 | 1.73 |
| | 150 | 0.76 | 0.06 | 0.10 | 1.35 | 2.43 |
| | 200 | 0.20 | 0.10 | 0.15 | 2.80 | 2.05 |
| | 250 | 0.19 | 0.13 | 0.20 | 3.60 | 2.25 |
| LTA-5A bead | | | | | | |
| | 25 | 0.85 | 0.01 | 0.09 | 1.73 | 1.91 |
| | 50 | 0.87 | 0.02 | 0.10 | 1.78 | 1.74 |
| | 100 | 0.80 | 0.03 | 0.12 | 1.97 | 1.65 |
| | 150 | 0.87 | 0.05 | 0.16 | 1.63 | 1.75 |
| | 200 | 0.79 | 0.06 | 0.18 | 1.44 | 1.58 |
| | 250 | 0.32 | 0.10 | 0.18 | 1.03 | 1.51 |

| | | | | | | |
|----------------|------|------|------|------|------|--|
| FAU-13X bead | | | | | | |
| 25 | 0.71 | 0.01 | 0.05 | 2.44 | 1.57 | |
| 50 | 0.70 | 0.02 | 0.07 | 2.71 | 1.94 | |
| 100 | 0.66 | 0.02 | 0.08 | 2.46 | 1.71 | |
| 150 | 0.91 | 0.05 | 0.13 | 1.59 | 2.41 | |
| 200 | 0.54 | 0.08 | 0.16 | 2.35 | 1.85 | |
| 250 | 0.23 | 0.09 | 0.18 | 3.51 | 1.99 | |
| FAU-13X powder | | | | | | |
| 25 | 0.49 | 0.04 | 0.09 | 2.86 | 1.53 | |
| 50 | 0.58 | 0.05 | 0.11 | 2.55 | 1.48 | |
| 100 | 0.72 | 0.06 | 0.17 | 2.16 | 1.59 | |
| 150 | 0.73 | 0.11 | 0.20 | 1.45 | 1.75 | |
| 200 | 0.30 | 0.14 | 0.29 | 1.62 | 1.69 | |
| 250 | 0.28 | 0.17 | 0.35 | 1.60 | 1.85 | |

Rate constants k_1 and k_2 were all found to follow the Arrhenius law, as shown for example in Figure 3.6 for powdered FAU-13X. The calculated activation energy (E_a) values are indicated in Table 3.3. According to Fletcher et al.,^[65] the DSE equation describes an adsorption involving two different kinetic processes. For the present application concerning water adsorption by zeolites, these kinetic processes could represent (i) a slow adsorption/diffusion through the narrow micropores of the zeolites with high activation energy and (ii) a fast adsorption/diffusion along pore entrance or at the zeolite surface with lower activation energy. E_a values given in Table 3.3 seem to confirm these assumptions as E_{a1} was found to be always higher than E_{a2} , corresponding to two different adsorption/diffusion processes. Furthermore, E_{a1} values were generally found to decrease with the increase of the zeolite pore size which could be related to the fact that molecular diffusion is less restricted in bigger pores (zeolites 5A and 13X).

Table 3.3. Activation energy (E_a) values related to the kinetic constants k_1 and k_2 in the DSE equation for zeolites LTA-(3A, 4A, and 5A) and FAU-13X

| Zeolite/form | E_{a1} (kJ/mol) | E_{a2} (kJ/mol) |
|--------------|-------------------|-------------------|
| 3A / bead | 13.25 | 11.57 |
| 4A / bead | 11.04 | 7.31 |
| 4A / powder | 11.99 | 9.83 |
| 5A / bead | 8.99 | 4.16 |
| 13X / bead | 9.49 | 6.82 |
| 13X / powder | 8.24 | 7.53 |

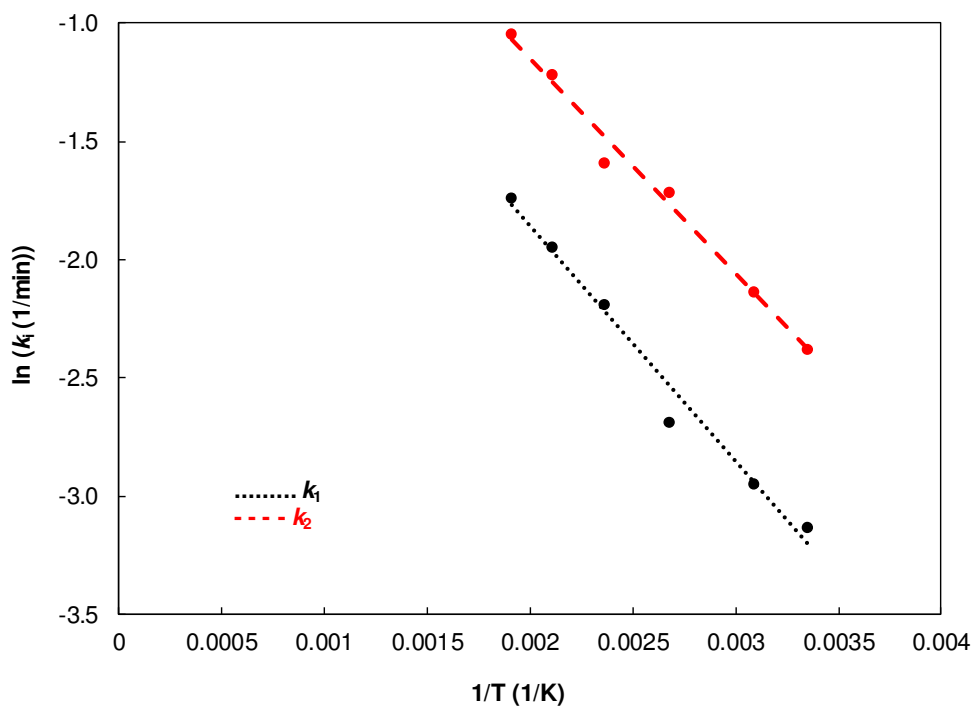


Figure 3.6. Arrhenius law verification for the rate constants given by DSE model; k_1 (black) and k_2 (red) for zeolite FAU-13X powder.

The analysis of the fractional contribution (A_1) for the kinetic process corresponding to the rate constant k_1 also revealed a certain trend. A_1 values tend toward a maximum at a

temperature of 150 °C for all adsorbents, suggesting that the contribution of the first kinetic process (water adsorption/diffusion inside the micropores) is on its maximum at this temperature. This optimum may be explained by the combination of the opposite trend of two phenomena: a decreasing adsorption tendency but an increasing diffusion with the temperature. Differential thermal analysis (DTA) curves obtained in the literature^[67] during thermogravimetric analysis (TGA) of different zeolites also revealed that water adsorption is still strong until around 130–150 °C and then a peak of desorption occurs. This peak of desorption involve a higher water mobility inside the zeolite and therefore, higher molecular diffusion inside the micropores (first kinetic process). No clear tendencies were observed for the exponents β_1 and β_2 .

3.3.3 Adsorbent Effect under SERP Conditions

As mentioned in the Experimental section, all powder zeolites (SOD, LTA-4A, and FAU-13X) were tested for in-situ water removal using the RWGS as a case study reaction. In these experiments, a small 10/10/5 mL/min H₂/CO₂/Ar flowrate was used to assure that the reaction equilibrium was achieved in the reactor, so that the effect of the adsorbent can clearly be seen. With the addition of an efficient water adsorbent inside the catalytic bed, an important increase of CO was expected, corresponding to the shift of equilibrium toward the products in a sorption enhanced process. Our results confirmed this behaviour, as it can be seen in Figure 3.7 where the CO concentration at the exit of the reactor was plotted against the time. After a delay time of around 2.5 min, CO concentrations increase sharply, reach maximal values and then decrease towards the equilibrium CO value dictated by the RWGS reaction. The increase of CO concentration versus the equilibrium value in the first 2.5–10 min of reaction is due to the water adsorption by the zeolite, allowing the equilibrium to be shifted towards the products. The fact that all curves reached again the equilibrium value after about 10 min indicated that the adsorbent became saturated in water. Water desorption under Ar flow showed a very good adsorption reversibility as several replicas of the experiments shown in Figure 3.7 have proved that the reproducibility of the results was within $\pm 8 \times 10^{-5}$ mol/L.

Clearly, FAU-13X shows the best water adsorption performance, followed by LTA-4A and SOD. This result agrees well with the previous findings obtained in this study and confirms

that SOD is not an efficient water adsorbent due to its very low adsorption kinetics. Integrating the curves from Figure 3.7 between 2.5 and 10 min allows to calculate the total amount of CO produced under the water adsorption regime and allows to compare this value with the amount produced in the absence of the adsorbent during the same period of time. The presence of FAU-13X in the reaction bed resulted in a huge increase of 60 % of CO production, while the corresponding values for LTA-4A and SOD are 26 % and -6 %, respectively. This negative value for SOD comes from the small interval of time (2.5 to 4 min) where the CO production in presence of SOD is inferior to the production at equilibrium due to the purge of Ar. It can be concluded that FAU-13X seems to be a very promising adsorbent candidate in SERP. A thorough study of the effect of different operating parameters is presently in progress in our laboratories.

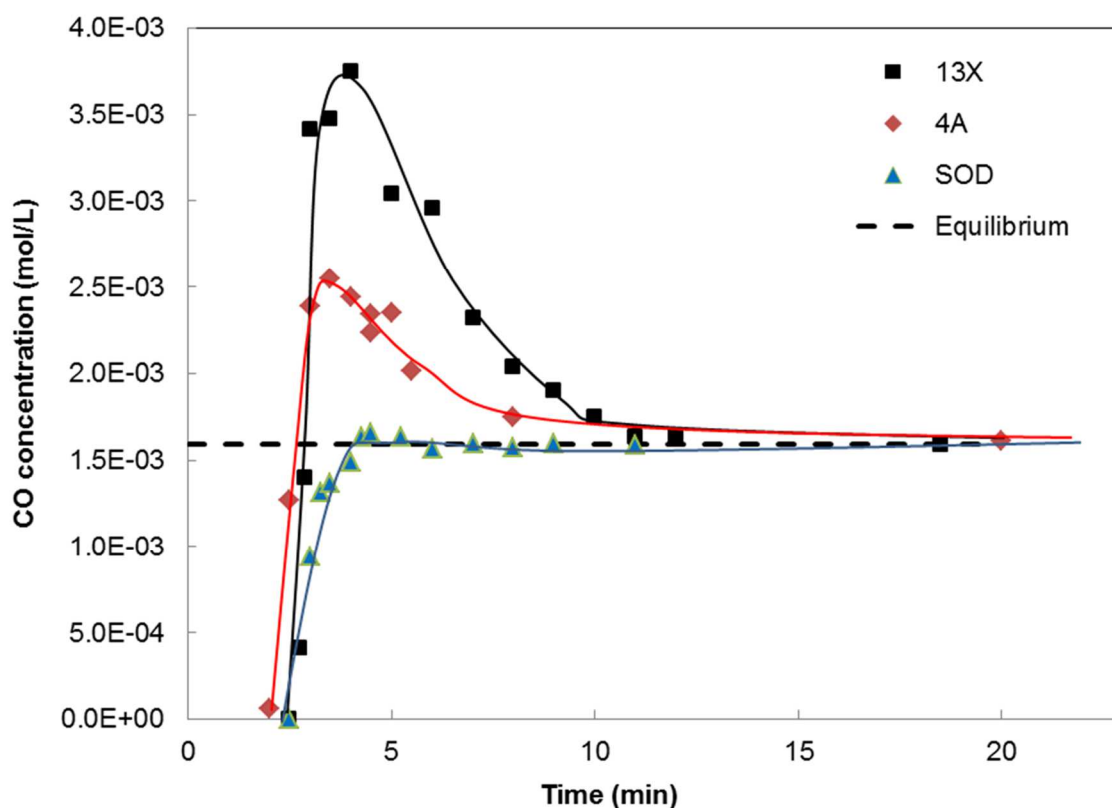


Figure 3.7. Effect of the addition of water adsorbents on CO concentration at the exit of RWGS reactor at 250 °C and 500 kPa.

3.4 Conclusion

In this work, water adsorption capacity and kinetics of zeolites LTA-(3A, 4A, and 5A), SOD and FAU-13X have been studied using an intelligent gravimetric analyzer at 100 kPa and under a wide range of temperature (25–250 °C) and water partial pressure (1.09–9.1 kPa). It was found that the water uptakes decrease significantly with temperature but are still significant at 250 °C. Zeolites like LTA, and especially FAU-13X, can be promising water adsorbents for application in sorption-enhanced reaction processes. FAU-13X powder was found to have the best adsorption capacity among the tested zeolites and its application in the RWGS reaction demonstrated experimentally the huge effect of in-situ water removal from the reaction media (increase of 60 % of the CO concentration at the exit of the reactor), in agreement with our previous modelling study.^[11] The kinetic constants of a DSE model were determined at several temperatures for LTA and FAU zeolites, along with the corresponding values of activation energy. All these results are very useful in modelling and designing efficient SERP processes. The adsorbent selectivity for water in the presence of other components of the reaction media (e.g., CO₂, methanol), as well as its structural stability and cyclic regeneration capacity are in progress in our laboratory and will be reported in an upcoming publication.

4 Conclusions générales et recommandations

La plupart des réactions de valorisation du CO₂ produisent l'eau comme sous-produit ce qui limite thermodynamiquement le processus et désactive le catalyseur. L'élimination de l'eau par adsorption permet de déplacer l'équilibre et d'augmenter la conversion et le rendement des réactions. Le procédé SERP qui combine le système réactionnel (ici, l'hydrogénation catalytique du CO₂) avec la séparation in-situ d'un produit (ici, l'eau) offre la possibilité d'éliminer l'eau du milieu réactionnel afin d'augmenter la conversion du CO₂ et le rendement et la sélectivité.

Dans ce travail, la capacité et la cinétique d'adsorption de l'eau par les zéolithes LTA- (3A, 4A et 5A), SOD et FAU-13X ont été étudiées en utilisant l'analyseur gravimétrique intelligent (IGA) à 100 kPa et en variant plusieurs paramètres comme la température (25 - 250 °C), la granulométrie (perle et poudre) et la pression partielle de l'eau (1,09 – 9,1 kPa).

Les résultats ont montré que pour les zéolithes étudiées, la capacité d'adsorption diminue significativement avec la température mais qu'elle reste encore significative à 250 °C. Les zéolithes de type LTA et FAU-13X ont montrées qu'elles peuvent constituer des adsorbants prometteurs pour l'application dans le procédé SERP. La poudre de FAU-13X s'est révélée avoir la meilleure capacité d'adsorption parmi les zéolithes testées. Ceci a été confirmé par les tests d'application dans les conditions du procédé SERP pour la réaction RWGS pour laquelle la concentration du CO à la sortie du réacteur a augmenté de 60%. La capacité d'adsorption de la zéolithe SOD n'a pas été évaluée avec précision car sa cinétique d'adsorption de l'eau est très faible, ce qui limite son utilisation. Afin de faire la modélisation et la conception des procédés SERP efficaces, les constantes cinétiques du modèle DSE ont été déterminées pour tous les adsorbants et à toutes les températures testées ainsi que les valeurs correspondantes de l'énergie d'activation.

Il est évident que la sélectivité vis-à-vis de l'eau est une propriété clé pour un choix efficace de l'adsorbant en raison de la complexité de toutes les réactions de valorisation du CO₂. Les études de sélectivité trouvées dans la littérature sont toutes réalisées à des températures inférieures à 180 °C pour le CO₂ et à 170 °C pour les alcools. La comparaison des

conditions opératoires des différentes études laisse à penser que la sélectivité de l'eau peut être favorisée en augmentant la température. Malgré cela, pour démontrer la sélectivité dans les conditions des réactions de valorisation du CO₂ par hydrogénation catalytique, des expériences de sélectivité à hautes températures doivent être réalisées et analysées. Cette étude est présentement en cours dans notre laboratoire et fera l'objet d'une prochaine publication.

Il faut mentionner aussi que dans le procédé SERP l'adsorbant doit être mélangé au catalyseur. Il est donc évident que la stabilité structurelle et la capacité de régénération cyclique sont des paramètres clés dans la réussite de ce procédé hybride. Des tests cycliques adsorption/désorption doivent donc être réalisés afin d'évaluer l'efficacité globale de ce type d'adsorbants dans des applications industrielles.

La température maximale étudiée dans ce projet est de 250 °C. D'autres expériences à des températures plus élevées doivent être faites afin de vérifier l'efficacité de l'adsorption et du procédé SERP pour d'autres réactions à plus haute température.

Pour la mise en conditions opératoires des adsorbants, l'étude de l'adsorption en milieu réactionnel permettra d'identifier les différents paramètres à optimiser comme la composition initiale du flux entrant, le ratio adsorbant/catalyseur et la durée des cycles adsorption/désorption afin de permettre le meilleur rendement de la réaction.

Finalement, le développement de nouveaux adsorbants plus performants constitue une autre perspective de ce projet en vue d'augmenter la capacité d'adsorption ainsi que la sélectivité et le rendement de la réaction.