



Article Ni and Ce Grafted Ordered Mesoporous Silica KIT-6 for CO₂ Adsorption

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Abstract: In this study, the Ni/KIT-6 and Ce/KIT-6 materials were prepared through the impregnation method and then amino-functionalized materials were obtained by the grafting of an aminosilane coupling agent 3-aminopropyl triethoxysilane (APTES). The samples were characterized by thermogravimetric analysis (TGA-DTA), Fourier transform infrared spectroscopy (FT-IR), X-ray diffraction, scanning electron microscopy (SEM) and nitrogen adsorption at 77 K. The study of CO₂ adsorption-desorption on prepared materials was investigated using thermogravimetric analysis (TGA-DTA) coupled with mass spectrometry (MS). The influence of metal oxides on the performance of CO₂ adsorption on functionalized mesoporous silica was presented. The results showed that doping the molecular sieve with cerium oxide can significantly increase the adsorption capacity of the amino-functionalized KIT-6. As the CO_2 adsorbents were prepared by functionalization through grafting with APTES, the amount of amine loading is one of the important factors which improves CO_2 adsorption capacity. Additionally, CO_2 adsorption performance depends on the textural properties and the temperature used for the adsorption process. The maximum adsorption capacity of Ce/KIT-6 Sil is 3.66 mmol/g, which is 2.4 times higher than Ni/KIT-6 Sil. After the nine cycles of cyclic CO₂ adsorption/desorption, the Ce/KIT-6 Sil still had higher adsorption capacities, indicating their good cyclical stability.

Keywords: molecular sieves; KIT-6; amine; CO₂; adsorption-desorption

1. Introduction

Today, global warming as a result of the unprecedented increase of carbon dioxide emissions, which are caused mainly through the combustion of fossil fuels, is a severe environmental issue. Considerable research efforts have been carried out to capture CO_2 , so in the short term it can be considered a promising way to reduce CO_2 emissions. Thus, the research directions have been aimed at obtaining materials with improved features for the CO_2 adsorption–desorption process [1–3]. Since the capture of carbon dioxide on a global scale can result in large quantities of gas, its prevention has been attempted, and one of the more effective methods is synthetic CO_2 hydrogenation in order to obtain combusted hydrocarbons and the CO_2 reforming of methane [4,5].

In addition to the mesoporous materials MCM-41, MCM-48 and SBA-15, considerable attention has been given to the mesoporous KIT-6 sieve by researchers in the fields of catalysis, adsorption–desorption or ion exchange. The mesoporous KIT-6 sieve is characterized by an easy synthesis method, its symmetric three-dimensional cubic structures I*a3d*, an average pore diameter of 4–12 nm and wall thickness of 4–6 nm [6,7].

The functionalization of the mesoporous sieves MCM-41, MCM-48, SBA-15 and KIT-6 with amines for CO_2 capture has been studied for a long time due to the high structural stability of the pore volume and adjustable pore dimensions [8–10].

The structure of KIT-6 is clearly superior to the other mesoporous supports due to the gyroid two-dimensional networks with pores that provide direct access to active sites,



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Copyright: © 2022 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). which facilitates insertion or diffusion inside the pores, thus allowing more reactants and precursor solutions through pore channels [11,12].

To improve the efficiency of the adsorption properties but also, implicitly, the catalytic properties of metal oxide materials that have applications in many industrial processes, researchers have attempted to immobilize metal oxide nanoparticles on porous supports with a large surface area and pore volume, such as zeolites or mesoporous sieves [13–18].

Sun et al. studied the method of increasing the adsorption capacity of CO_2 and cyclic stability for CaO by impregnating CaO into a mesoporous silica structure, namely KIT-6 [19]. The prepared CaO supported KIT-6 has a good cycling stability of over 10 cycles of carbonation/calcination. The performance increase for CO_2 capture is due to the interaction between the structure of KIT-6 and active CaO, through the formation of interfacial mixed oxides, which enhanced the sintering-resistant properties of CaO.

Puertolas et al. studied the cerium oxide supported on mesoporous KIT-6 prepared by the impregnation of $Ce(NO_3)_3$ on siliceous KIT-6. These cerium oxide doped materials Ce-KIT-6 have been tested as catalysts for the total oxidation of naphthalene and display excellent activity, remarkably higher than commercial CeO_2 [20].

The advantages of mesoporous CeO_2 materials for glycerol conversion were demonstrated by Ruiz et al. [21], showing that the acidic properties of CeO_2 proved to be a determining factor for the selectivity towards acetol and acrolein. Mahfouz et al. [22] investigated the effect of the promotion of cerium on Ni and/or Ru KIT-6 mesoporous catalysts for the CO_2 reformation of methane, with the catalysts being synthesized using the wet impregnation technique.

The low cost and wide range of applications have led to detailed studies of nickelbased catalysts [23,24]. In order to obtain a high catalytic activity, studies were conducted on the production of nickel nanoparticles, controlling the dimensions at the nanometer scale using various synthesis methods [25–29]. These catalysts have high catalytic activity and are prepared by simple methods, making them appropriate for different applications, such as the gas cleaning of polycyclic aromatic hydrocarbons from gas exhaust. Additionally, they could be used as supports for different metals and oxides which are catalytically active and in other applications for the protection of the environment from harmful emissions.

In the present study, materials containing Ni and Ce were prepared by impregnating the hydrothermally prepared mesoporous KIT-6 support with 30 wt% total metal oxide content. Then amino-functionalized materials were obtained by the grafting of an aminosilane coupling agent 3-aminopropyl triethoxysilane (APTES) on previously prepared samples.

The three-dimensional mesoporous structure of the KIT-6 support and Me/KIT-6 (Me= Ni and Ce) was confirmed by small angle X-ray diffraction (SAXRD) patterns. N₂ adsorption–desorption analysis results confirmed that the mesoporous structure of KIT-6 and Me/KIT-6 was preserved after metal oxide loading. The structural bonds of KIT-6 support and prepared amino-functionalized materials were determined by Fourier transform infrared (FT-IR) spectroscopy. As far as we know, there are no reports available in the literature regarding Ni/KIT-6 and Ce/KIT-6 composites modified with APTES used for CO₂ adsorption–desorption studies. Compared with other mesoporous silica composites, the CO₂ adsorption–desorption experiments clearly reveal that Ce/KIT-6 composites modified with APTES in particular are very efficient adsorbents.

The CO₂ adsorption capacity and amine efficiency for all prepared amino-functionalized materials were measured by CO₂ adsorption/desorption experiments at adsorption temperatures of 40, 50, 60 and 70 °C, using thermogravimetric analysis. Some representative samples from studied amino-functionalized materials were also tested for stability and recyclability during prolonged operation to justify their consistency for practical applications.

2. Results and Discussion

2.1. Physical–Chemical Characterization

The low angle XRD patterns of KIT-6, Ni/KIT-6 and Ce/KIT-6 are shown in Figure 1 and to large angle in Figure 2. It can be seen that KIT-6, Ni/KIT-6 and Ce/KIT-6 exhibit

similar characteristic peaks, which suggest and confirm that the cubic structure Ia3d specific to the mesoporous sieves of KIT-6 type was still maintained after the addition of Ni- and Ce-active metals. Anyway, in the case of Ni/KIT-6 and Ce/KIT-6, the peaks were also retained but the intensities decreased.



Figure 1. Small-angle XRD patterns of (a) KIT-6, (b) KIT-6 Sil and (c) Me/KIT-6.



Figure 2. Large-angle XRD patterns of Ni/KIT-6 and Ce/KIT-6.

Figure 2 shows the large-angle XRD patterns of Ni/KIT-6 and Ce/KIT-6 materials. The characteristic diffraction peaks observed at $2\theta = 44.3^{\circ}$ and 52.5° were indexed as the plane (111) and (220) of the face-centered cubic NiO (JCPDS No.04-0850) [22] and CeO₂ [21] at $2\theta = 28.8^{\circ}$, 33.1° , 47.5° and 56.4° peaks, corresponding to the (111), (220), (311) and (200) planes of cerium oxide spacegroup Fm3m (225), with cubic fluorite structure (JCPDS No. 34–0394).

The N₂ adsorption–desorption isotherms of KIT-6 support and metal oxideimpregnated materials are the type IV hysteresis loop, which, according to the IUPAC classification, is the indication of a mesoporous structure (Figure 3). It could be observed a sharp increase in volume adsorbed at $p/p_0 = 0.5$ –0.8 is characteristic of the highly ordered pores of composites. Even after metal oxide loading, the preservation of mesoporous structure was confirmed by XRD and N₂ adsorption–desorption analyses.



Figure 3. Nitrogen adsorption–desorption isotherms and the pore size distribution of KIT-6 and KIT-6 Sil (**A**), Ni/KIT-6 and Ni/KIT-6 Sil (**B**) and Ce/KIT-6 and Ce/KIT-6 Sil (**C**).

As can be seen from Table 1, the largest surface area ($S_{BET} = 813 \text{ m}^2/\text{g}$) and pore volume (Vp = 0.99 cm³/g) were recorded for the KIT-6 support. The specific surface areas and pore volumes decreased, respectively, to 649 m²/g and 0.49 cm³/g for Ce/KIT-6 and 551 m²/g and 0.65 cm³/g for Ni/KIT-6. This is an anticipated consequence of pore filling during the impregnation process.

The pore parameters of amino-functionalized molecular sieves reveal that the surface areas of KIT-6 Sil, Ni/KIT-6 Sil and Ce/KIT-6 Sil decreased after modification with amino-silane coupling agent 3-aminopropyl triethoxysilane. The reduction in surface areas can be attributed to the increase in the agglomeration of silica particles and/or the occupation of pores after modification with APTES.

No.	Sample	Specific Surface Area (m²/g)	Pore Volume BJH _{Des} (cc/g)	Average Pore Diameter BJH _{Des} (nm)
1	KIT-6	813	0.991	7.867
2	KIT-6 Sil	561	0.950	5.462
3	Ni/KIT-6	551	0.650	4.723
4	Ni/KIT-6 Sil	260	0.395	5.666
5	Ce/KIT-6	649	0.490	4.896

Table 1. Textural properties of KIT-6, Me/KIT-6 and amine-grafted samples.

As can be seen in Figure 4, the FT-IR spectra of all the samples display three bands at 461, 803, and 1075 cm^{-s}, which are typical for Si-O-Si bands and are related to the presence of a condensed silica network. The adsorption peaks at 461 cm^{-m}, 803 cm^{-m8} and 1075 cm^{-md} are the bending vibration peak and the symmetric and asymmetric stretching vibration peaks of Si-O-Si bonds in the KIT-6 network [28].







Figure 4. FTIR spectra of parent KIT-6, KIT-6 Sil, Ce/KIT-6 Sil and Ni/KIT-6 Sil (**a**) and detailed spectra in the intervals of interest (**b**,**c**).

In order to confirm the presence of the APTES in the amino-functionalized molecular sieves, the FT-IR spectra were recorded in the range 500–4000 cm^{-a} (Figure 4). In the APTES-grafted materials, the peaks at 1383 cm⁻⁽ and 1547 cm^{-a}, representing the $-NH_2$ and -NH groups associated with the materials surface [16]. The broad peak at around 3734 represents the -OH stretching vibrations, and its intensity is lower for amino-functionalized materials than for the parent KIT-6. The other peaks at 2941 cm^{-o} and 1635 cm^{-a} represent the asymmetric deformation of CH₂ groups present in APTES and the physically adsorbed water [14].

The Si-O-Si symmetric stretching vibrations of Ni/KIT-6 and Ce/KIT-6 materials presented a slight shift toward lower wavenumbers in comparison with KIT-6, which was probably because Ni and Ce species were introduced into the 3D-mesopores of KIT-6.

Scanning electron micrographs images were used to analyze the morphology of the KIT-6, KIT-6 Sil and Ni/KIT-6 Sil particles (Figure 5). The picture of KIT-6 shows that the particles appear to be spherical due to the aggregation of the fine threads of KIT-6. It can be seen that the spherical morphology is modified by the introduction of APTES after amine functionalization, as the threads are dispersed and thus destroy the spherical morphology [14,30]. From the EDX spectrum it was confirmed that Ni and Ce elements have 30% loading.



Figure 5. SEM micrographs images of the KIT-6 and KIT-6 Sil particles.

2.2. The Adsorption-Desorption Process CO₂

The adsorption–desorption process of CO₂ was studied for amine-grafted KIT-6 Sil, Ni/KIT-6 Sil and Ce/KIT-6 Sil adsorbents. It should be mentioned that non-functionalized materials were not active for CO₂ capture. The CO₂ adsorption capacity of the adsorbent in mmol of CO₂ per gram of the adsorbent was determined from the mass gain of the sample in the adsorption process step (Figures 6a and 7). The steps of pre-treated samples during adsorption–desorption processes are: first, each sample was pre-treated in flowing N₂ at 150 °C (1/2 h) and temperature is then decreased to the desired adsorption temperature (40, 50, 60, 70 °C) and held there for 30 min under N₂ flow. Following this, the sample was exposed to the adsorption process is ended, the samples are maintained for another 30 min in N₂ flow in order to remove the physisorbed CO₂ from the sample.



Figure 6. CO_2 adsorption–desorption steps of functionalized samples KIT-6 Sil with an adsorption isotherm at 40–70 °C (**A**) and MS for KIT-6 Sil composites at 40 °C (**B**).



Figure 7. CO_2 adsorption–desorption steps of functionalized samples KIT-6 Sil (a), Ni/KIT-6 Sil (b) and Ce/KIT-6 Sil (c) with an adsorption isotherm at 40 °C.

The desorption step of the chemisorbed CO₂ from the amine-grafted materials was carried out from the adsorption temperature until 180 °C, with an increasing temperature rate of 10 °C/min and with an isotherm at 180 °C for 30 min. From the MS spectra (Figure 6b) the evolution of CO₂ (at a specific mass-to-charge ratio m/z = 46, 45, 44, 43, 23, 22, 16, 12 and 11) during all steps of the adsorption–desorption process was observed. During adsorption process, the MS signal of CO₂ increased and then remained relatively constant for 90 min when the sample was exposed to the adsorption gas mixture. After the CO₂ / N₂ mixture flow was stopped, the MS signal of CO₂ decreased when the samples were maintained for another 30 min in the N₂ atmosphere only (when the physisorbed CO₂ is removed from the sample). The CO₂ signal increased again during the desorption step of the chemisorbed CO₂ from the adsorption temperature until 180 °C (selected area in the Origin graphs of Figure 6b).

In Table 2, the amounts of the captured CO₂ on KIT-6 Sil adsorbent in the temperatures: 40, 50, 60 and 70 °C are shown. By increasing the temperature, the adsorption capacity and efficiently of amino groups decrease from 2.23 to 0.95 mmol CO₂/g SiO₂ and from 0.51 to 0.22 mmol CO₂/mmol NH₂, respectively. The best result was obtained for KIT-6 Sil at 40 °C, which means an adsorption capacity of 2.23 mmol CO₂/g SiO₂ and an efficiency of amino groups of 0.51 mmol CO₂/mmol NH₂. The levels of the capture CO₂ using KIT-6 Sil at different temperatures were calculated from mass gain during the adsorption step. The

same calculation method was applied to KIT-6 Sil, Ni/KIT-6 Sil and Ce/KIT-6 Sil at 40 °C by using the following calculation formulas:

$$m_{KIT-6 \ Sil(ini)} - m_{H_2O(mass \ loss \ total)} = m_{KIT-6 \ Sil(dry)} \tag{1}$$

$$n_{SiO_2} = \frac{m_{KIT-6\ Sil(dry)}}{60} \tag{2}$$

$$n_{CO_2} = \frac{m_{CO_2(ads)}}{44} \tag{3}$$

$$\frac{n_{CO_2}}{n_{SiO_2}} * 60 = x \ mmoleCO_2/gSiO_2 \tag{4}$$

$$\frac{n_{\rm CO_2}}{n_{\rm NH_2}} = x \ mmole \ CO_2 / mmole \ NH_2 \tag{5}$$

where $m_{KIT-6 \ Sil(ini)}$ is the initial mass of KIT-6; $m_{H2O(mass \ loss \ total)}$ is water loss until 150 °C; $m_{KIT-6 \ Sil(dry)}$ is the dried mass of KIT-6; and n_{CO_2} , n_{SiO_2} and n_{NH_2} are the number of mmole.

Table 2. The amounts of the capture CO₂ using KIT-6 Sil at different temperatures.

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No.	Sample	Temp (°C)	n _{CO2} /gSiO ₂ (mmol/gSiO ₂)	n _{CO2} /n _{NH2} (mmol/mmol)
1	KIT-6-Sil	40	2.23	0.51
2	KIT-6-Sil	50	1.76	0.40
3	KIT-6-Sil	60	1.31	0.29
4	KIT-6-Sil	70	0.95	0.22

The results are promising and showed that both the adsorption capacity (mmol CO_2/g adsorbent) and the efficiency of amino groups (mmol $CO_2/mmol NH_2$) depend on the temperature at which the experiment is performed. The rate of CO_2 adsorption reaches maximum values at 40 °C and then decreases at higher temperatures. One of the external energy sources that can activate the CO_2 molecule is temperature, among others such as light or electricity. So, the CO_2 adsorption capacity is influenced by the temperature as a result of the activation of the CO_2 molecule by facilitating charge transfer (mainly electron injection) processes to the molecule from, for instance, a catalytic surface. It is probably a question of equilibrium between the processes of CO_2 adsorption and desorption processes, respectively. Until 40 °C, the adsorption process in favorably influenced by the temperature; however, with increasing temperature, desorption is the process favored by the temperature.

The evolution of the CO_2 uptake with time and also its time derivative—which is taken as a measure of adsorption rate—is shown in Figure 8a,b for KIT-6 Sil, Ni/KIT-6 Sil and Ce/KIT-6 Sil adsorbents at 40 °C. The rate of CO_2 adsorption has reached the maximum values for Ce/KIT-6 Sil and then decreases for the other adsorbents.



Figure 8. Carbon dioxide adsorption and (**A**) carbon dioxide adsorption rate of KIT-6 Sil, Ni/KIT-6 Sil and Ce/KIT-6 Sil at temperatures between 40 $^{\circ}$ C (**B**).

The efficiency of the adsorbent (measured in mmol CO₂/mmol NH₂), was calculated from the mass loss during the desorption step of CO₂ (Table 3). CO₂ adsorption isotherms of functionalized samples at 40 °C showed that the adsorption capacity (mmol CO₂/g ads) is higher for KIT-6 Sil, while the efficiency of the amino group is higher for Ce/KIT-6 Sil (Figure 9). The higher adsorption capacity of Ce/KIT-6 Sil compared to Ni/KIT-6 Sil can be explained by the fact that the anchoring of nickel oxide on the inner surface of the 3D mesopores was more uniform and in depth, owing to its lower volume ($r_{Ni-O} = 2.112$ Å, Ni²⁺ =0.69 Å, O²⁻ = 1.40 Å and V_{NiO} = 74.97 Å³,) in comparation with that of cerium oxide ($r_{Ce-O} = 2.37$ Å, Ce³⁺ = 0.97 Å, O²⁻ = 1.40 Å and V_{CeO2} = 163.44 Å³). Additionally, a higher decrease in specific surface area and pore volume can be observed in the case of Ni/KIT-6 Sil with APTES grafting, which suggests that a part of the pores was blocked, hindering CO₂ access to the active sites.

Table 3. The amount of the captured CO₂ at 40 °C using KIT-6 Sil, Ni/KIT-6 Sil and Ce/KIT-6 Sil.

No.	Sample	Temperature (°C)	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	Ce/KIT-6 Sil	40	3.66	0.256



Figure 9. The adsorbed amounts of CO₂ by KIT-6 Sil, Ni/KIT-6 Sil and Ce/KIT-6 at 40 °C.

As we mentioned before, the modifications to the surface chemistry of the silica porous materials by incorporating basic organic group (various amines) and inorganic metal oxides increase CO_2 adsorption capacity. The interaction of CO_2 with amine groups in a water-free environment gives rise to carbamates, via the formation of the CO_2 -amine zwitterion, such as R-NH₂ ⁺COO. Overall, this reaction requires two amine groups per CO_2 molecule, i.e., adsorption efficiency, defined as the CO_2/N molar ratio, equal to 0.5. The chemical interaction between CO_2 and amine (APTES) can be expressed as follows:

$$R-NH_2 + CO_2 \rightarrow R-NH_2^+COO^-$$
(6)

$$R-NH_2+COO^- + R-NH_2 \rightarrow R-NHCOO^- + RNH_3^+$$
(7)

While the desorption of CO₂ and regeneration of grafted mesoporous silica is expressed as follows:

$$R-NH-COO^{-} + R-NH_{3}^{+} + Heat \rightarrow CO_{2} + 2R-NH_{2}$$
(8)

The formation of the carbamate involves equilibrium and is, therefore, reversible. It is also important to point out that, while this mechanism corresponds to chemisorption, physisorption also takes place at higher partial pressures [31,32].

Kishor and Ghoshal [7] investigated KIT-6 performance as absorbent, for CO_2 adsorption using APTES as silanization agent. At different amine loadings quantities of 1.43, 1.50 and 1.72 mmol/g, they obtained CO_2 adsorption capacities of 0.79, 0.90 and 0.83 mmol CO_2/g , respectively, and a stable performance after 10 cycles of adsorption– desorption. Muchan et al. [33] concluded that high surface area does not represent the only important factor that influences the adsorption capacity, as pore-size diameter and the level of amine loading must also be taken into account. The presence of mesopores channels in the KIT-6 structure provides a better mass transfer of CO_2 throughout the adsorbent, and APTES addition increases the CO_2 adsorbed quantity to 1.30 mmol CO_2/g . Analyzing the adsorption–desorption cycle it was found that the regeneration efficiency at 100 °C for unmodified KIT-6 and modified KIT-6/APTES adsorbent reaches 95%, representing good regenerability and stability. Yilmaz S.M. [34] studied KIT-6 mesoporous silica via partitioned cooperative self-assembly method. CO₂ adsorption-desorption experiments were performed at the different temperatures of 25, 75, and 100 °C, and the maximum adsorption capacity, 0.65 mmol/g, was achieved at the 25 °C adsorption temperature. J.A.A. Gibson et al. [35] investigated how the different amine loadings influenced the CO_2 uptake at 0.1 bar partial pressure on two different carbon porous materials. In the case of micro-AC, the results show that for optimum amine loading, the absorbed amount of CO_2 is 1.05 mmol g^{-1} . After four cycles of the adsorption-desorption experiment, the CO₂ efficiency proved to be relatively constant in case of both micro-AC and meso-AC studied materials.

The cycles of CO₂ adsorption–desorption of the functionalized sample Ce/KIT-6 Sil are shown in Figure 10. Nine cycles of CO₂ adsorption/desorption measurements were performed on grafted samples with the highest CO₂ absorption at 40 °C, which means that Ce/KIT-6 Sil can be used to assess their potential for recycling. Every test was pretreated in N₂ flowing at 120 °C for 10 min, then cooled to a 40 °C adsorption temperature and exposed to 30% CO₂ in N₂ for 40 min. CO₂ desorption was performed by heating the sample to 120 °C with 10 °C/min. An examination of the adsorption/desorption cycle data shows that the performance of the Ce/KIT-6 Sil adsorbent is relatively stable, with a low decrease in the adsorption capacity after nine adsorption–desorption cycles.



Figure 10. Cycles of CO₂ adsorption–desorption of functionalized samples Ce/KIT-6 Sil with adsorption at 40 $^{\circ}$ C.

3. Experimental

3.1. Preparation of sample

Mesoporous silica KIT-6 type was prepared according to the method described by Kleitz et al. [36]. First, 3.69 g triblock copolymer Pluronic P123 (EO₂₀PO₇₀EO₂₀) (Merck,

Darmstadt, Germany) was dissolved in 132 g distilled water and 6.75 g 37% HCl under vigorous stirring at 35 °C for 8 h. After total dissolution, 3.63 g n-butanol (\geq 95.0% Reactivul, București, Romania) was added to initial solution. The mixture remained under stirring at 35 °C for 1 h. Then, 7.92 g tetraethyl orthosilicate (TEOS, \geq 99% Merck, Darmstadt, Germany) was added to the homogeneous solution and stirred for 24 h at 35 °C. This mixture was transferred into a Teflon-lined stainless steel autoclave and heated at 100 °C for 24 h under static hydrothermal conditions. After hydrothermal treatment, the obtained solid material was separated by vacuum filtration and washed with a 2% HCl-ethanol solution. At the end, the samples were calcined in air atmosphere at 550 °C for 6 h to remove the organic template. The resulting sample was denoted as KIT-6.

The Ni/KIT-6 and Ce/KIT-6 materials with 30% Ni and Ce loading were prepared by the impregnation method. An adequate amount of Ni(NO₃)₂·6H₂O (Merck, Darmstadt, Germany) and Ce(NO₃)₃·6H₂O (Merck, Darmstadt, Germany), respectively, was dissolved in 0.6 mL deionized water. Then the support KIT-6 was added in the solution and the mixture was stirred for 2.0 h. Next, the formed slurry was further filtered to obtain dried powder samples, and the obtained powder samples were dried at 80 °C overnight. Finally, the powder samples were calcined at 250 °C for 4.0 h.

Modified KIT-6 and Me/KIT-6 denoted as KIT-6 Sil and Me / KIT-6 Sil (Me= Ni and Ce) were prepared as follows: 0.5 g of KIT-6 was dispersed in 50 mL toluene and 0.79 mL of 3-aminopropyl triethoxysilane (APTES, \geq 98.0% Merck, Darmstadt, Germany) was later added to the solution. The grafting reaction was carried out at 110 °C for 5 h. After filtration and drying, the absorbents were obtained as white solids.

3.2. Characterization of the Samples

The thermal analysis was carried out using a thermoanalyzer system Mettler TGA/SDTA 851/LF/1100 (Columbus, OH, USA) coupled with mass-spectrometry (MS). The measurements were conducted in dynamic atmosphere of air (50 mL/min), using the alumina plates crucibles of 150 μ L.

The FTIR absorption spectra were recorded with a Jasco 430 spectrometer (Tokio, Japan) in the spectral range 4000-400 cm⁻¹ range, 256 scans and resolution 2 cm⁻¹, using KBr pellets.

Powder X-ray diffraction data were obtained with a XD 8 Advanced Bruker diffractometer (Karlsruhe, Germany) using the CuK α radiation in the range $2\theta = 0.5 \div 50$ and $2\theta = 5 \div 600$. The specific surface areas of samples were calculated from the nitrogen adsorption–desorption isotherms using a Quantachrome instrument, Nova 2000 series (Boynton Beach, FL, USA).

Scanning electron micrographs (SEM) were recorded using Jeol JMS 6460 LV instrument (Tokio, Japan) equipped with an Oxford Instruments EDS (energy dispersive spectroscopy) analyzer.

The tests of CO₂ adsorption–desorption were obtained using the same thermogravimetric analyzer coupled with MS used for thermal analysis. High-purity CO₂ and 30% CO₂ in N₂ at 1 atm was used for the adsorption experiments, and N₂ was used as purge gas for CO₂ desorption. Each sample was pretreated in N₂ atmosphere at 150 °C, then was cooled to the desired adsorption temperature (40–70 °C) and finally exposed to 30% CO₂/N₂ (70 mL/min) for 90 min. The CO₂ adsorption capacity of the adsorbent in milligrams of CO₂ per gram of adsorbent was calculated from the weight gain of the sample in the adsorption process.

4. Conclusions

In this paper, the Ni/KIT-6 and Ce/KIT-6 materials with 30% Ni and Ce loading were prepared by the impregnation method. Then amino-functionalized materials were prepared by grafting of a silane coupling agent 3-aminopropyl triethoxysilane (APTES) on previous prepared samples.

The small angles of XRD showed that KIT-6 has a cubic structure, which indicates that the synthesis was successfully carried out. For the KIT-6-Sil sample a decrease in

peak intensity appears because the APTES was successfully grafted onto KIT-6. The FT-IR indicated that the KIT-6-Sil is present all the characteristic bands of amino-functional groups, confirming the grafting of amines onto KIT-6.

The CO₂ adsorption/desorption of KIT-6-Sil showed that both the adsorption capacity (mmolCO₂/g adsorbent) and the efficiency of amino groups (molCO₂/mol NH₂) depend on the temperature. The best results were obtained for KIT-6-Sil at 40 °C. Good CO₂ adsorption capacities were obtained for all prepared adsorbents, especially for the Ce/KIT-6 Sil sample. After nine adsorption–desorption cycles, the performance of the Ce/KIT-6 Sil adsorbent is relatively stable, with a low decrease in the adsorption capacity. In the case of the Ni/KIT-6 Sil adsorbent, a lower adsorption capacity was displayed. These studies show the potential of mesoporous silica for carbon dioxide capture. The ability of KIT-6 mesoporous sieves to change their structure with metal ions and organic functional groups opens the door for CO₂ adsorption.

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