The cyclic adsorption-desorption of CO_2 on KIT-6 and Ni/KIT-6 studied by Temperature-Programmed Desorption

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INTRODUCTION

Carbon dioxide is the primary greenhouse gas, responsible for about three-quarters of emissions. It can linger in the atmosphere for thousands of years. Thus, the research directions were directed towards obtaining materials with CO_2 adsorption-desorption properties [1-4].

This study investigates the cyclic adsorption-desorption of CO_2 on KIT-6 sil and Ni/KIT-6 sil by Temperature-Programmed Desorption. The samples were evaluated by the adsorption of CO_2 and its temperature-programmed desorption TPD. Thermal stability was investigated by TGA and DTA methods.

The adsorption of CO_2 and its temperature programmed desorption using thermogravimetry were studied for amino-functionalized molecular sieves at 40 and 60 °C.

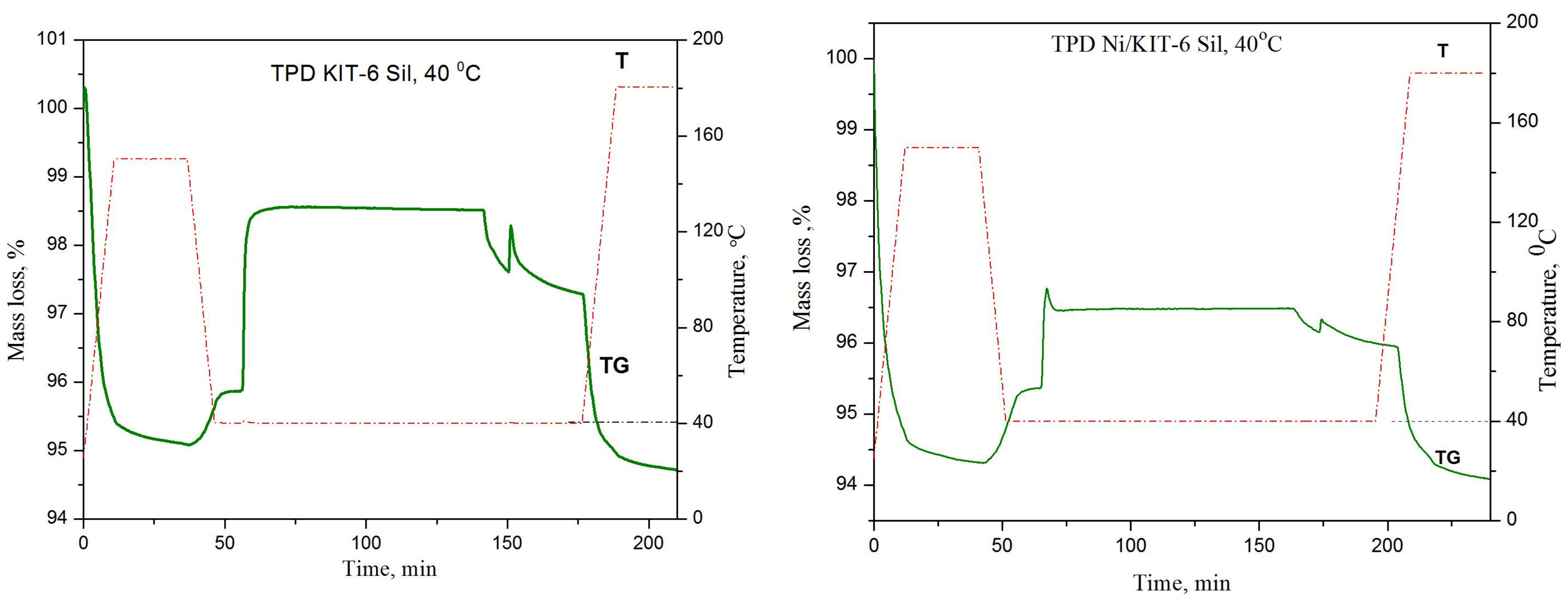
EXPERIMENTAL

KIT-6 mesoporous silica was synthesized following the method described by *Kleitz et al.* [5].

Modified KIT-6 denoted as KIT-6 Sil was prepared as follows: 0.5 g of KIT-6 was dispersed in 50 ml toluene and 0.79 ml of 3-aminopropyl triethoxysilane was added later to the solution. The above mixture was refluxed at 110 °C for 12 h, and then the solid was collected by filtration, washed by ethanol and air-dried at 80 °C. The grafting reaction was carried out at 110 °C for 5 h. After filtration and drying, the absorbents were obtained as white solids.

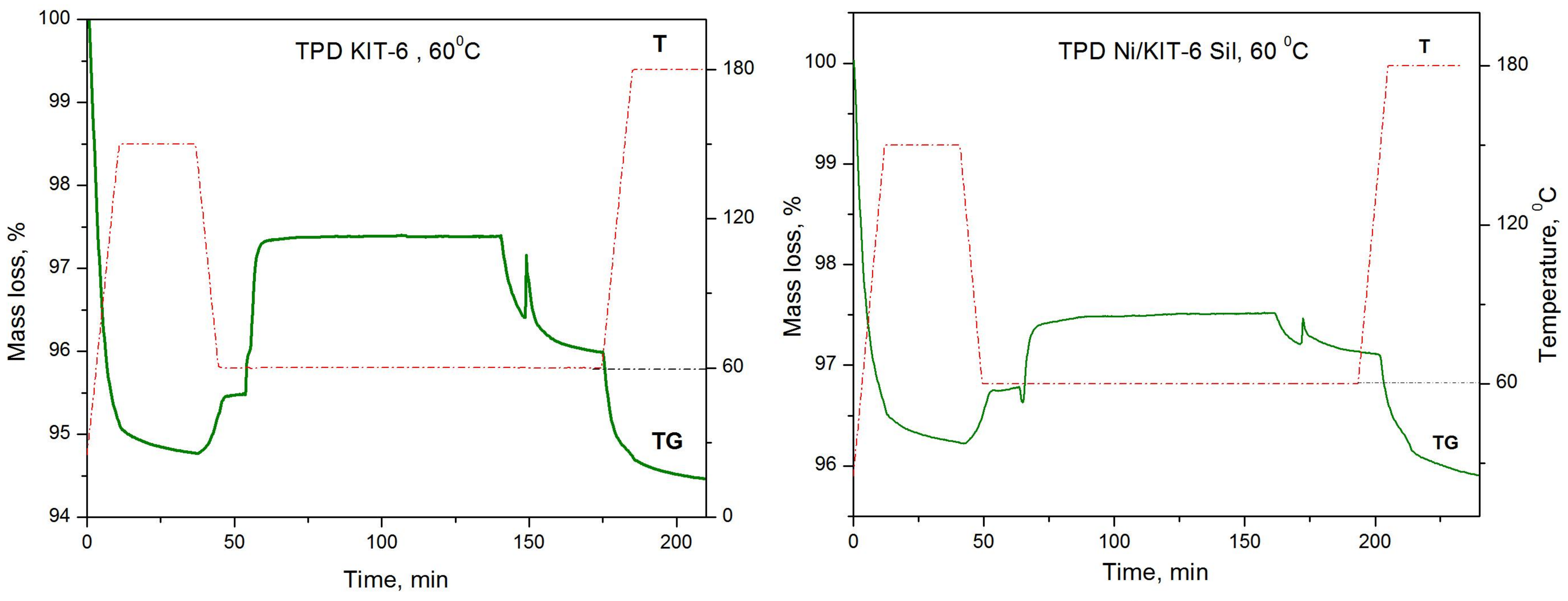
The Ni/KIT-6 Sil was prepared by addition $Ni(NO_3)_2 \cdot 6H_2O$ by wet impregnation.

RESULTS AND DISCUSION



(a) (b)

Fig.1. CO_2 adsorption-desorption steps of functionalized sample KIT-6 Sil (a) and Ni/KIT-6 Sil (b) with an isotherm at 40°C



(a) (b)

Fig. 2. CO_2 adsorption-desorption steps of functionalized sample KIT-6 Sil (a) and Ni/KIT-6 Sil (b) with an isotherm at 60°C

The adsorption capacity of mesoporous silicates KIT-6 Sil and Ni / KIT-6 Sil at different temperatures is given by **Fig. 1**. and **Fig. 2**. It is observed that the adsorption capacity decreases by increasing temperatures, a specific phenomenon of physiosorption.

The efficiency of the adsorbent (measured in mmol CO_2/mmol NH_2) , was calculated from the mass loss during the desorption step (**Table. 1**). The adsorption efficiency is an important parameter, since it offers valuable information about the CO_2 adsorption performance of the amino incorporated groups.

Table 1. The amount of the captured CO_2 using KIT – 6 Sil and Ni/KIT-6 Sil

	Sample	Temp [ºC]	n_{CO2}/g SiO_2 [mmol/g SiO_2]	n_{CO2}/n_{NH2} [mmol/mmol]
1	KIT-6 Sil	40	2.23	0.512
2	Ni/KIT-6 Sil	40	1.63	0.188
3	KIT-6 Sil	60	1.31	0.294
4	Ni/KIT-6 Sil	60	1.07	0.115

Nickel-based catalysts have been extensively studied in the last years. Nickel is more readily available, active and relatively inexpensive compared to noble metals, i.e. Pt, Pd, Ru, Rh and Ir. [6].

The stability of the adsorbent adhesive during prolonged operation for CO_2 capture is an important factor.

Nine cycles of CO_2 adsorption / desorption measurement were performed on grafted samples with the highest CO_2 absorption at 40 ° C, which means that KIT-6 Sil can be used to assess their potential for cycling. Every test was pretreated in N_2 flowing at 120 °C for 10 minutes, then cooled up to 40 °C adsorption temperature and exposed to 30% CO_2 in N_2 for 40 min. CO_2 desorption was per- formed by heating the sample to 120 °C with 10 °C / min.

Temperature is the dominant factor in the adsorption-desorption cycles of the absorbent functionalized with amine due to chemical interactions between CO_2 and amine.

The cycles of CO_2 adsorption–desorption of functionalized sample KIT-6 Sil are shown in **Fig. 3**. and Ni/KIT-6 Sil are show **Fig. 4.**

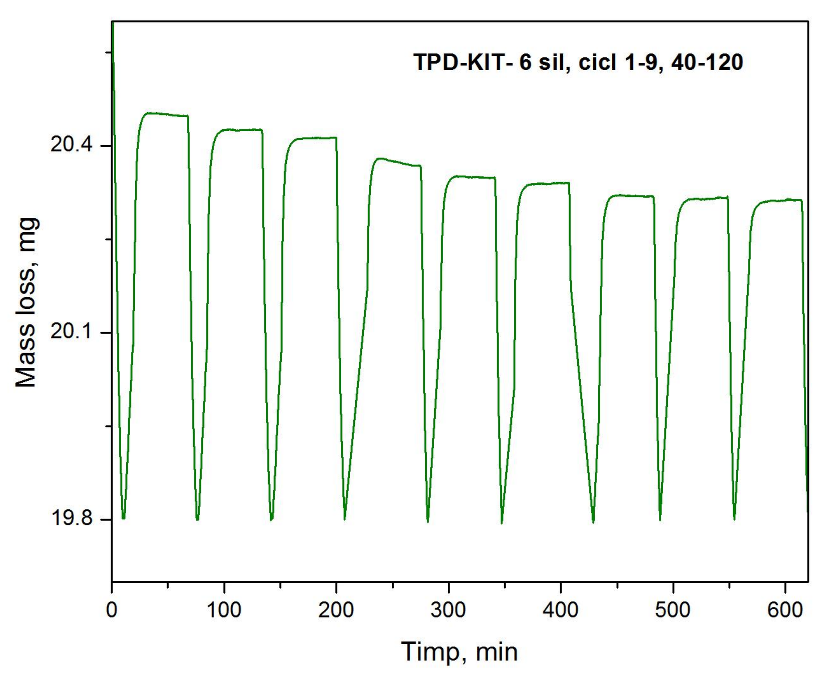


Fig. 3. Cycles of CO_2 adsorption–desorption of functionalized sample KIT-6 Sil with adsorption at 40 °C

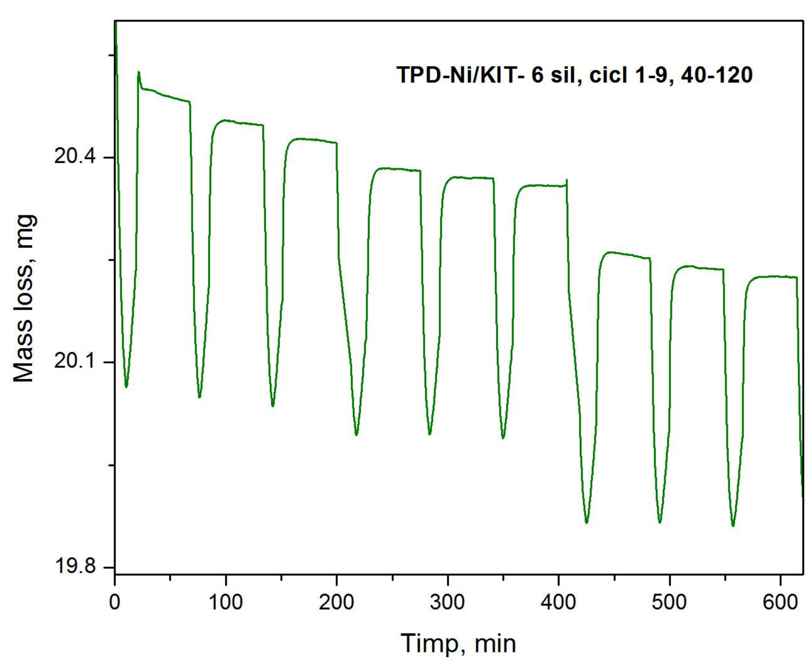


Fig. 4. Cycles of CO_2 adsorption–desorption of functionalized sample Ni/KIT-6 Sil with adsorption at 40 °C

Examination of the adsorption/desorption cycles data shows that the performance of the KIT-6 Sil adsorbent is relatively stable, with the low decrease in the adsorption capacity (0.10 mmol/g of CO_2, i.e., 2.23% of initial capacity) after nine adsorption–desorption cycles and Ni/KIT-6 Sil with the low decrease in the adsorption capacity. (0,30 mmol/g of CO_2, i.e., 1,63% of initial capacity) after nine adsorption–desorption cycles.

CONCLUSIONS

- The preparation by grafting of amino-functionalized KIT - 6 molecular sieve by using a silane coupling agent 3-aminopropyl triethoxysilane which was first grafted on the KIT – 6.
- The CO_2 adsorption/desorption of KIT-6 Sil showed that both the adsorption capacity (mmoleCO_2/g adsorbent) and the efficiency of amino groups (moleCO_2/mole NH_2) depend on the temperatures. The best results were obtained for KIT-6-Sil at 40 °C.
- After nine adsorption–desorption cycles, the performance of the KIT-6 Sil adsorbent is relatively stable, with a low decrease in the adsorption capacity. In the case of Ni / KIT-6 Sil showed a lower adsorption capacity than KIT-6- Sil.

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