

Improvement of Methanol Production from Carbon Dioxide and Hydrogen by a Sorption Enhanced Reaction Process

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Climate change caused by carbon dioxide emissions is one of the most concerning problems worldwide. CCS (Carbon Capture and Storage) technologies are not enough to achieve climatic goals, so there is the need to embrace new processes, like CCUS (Carbon Capture Utilization and Storage). Hydrogenation of CO₂ to produce methanol is one of the most feasible ways, however, the conversion rates are small. It could be solved by a SERP process (Sorption Enhanced Reaction Process), displacing the reaction equilibrium through the adsorption of the products, water and methanol.

There is scarce information of the adsorption of these compounds, especially methanol, at the reaction temperature (200-300 °C). In this work, adsorption equilibrium and diffusional parameters for water and methanol are obtained for the design of a SERP process. 3A zeolite, silica gel and silica-alumina have been studied at temperatures of 200-300°C by a chromatographic method. The performance of these adsorbents in a PSA reactor for CO₂ hydrogenation with a commercial catalyst (Cu/ZnO/Al₂O₃) is compared by simulation.

1. Introduction

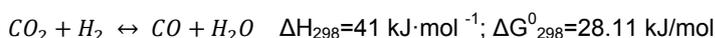
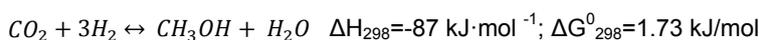
Nowadays, one of the main objectives of science is the substitution of fossil fuels for clean sources of energy; however, the sustainable transition progresses too slowly. (*World Energy Council, World Energy Scenarios 2019*) Despite the actual COVID-19 crisis has decreased the global energy demand and CO₂ emissions in 2020, some scenarios put back both to pre-crisis values between 2023 and 2025, and a growing tendency the next years. (*IEA World Energy Outlook 2020*)

Numerous countries over the world aim to achieve net-zero emissions at 2050, but to accomplish that, a huge investment and development is needed. In this energy transition CCUS technologies take an important role (*IEA World Energy Outlook 2020*)

One of the most viable and simple way to utilize captured CO₂ is the synthesis of methanol. Methanol is one of the largest raw materials in the organic chemical industry and a promising substitute of fossil fuels, like gasoline or diesel. Moreover, methanol could be obtained from any source of CO₂. (*Goepfert et al. 2014*)

Methanol can be produced by many ways, although the most developed and efficient is catalytic hydrogenation with H₂. (*Goepfert et al. 2014*) H₂ can also be obtained by renewable sources, so the entire process is environmentally friendly.

The hydrogenation of CO₂ involves two equilibrium reactions (*Van-Dal and Bouallou, 2013*) showing that methanol production is favored at low temperatures because the reaction is exothermic.



CO₂ conversion and methanol yield could be improved by mixing the catalyst with a selective adsorbent, and removing the products in a SERP process (Sorption Enhanced Reaction Process) (Carvill *et al.*, 1996)

2. Materials and methods

Zeolite 3A pellets supplied by Bayer AG, silica-alumina, silica gel Davisil™ supplied by Sigma-Aldrich have been used as selective adsorbents. Helium (>99.999%) supplied by Carbueros Metálicos has been utilized as carrier gas. Methanol (HPLC grade, >99.9%) supplied by Sigma-Aldrich, and ultrapure water have been used as liquid adsorbates. The physicochemical characterization of the adsorbents is shown below in Table 1.

Table 1: Physicochemical properties of the adsorbents

| Adsorbent | Particle diameter (mm) | Particle density (kg/m ³) | Particle porosity | Specific surface area (m ² /g) | Total pore volume (cm ³ /g) | Pore size width (Å) | Si/Al (molar) |
|----------------|------------------------|---------------------------------------|-------------------|---|--|---------------------|---------------|
| 3A | 1.4 | 1638 | 0.301 | 280 | 0.184 | 42* | 0.98 |
| Silica gel | 0.5-0.25 | 635 | 0.690 | 282 | 1.103 | 147 | ∞ |
| Silica-alumina | 1-0.71 | 1256 | 0.480 | 381 | 0.430 | 45 | 0.26 |

*Microporous pore size around 3 Å

Adsorption equilibrium and diffusional parameters were obtained through pulse experiments by a chromatographic method. The method is like the Zero Length Column method, which consist of using a small amount of the adsorbent in a packed bed and follow the desorption of the adsorbates (Ruthven and Post, 2001)

Pulse experiments are carried out in a packed bed inside the oven of a gas chromatograph Varian Star 3400 CX coupled with a TCD detector. In each pulse, 1 µL of the adsorbate is injected using helium as a carrier gas. Dead volume and global dispersion of the installation, including dispersion of the detector, were determined by air pulses. Packed bed properties and operation conditions are shown in Table 2.

Table 2: Properties of the packed bed and operation conditions

| Adsorbent | Bed length (cm) | Mass of pellets (g) | Porosity between particles | Bed diameter (cm) | Temperature (°C) | Gas flow rate (mL·s ⁻¹) |
|----------------|-----------------|---------------------|----------------------------|-------------------|------------------|-------------------------------------|
| 3A | 1.91 | 0.250 | 0.580 | 0.49 | 200-300 | 1.5 |
| Silica gel | 1.91 | 0.069 | 0.699 | 0.49 | | |
| Silica-alumina | 1.91 | 0.115 | 0.746 | 0.49 | | |

The adsorbents were regenerated inside the packed bed under helium flow rate at 623 K overnight. Gas flow rate and temperatures were set with the controllers of the chromatograph.

3. Results and discussion.

3.1 Henry's equilibrium adsorption constant and reciprocal diffusional time constant.

Henry's equilibrium adsorption constants and reciprocal diffusional time constants of water and methanol have been determined by pulse experiments in a gas chromatograph at 200-300 °C, the range of temperatures in which hydrogenation of carbon dioxide to methanol take place.

Experimental pulses of water, methanol and air at 250°C on 3A zeolite, silica-alumina and silica gel are shown below in Figure 1 and Figure 2. Air has been used as gas tracer, determining with the pulses the dead volume and the dispersion of the installation.

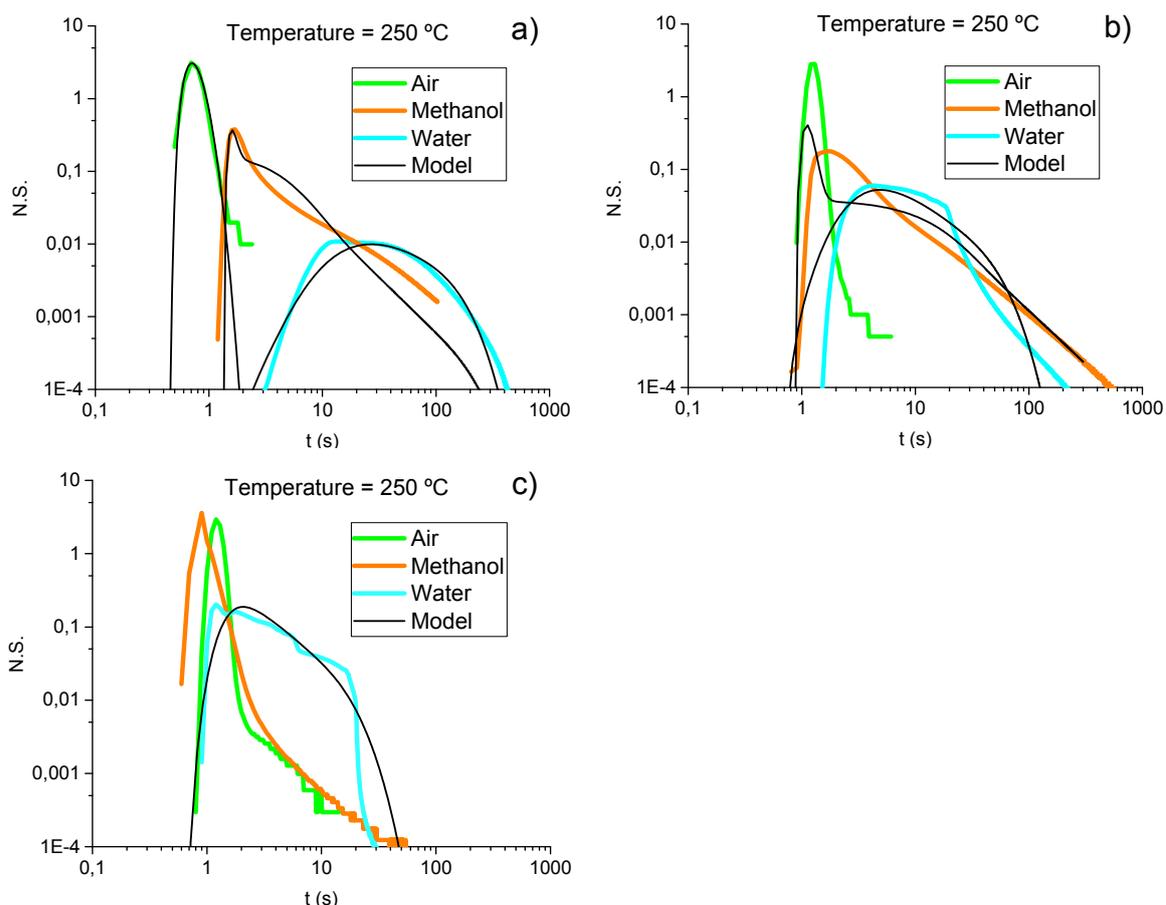


Figure 1: Pulses of water, methanol and air at 250 °C and $1.5 \text{ mL}\cdot\text{s}^{-1}$ total gas flow rate. a) 3A zeolite b) Silica-alumina c) Silica gel

Figure 1a shows that the peak signal of water is lower and appears later than the peak of methanol, meaning that water has greater affinity for 3A zeolite being the strongest adsorbate. Even so, the peak of methanol is still lower than the peak of air, and has a significant tail, what indicates that methanol is notably adsorbed too. Furthermore, the pulse of methanol rises faster than water, and has a longer tail, deducing that methanol presents higher steric hindrance due to his higher kinetic diameter. Methanol cannot enter in to the pores of the adsorbent, as water do, and desorption is slower, due to the high mass transfer resistance.

Figure 1b shows that the pulses of methanol and water in silica-alumina are similar, appearing almost at the same time and rising fast with a steep slope. It indicates that both are adsorbed on-to silica-alumina. Methanol has a greater tail as in the case of 3A zeolite, due to its higher affinity.

From the comparison pulses of air and methanol in Figure 1c, it is deduced that methanol is not adsorbed on silica gel at 250 °C. The broad peak of water indicates that is adsorbed. However, it appears very soon and rises fast, indicating that water has low affinity for the adsorbent. Also, the tail is not too long, so the diffusion resistance is not significant due to the high pore size.

Figure 2 presents the influence of the adsorbent on the water and methanol adsorption at 250°C.

In Figure 2a the pulse signal of water on 3A zeolite is lower and rise slower, so is widely adsorbed compared with silica gel and silica-alumina. The peak decreases faster in the silica gel and in the silica-alumina, indicating that the affinity for the 3A zeolite is higher, due to the smaller pore size and the interactions of the water molecule with the cations of the zeolite.

In Figure 2b, it is observed that methanol pulses of 3A zeolite and silica alumina are alike, so they are adsorbed with similar strength. The tails of methanol are almost identical too, so the mass transfer resistance observed is practically the same in the 3A zeolite and the silica-alumina. Methanol adsorption in silica gel at 250 °C is negligible, as it was previously discussed.

Henry's equilibrium constants have been calculated from dimensionless Henry's constant through the first momentum of the pulses. (Delgado et al. 2014) The values obtained for Henry's constants for methanol and water are shown in Table 4.

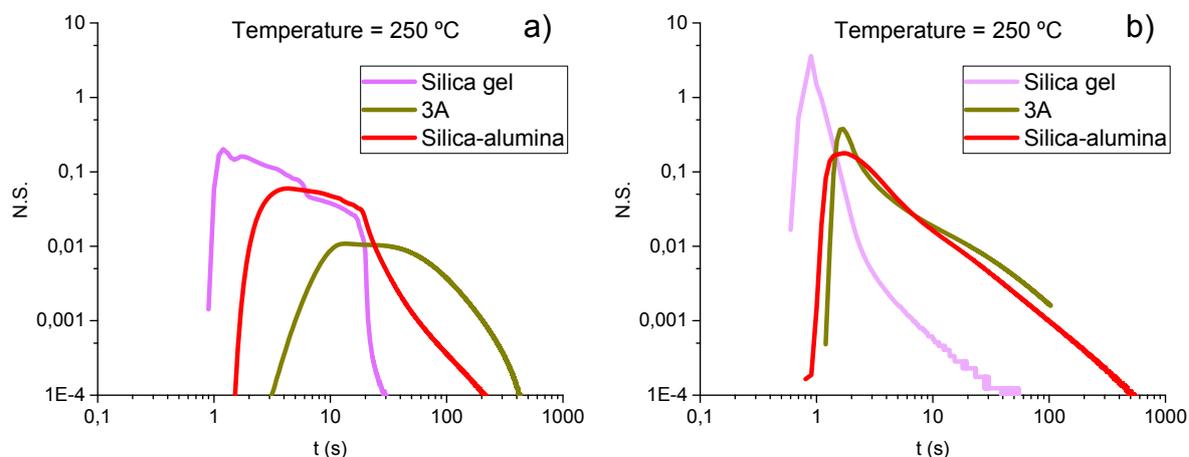


Figure 2: Comparison of a) water and b) methanol pulses on different adsorbents at 250 °C and 1.5 mL·s⁻¹

Table 4: Henry's equilibrium adsorption constants for methanol and water

| Adsorbent | Temperature (°C) | K _H methanol (mol·kg ⁻¹ ·Pa ⁻¹) | Adsorbent | Temperature (°C) | K _H water (mol·kg ⁻¹ ·Pa ⁻¹) |
|----------------|------------------|---|----------------|------------------|--|
| 3A | 200 | 8.25·10 ⁻⁵ | 3A | 200 | 6.54·10 ⁻⁴ |
| 3A | 250 | 4.49·10 ⁻⁵ | 3A | 250 | 2.12·10 ⁻⁴ |
| 3A | 300 | 4.03·10 ⁻⁵ | 3A | 300 | 8.04·10 ⁻⁵ |
| Silica gel | 200 | 6.42·10 ⁻⁶ | Silica gel | 250 | 5.30·10 ⁻⁵ |
| Silica gel | 250 | Non-adsorbable | Silica gel | 300 | 2.28·10 ⁻⁵ |
| Silica gel | 300 | Non-adsorbable | Silica-alumina | 200 | 1.29·10 ⁻⁴ |
| Silica-alumina | 200 | 4.33·10 ⁻⁴ | Silica-alumina | 250 | 1.08·10 ⁻⁴ |
| Silica-alumina | 250 | 3.20·10 ⁻⁴ | | | |
| Silica-alumina | 300 | 1.62·10 ⁻⁴ | | | |

Affinity between adsorbate and adsorbent, related to Henry's constants, decreases with the temperature in all cases as it is expected for physical adsorption mechanism, being more accused the effect at higher affinities. The Henry's constant of water in zeolite 3A is higher due to the stronger interactions with the zeolite cations caused by its high dipole moment. That explains why Henry's constant is higher for water than for methanol and the higher affinity observed in Figure 1a. Water has also greater affinity for silica gel than methanol. Silica gel does not adsorb methanol significantly at temperatures above 200 °C. Silica-alumina presents higher affinity for methanol than for water, but the values of Henry's constant for both adsorbates are of the same order of magnitude.

Diffusional reciprocal time constants have been determined by adjusting the experimental pulses with a theoretical model. The model is based on a plug flow, which represents the dead volume, followed by perfect mixed tanks-in-series. (Delgado et al. 2014) The values obtained for the diffusional parameters for methanol and water are presented below in Table 5.

The reciprocal diffusional time constant is higher for water than for methanol in 3A zeolite due to the greater steric hindrance detailed before. In silica-alumina, the diffusion rate for methanol is lower due to its higher affinity.

Diffusional parameters of 3A zeolite are lower than those of silica gel and silica-alumina due to the smaller pore size and the greater interactions of water with the cations of the zeolite. Diffusional parameters of silica gel are notably higher because of the significant greater pore size. Diffusional parameters increase with the temperature due to the higher mobility of the molecules, being the effect more pronounced at higher hindrance resistance.

Table 5: Diffusional reciprocal time constants for methanol and water

| Adsorbent | T (°C) | D_c/r_c^2 methanol (s ⁻¹) | r ² | Adsorbent | T (°C) | D_c/r_c^2 water (s ⁻¹) | r ² |
|----------------|--------|---|----------------|----------------|--------|--------------------------------------|----------------|
| 3A | 200 | $5.77 \cdot 10^{-4}$ | 0.86 | 3A | 200 | $1.04 \cdot 10^{-3}$ | 0.98 |
| 3A | 250 | $1.33 \cdot 10^{-3}$ | 0.90 | 3A | 250 | $2.77 \cdot 10^{-3}$ | 0.94 |
| 3A | 300 | $1.40 \cdot 10^{-3}$ | 0.87 | 3A | 300 | $4.00 \cdot 10^{-3}$ | 0.78 |
| Silica gel | 200 | $1.35 \cdot 10^{-2}$ | 0.97 | Silica gel | 250 | $2.16 \cdot 10^{-2}$ | 0.86 |
| Silica gel | 250 | Non-adsorbable | | Silica gel | 300 | $4.55 \cdot 10^{-2}$ | 0.60 |
| Silica gel | 300 | Non-adsorbable | | Silica-alumina | 200 | $2.83 \cdot 10^{-3}$ | 0.97 |
| Silica-alumina | 200 | $2.60 \cdot 10^{-4}$ | 0.99 | Silica-alumina | 250 | $7.32 \cdot 10^{-3}$ | 0.92 |
| Silica-alumina | 250 | $3.20 \cdot 10^{-3}$ | 0.64 | | | | |
| Silica-alumina | 300 | $4.66 \cdot 10^{-3}$ | 0.67 | | | | |

3.2 Simulation of a PSA reactor for methanol production in a SERP process.

A SERP process based on a PSA reactor has been simulated, with the adsorbents studied before, using the PSASIM® software (Delgado *et al* 2017). The interior of the PSA reactor consists of a mixture of the adsorbent and a commercial Cu/ZnO/Al₂O₃ catalyst, which kinetic model has been taken from bibliography (Bussche and Froment, 1996, Graaf *et al*, 1986). The PSA cycle used in the simulations consist of the following steps: 1) reaction/adsorption 2) rinse/adsorption 3) blowdown 4) backfill (Carvill *et al*, 1996, Ruthven *et al*, 1994)

The results of the simulation and the operation conditions are presented below in Table 6. These operation conditions are settled as reference conditions to compare the performance of the adsorbents but are not optimized for each adsorbent and case of study.

Table 6: Operation conditions and results of the PSA reactor simulation

| Adsorbent | CO ₂ conversion (%) | CH ₃ OH selectivity (%) | CH ₃ OH productivity (mol·m ⁻³ ·s ⁻¹) | CH ₃ OH recovery (%) |
|----------------|--------------------------------|------------------------------------|---|---------------------------------|
| 3A | 42.32 | 67.03 | 0.0616 | 50.74 |
| Silica gel | 40.84 | 67.81 | 0.0580 | 38.58 |
| Silica-alumina | 39.54 | 70.91 | 0.0489 | 36.79 |

*Reference conditions: Temperature = 250 °C, high pressure = 50 bar, low pressure = 10 bar, mass catalyst fraction = 0.5, feed superficial velocity = 0.05 m·s⁻¹

Table 6 shows that using whatever adsorbent in the SERP process, CO₂ conversion and methanol selectivity are improved. The equilibrium values calculated without adsorbent at 50 bar and 250 °C, using the kinetic model cited before, are 24.4% and 63.8% for CO₂ conversion and methanol selectivity respectively. The conversion and selectivity to methanol are very similar to all the adsorbents, even so, methanol productivity is quite higher for 3A zeolite and the recovery increase notably with this adsorbent, which can be attributed to its higher water and methanol adsorption capacity.

4. Conclusions

Adsorption of water and methanol have been studied on 3A zeolite, silica gel and silica-alumina through pulse experiments. Henry's equilibrium adsorption constant and reciprocal diffusion time constant have been determined. 3A zeolite has greater affinity for water than silica-alumina and silica gel as it is observed in the pulse experiments and in the higher values of Henry's constant. Methanol is not adsorbed on silica-gel at high temperatures (>200°C), and it is adsorbed stronger on silica-alumina than 3A zeolite.

Diffusional reciprocal time constants shows that methanol diffusion is slower than water due it higher kinetic diameter. Also, water diffusional parameters are lower for 3A zeolite than silica-alumina and specially silica gel. It is caused by the smaller micropore size of zeolite and the higher interactions with the cations.

Once determined the equilibrium and diffusional parameters, a PSA reactor has been simulated. In all cases, the equilibrium conversion and selectivity are improved by using the SERP process for carbon dioxide hydrogenation to methanol. Moreover, 3A zeolite presents the best performance showing higher methanol productivity (0.0616 mol·m⁻³·s⁻¹), and a significant greater recovery of methanol (50.74%) than the other adsorbents.

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