

Intrinsic reaction kinetics for CO₂ reacting in supported amine sorbents

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Highlights

- Development of method to determine intrinsic reaction kinetics for CO₂ on amine sorbents
- Intrinsic reaction kinetics determined for a supported primary amine sorbent

1. Introduction

Application of carbon capture from flue gases of power plants is technically feasible. However, applying state-of-the-art technology will increase the price of electricity by 30-60% [1]. Switching the conventional aqueous amine solvent by solid amine sorbents will significantly reduce both the capital and operating expenditure. Savings in operational costs are mainly due to a lower heat capacity of the sorbent and avoiding solvent evaporation. The capital savings are related to higher volumetric productivities, as found experimentally [1]. The higher productivities are partly related to fast gas-solid mass transfer (in comparison with gas-liquid mass transfer) and, apparently, a fast chemical reaction with active groups inside the sorbent.

In this work, a study is reported to determine the sorption kinetics for a typical amine sorbent. In literature often overall apparent kinetic parameters are determined by fitting breakthrough curves [2–4] or an analytical solution [5]. This study will describe –for the first time – a method of measuring intrinsic reaction kinetics of solid amine sorbents and results for a primary amine sorbent. Challenge in this work is to unravel the apparent kinetics by taking into account diffusional transport, reaction kinetics, heat of reaction, heat transport and the reversibility of the reaction.

2. Methods

The experimental method is based on pressure swing adsorption. The sorbent is loaded in a so-called pancake reactor where a monolayer of sorbent is in contact with the actively heated bottom plate of the reactor. The sorbent is heated to 80°C and the pressure is reduced below 1 mbar by a vacuum pump in order to remove all adsorbed components from the sorbent. The buffer vessel (V-400,85mL, Figure 1) is filled with grade 5.3 CO₂ and the sorbent is cooled to the desired temperature. Next, the pressure in the reactor is set by a pressure control valve and the adsorption rate is monitored by the pressure indicator in the buffer vessel. By using reduced absolute pressure and pure CO₂ external mass transfer limitations have been eliminated.

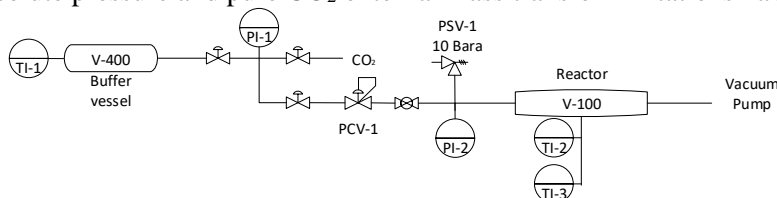


Figure 1. Flowsheet of the setup, including the CO₂ buffer vessel (V-400) and the pancake reactor (V-100)

3. Results and discussion

A first set of experiments has been performed at a pressure of 100mbar CO₂. Figure 2 shows that the initial reaction rate is indeed very high and 50% of the equilibrium loading is reached within the first 15 seconds. However, it should be noticed that the reactor pressure is also still increasing within this 15 seconds. Therefore, the experimental adsorption rate could be partly supply limited. This effect will be analyzed in more detail in the coming months with the purpose to eliminate any supply limitations in the experiment.

Furthermore, in Figure 3 can be seen that the reactor temperature is not increasing during the experiment, even though the adiabatic temperature rise of the sorbent is 40°C per mole of CO₂ adsorbed. As the sorbent has a low thermal conductivity, heat effects inside the particle might influence the experimental results. A particle model is constructed to analyze internal heat effects as well as any internal mass transport limitations.

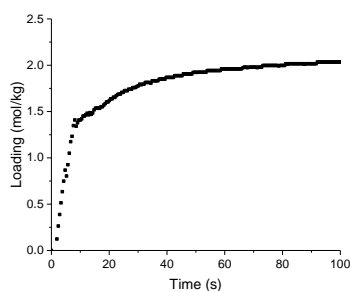


Figure 2. Loading curve for a typical experiment: 100mbar CO₂ and 40°C.

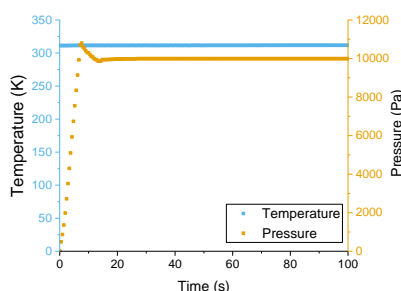


Figure 3. Reactor pressure and temperature for a typical experiment

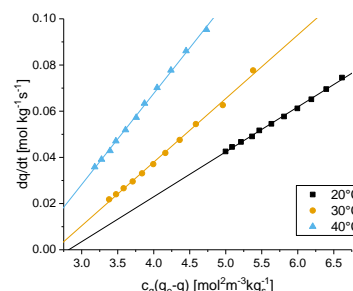


Figure 4. Kinetic constants at 100mbar CO₂ using $dq/dt = k_{ads} C_g (q_e - q)$.

The intrinsic reaction rate is found by linearization of the reaction rate equation ($dq/dt = R_a = k_{ads} C_g (q_e - q)$) proposed in literature [1]. By plotting the experimental adsorption rate against the bulk gas concentration times the number of free site ($q_e - q$) the kinetic constant k_{ads} can be found, see Figure 4. The results shown in Figure 4 are fitted to the first 10 data points with constant pressure ($t > 10s$). However, it should be noted that the loading was already above 1.25 mole/kg (above 50% of the equilibrium capacity) for all experiments which might influence adsorption rates. The kinetic constant at 20°C for the range of 50%-90% capacity is in the same order of magnitude as the value presented by Veneman et al. [1]. The found activation energies are in the range of 25-35kJ/mole which are in line with values presented for aqueous amines [6]. Note that, as shown in Figure 2, the adsorption rate is significantly larger in the first 10 seconds. Therefore, transfer limitations (of mass or heat) might be present. This shows the importance of the removal of supply limitations and analyzing the heat and mass transfer effects via the particle model, which is currently ongoing and will be reported in the full manuscript.

4. Conclusions

A method for the measurement of intrinsic kinetics of CO₂ adsorption on solid sorbents is shown. First experiments show that the initial reaction kinetics are very fast. For sorbents loaded for 50-90% the reaction kinetics are in line with apparent sorption kinetics found in literature. The activation energy is in the range of activation energies presented in literature of liquid amine solvents. At the moment, activities are ongoing to exclude any influence of mass and heat transfer limitations on the derived chemical reaction kinetics for the initial stage of reaction (0-50% loading).

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