The synthesis of zirconium and tetraethylenepentamine bi-functionalized TiO₂ for efficient CO₂ adsorption

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ABSTRACT

In the present work, zirconium-doped metal oxide of TiO₂(Zr_x) was synthesized and functionalized with different amount of tetraethylenepentamine (TEPA). The physical properties of the materials were tested using temperature-programmed desorption of NH₃, X-ray diffractometer, X-ray photoelectron spectrometer, scanning electron microscope, transmission electron microscope, energy dispersion spectrum, Inductively coupled plasma atomic emission spectroscopy, Infrared spectrometer, N₂ adsorption-desorption analyzer, energy dispersion spectrum and thermogravimetric analyzer. Zr species has a positive effect on the enhancement of the thermal stability and amine utilization. After the introduction of Zr, the decomposition temperature of TEPA is improved to 180°C. Over TEPA decorated adsorbents, physical adsorption and chemical adsorption occurs simultaneously. When the adsorption time is 75°C, CO₂ flow rate is 20 mL/min, the adsorbent of TEPA(40)/TiO₂(Zr_{0.1}) exhibit a remarkable amine utilization of 83.5%.

Keywords: Adsorption, CO₂, Tetraethylenepentamine, TiO₂, ZrOCl₂

1. Introduction

Carbon dioxide (CO₂) is one of important raw materials in C1 family [1, 2]. However, it is also a greenhouse gas blamed for the change of global climate [3-5]. Consequently, CO₂ mitigation is arousing wide concern all over the world. In CO₂ mitigation technologies, CO₂ adsorption with kinds of solid adsorbents receives a great attention because of the large adsorption capacity and less corrosion to the equipment [6]. For efficient adsorption, various organic amine functionalized adsorbents are developed, such as molecular sieves [7-10], carbon [11-14], metal-organic framework (MOFs) materials [15-18], polymer [19-21] and bimetal materials [22]. However, only a little amine based metal oxides are reported for CO₂ adsorption [23, 24].

Compared with the above materials, the most of metal oxides are difficult to be modified with organic amines on account of little functional species on the surface. Recently, heteroatom-doped molecular sieves, such as Zr-MCM-41 [25] and Zr-SBA-15 [26], were synthesized for the loading of organic amines. Over Zr-MCM-41, Zr species was introduced to the framework, leading to the form of Zr-O-Si bonds and the enhancement of Lewis acidity

[25]. Based on this, more amines were grafted on the pore channels, resulting in the improvement of thermal stability and CO₂ adsorption capacity. The similar phenomenon was also observed over poly-ethyleneimine loaded Zr-SBA-15 [26]. The interesting results inspire us to design a new type of metal oxide for the successful loading of organic amines and the improvement of CO₂ adsorption performance. Compared with amine decorated traditional supports, the adsorbents synthesized in this way may exhibit a high thermal stability and a large amine utilization.

The surface properties of titanium dioxide (TiO₂) could be modified by introducing heteroatoms to the framework [23, 24]. Therefore, heteroatom-doped TiO₂ could be used as the support for the synthesis of amine immobilized adsorbent. Zirconyl chloride octahydrate (ZrOCl₂·8H₂O), a Lewis acid with many electron holes, is a good candidate for the doping of Zr species [25, 26]. Besides, tetraethylenepentamine (TEPA) is a good agent for CO₂ adsorption based on the following properties: 1) TEPA has enough basic sites (N atoms) for the coordination with acidic sites (Zr species). 2) In small organic amines, TEPA has a high N content (37%) which is used as affinity sites in CO₂ adsorption. 3) Compared with poly-amine, TEPA with small volume and low viscosity is easier to be dispersed well on the surface of porous materials. 4) TEPA

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is easy to be dissolved in the traditional solvents compared with polyamine. In the present work, Zr-doped metal oxide of $\text{TiO}_2(\text{Zr}_N)$ was first successfully prepared and then functionalized with different amount of TEPA. The TEPA based adsorbents were tested for CO_2 adsorption under different conditions. In addition, the optimal adsorbent before and after CO_2 adsorption was characterized using Infrared spectroscopy to investigate the adsorption mechanism.

2. Experimental

2.1. Synthesis of TiO_2 , $\text{TiO}_2(\text{Zr}_N)$ and $\text{TEPA}(n)/\text{TiO}_2(\text{Zr}_N)$

3 g of polyethylene glycol (PEG) and a desired amount of $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ were dissolved in 100 g of deionized water, and 13.7 g of tetrabutyl titanate was then added dropwise to the above solution. After being stirred for 3 h at 70°C , the resulting mixture was hydrothermally treated at 180°C for 48 h. The product was washed thoroughly with deionized water and dried overnight at 120°C . Finally, PEG was removed through the calcination at 500°C for 6 h. The synthesized material is named as $\text{TiO}_2(\text{Zr}_N)$, where N stands for the molar ratio of Zr/Ti and the value is 0, 0.025, 0.05, 0.075, 0.1 and 0.125, respectively. When N is 0, no $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ is added to the solution. In this situation, TiO_2 was synthesized.

Tetraethylenepentamine (TEPA) functionalized $\text{TiO}_2(\text{Zr}_N)$ was synthesized by a wet impregnation method [22, 25]. Typically, a desired amount of TEPA was dissolved in 10 g of ethanol, and followed by the addition of 0.5 g of as-synthesized $\text{TiO}_2(\text{Zr}_N)$. The product was stirred for 3 h, and then dried at 120°C for 24 h. The synthesized adsorbents are labelled herein as $\text{TEPA}(n)/\text{TiO}_2(\text{Zr}_N)$, where n represents the mass ratio of $\text{TEPA}/\text{TiO}_2(\text{Zr}_N)$.

2.2. Characterization

Zr-doped TiO_2 adsorbents before and after functionalization with TEPA were characterized using: 1) temperature-programmed desorption of NH_3 (NH_3 -TPD) in order to analyze the acidic properties; 2) powder X-ray diffraction (XRD) in order to get the information of their phase; 3) X-ray photoelectron spectroscopy (XPS), inductively coupled plasma atomic emission spectroscopy (ICP), infrared spectroscopy (IR) and energy dispersive spectroscopy (EDS) to analyze their structure and element content; 4) N_2 adsorption-desorption to prove their pore structure; 5) thermogravimetric analysis (TGA) to illustrate their thermal stability. 6) scanning electron microscope and transmission electron microscope to characterize the morphology and the loading to amine.

2.3. CO_2 Adsorption Measurement

Although the concentration of CO_2 originating from many industrial processes is about 10–15%, the concentration of CO_2 in the atmosphere is much less than this standard value. Moreover, a great number of adsorbents exhibit a large decrease on CO_2 adsorption capacity as the diminution of CO_2 concentration. Therefore, a lower concentration of CO_2 is necessary for the promotion of CO_2 adsorption in atmosphere. For this purpose, 5% CO_2 and a lower concentration have been used [25, 27, 28].

Similar to our previous work, CO_2 adsorption experiment was

carried out using a Micromeritics AutoChem II 2920 Chemisorption analyzer [22, 25]. Typically, a desired amount of adsorbent was exposed to a pure argon flow at 100°C in order to remove the impurities adsorbed on the surface. Then, the gas flow was altered to 5% CO_2 for the adsorption. In this study, CO_2 adsorption capacity was achieved through the integration of the resulted breakthrough curve, which was obtained by detecting CO_2 concentration in the residual gas. After 10 min, the adsorbent was regenerated at 100°C in a stream of pure argon flow (100 mL/min). Similar to the previous work [29], CO_2 desorption in the system with enough inert gas of Ar is easier than that in the air. In this situation, the majority of CO_2 adsorbed in the surface of amine immobilized porous materials could be removed, leading to the regeneration of the adsorbent.

3. Results and Discussion

3.1. Characterization

3.1.1. NH_3 -temperature-programmed desorption (NH_3 -TPD)

Fig. 1 shows the NH_3 -TPD tested results of TiO_2 before and after the doping with Zr species. For all of the supports, the desorption peaks within 100 to 500°C are observed. In addition, the acidity increases first and then declines with the rise of Zr/Ti molar ratio. When the molar ratio of Zr/Ti is 0.1, the maximum surface acidity of 0.679 mmol/g is obtained, which is 1.87 times higher than that of TiO_2 without Zr species. According to the previous work [25, 26], the ratio of Zr/Si is very important in the adjustment of surface properties. When Zr/Ti ratio is less than 0.1, Zr species could be dispersed well in the framework of the support. The Lewis acidity increases with the rise of the Zr/Ti molar ratio. In this case, more and more amines react with the support, resulting in the increase of CO_2 affinity sites. As a result of this, CO_2 adsorption capacity is enhanced. When the Zr/Ti molar ratio is 0.1, the Lewis acidity reaches the maximum value, leading to the maximum amount of CO_2 adsorption capacity. Further increase of the Zr/Ti molar ratio causes a distortion of the TiO_2 network. In addition,

Fig. 1. NH_3 -TPD profiles of TiO_2 and $\text{TiO}_2(\text{Zr}_N)$.

the high Zr content results in the low ordering of the structure, even the collapse of the mesoporous structure. Because of these, less amines could be grafted on the support, leading to the decrement of CO_2 adsorption capacity. Therefore, Zr/Ti molar ratio of 0.1 is selected for the grafting of TEPA and good CO_2 adsorption performance.

3.1.2. Powder X-ray diffraction (PXRD)

Fig. 2 displays the XRD results of TiO_2 , $\text{TiO}_2(\text{Zr}_{0.1})$ and the modifier of TEPA(40)/ $\text{TiO}_2(\text{Zr}_{0.1})$. The diffraction pattern of TiO_2 is according to that of PDF#29-1360. The peaks at 25.339° , 27.488° , 30.807° , 37.933° , 48.011° , 54.203° , 55.710° and 63.414° are assigned to the crystals of (111), (110), (121), (131), (211), (231), (320) and (151) [30]. With the doping of Zr, the diffraction patterns does not change, indicating that the structure is preserved. However, the intensity of the (111) peak drops a lot. The (111) peak is a characteristic diffraction peaks of orthorhombic TiO_2 which is made up by Ti and O atoms. With the doping of Zr, part of Ti atoms in the lattice are replaced by Zr species, leading to the decrement of (111) peak intensity. Over $\text{TiO}_2(\text{Zr}_{0.1})$, no diffraction peak of ZrO_2 is detected, indicating that Zr species is dispersed well in the framework of TiO_2 . After the loading of 40% of TEPA, the intensity of the diffraction peaks decreased, which is possibly caused by the filling of TEPA. Besides, the peak shift of (110) plane from 27.488° to 27.446° is observed, which could be explained by the reaction between TEPA and the support [31].

Fig. 2. XRD results of TiO_2 , $\text{TiO}_2(\text{Zr}_{0.1})$ and TEPA(40)/ $\text{TiO}_2(\text{Zr}_{0.1})$.

3.1.3. Infrared spectroscopy (IR)

Fig. 3 reveals the IR images of TiO_2 , $\text{TiO}_2(\text{Zr}_{0.1})$ and TEPA(40)/ $\text{TiO}_2(\text{Zr}_{0.1})$. As seen, the peak at 663 cm^{-1} on TiO_2 is attributed to the Ti-O-Ti bond [30]. The peak moves to 568 cm^{-1} after the doping of Zr, which could be explained by the formation of Zr-O-Ti bond [32]. On $\text{TiO}_2(\text{Zr}_{0.1})$, the peak at $1,626\text{ cm}^{-1}$ is assigned to the bending vibration of physically adsorbed H_2O [30]. Compared with $\text{TiO}_2(\text{Zr}_{0.1})$, TEPA(40)/ $\text{TiO}_2(\text{Zr}_{0.1})$ shows some new peaks. The peaks: 1) at $3,276\text{ cm}^{-1}$ is assigned to N-H stretching vibrations [33]; 2) at $2,939\text{ cm}^{-1}$ and $2,826\text{ cm}^{-1}$ are attributed to the symmetric and

Fig. 3. FT-IR spectra of TiO_2 , $\text{TiO}_2(\text{Zr}_{0.1})$ and TEPA(40)/ $\text{TiO}_2(\text{Zr}_{0.1})$.

asymmetric stretching vibration of C-H [33, 34]; 3) at $1,667\text{ cm}^{-1}$ and $1,542\text{ cm}^{-1}$ are related to N-H bending vibration [33, 34]. 4) at $1,441\text{ cm}^{-1}$ and $1,368\text{ cm}^{-1}$ are associated with the deformation of C-H bond [34]. The IR results demonstrating that TEPA is successfully incorporated.

3.1.4. X-ray photoelectron spectroscopy (XPS) and inductively coupled plasma atomic emission spectroscopy (ICP)

Fig. 4 reveals the XPS survey scan results of TiO_2 , $\text{TiO}_2(\text{Zr}_{0.1})$ and TEPA(40)/ $\text{TiO}_2(\text{Zr}_{0.1})$. As seen in the full spectra, Ti and O are detected on TiO_2 , Ti, Zr and O species are detected on $\text{TiO}_2(\text{Zr}_{0.1})$. The appearance of C atom is related to the adsorbed CO_2 on the materials. Besides, Zr-O bonds at 181.9 and 184.3 eV are also observed in the spectra of Zr(3d) over $\text{TiO}_2(\text{Zr}_{0.1})$ (Fig. 4(c)) [35]. The results are in line with that of IR, suggesting that Zr atoms are successfully introduced to the framework of TiO_2 . After the loading of TEPA, the peaks at 181.9 and 184.3 eV shift to 181.3 and 183.7 eV , respectively. For $\text{TiO}_2(\text{Zr}_{0.1})$, the peaks at 181.9 and 184.3 eV are related to the formation of Zr-O bond. Besides, $\text{TiO}_2(\text{Zr}_{0.1})$ has an acidity of 0.679 mmol/g because of the introduction of Zr species. With the loading of TEPA, amine groups with lone-pair electrons react with Zr atoms. Therefore, the peaks shift are detected. In addition, the signals at 398.1 , 399.2 and 400.1 eV assigned to N-Zr, N-H and N-C bonds are detected over the modifier (Fig. 4(d)). The results are in accordance with the previous work [22], which is attributed to the reaction between Zr atoms coming from $\text{TiO}_2(\text{Zr}_{0.1})$ and N species originating from TEPA. The XPS results provide further evidence for the successful synthesis of $\text{TiO}_2(\text{Zr}_{0.1})$ and TEPA(40)/ $\text{TiO}_2(\text{Zr}_{0.1})$.

ICP and XPS are used in combination for the detection of elements content. First, the ICP result displays that the content of Zr and Ti are 0.4567 and 2.417 g/L , respectively. Therefore, Zr/Ti molar ratio is 0.0992 . The result is very close to the theoretical value of 0.1 , demonstrating that Zr has been successfully introduced to $\text{TiO}_2(\text{Zr}_{0.1})$. Then, the XPS results show that Ti, Zr, O, C atoms are detected over $\text{TiO}_2(\text{Zr}_{0.1})$ (Table S1). The appearance of Zr and C species are due to the introduction of Zr in the framework of TiO_2 and the adsorption of CO_2 on the surface. According to the

Fig. 4. XPS spectra of TiO_2 , $\text{TiO}_2(\text{Zr}_{0.1})$ and $\text{TEPA}(40)/\text{TiO}_2(\text{Zr}_{0.1})$. (a), (b) the full spectrum of TiO_2 and $\text{TiO}_2(\text{Zr}_{0.1})$; (c) $\text{Zr}(3d)$ spectrum over $\text{TiO}_2(\text{Zr}_{0.1})$ and $\text{TEPA}(40)/\text{TiO}_2(\text{Zr}_{0.1})$; (d) $\text{N}(1s)$ on $\text{TEPA}(40)/\text{TiO}_2(\text{Zr}_{0.1})$.

results, the Zr/Ti molar ratio of 0.0993 is calculated. The value is in accordance with that of ICP, demonstrating that $\text{TiO}_2(\text{Zr}_{0.1})$ is successfully prepared. After the functionalization, N is observed on $\text{TEPA}(n)/\text{TiO}_2(\text{Zr}_{0.1})$. With the rise of TEPA immobilization, the content of N species increases rapidly. However, some C, N and O species in the air are also be detected, leading to a little deviation. The results of XPS provide further evidence for the successful introduction of TEPA.

3.1.5. N_2 adsorption-desorption

Fig. S1 and Table S2 illustrate the N_2 adsorption-desorption results of $\text{TiO}_2(\text{Zr}_N)$ and $\text{TEPA}(n)/\text{TiO}_2(\text{Zr}_{0.1})$. All of Zr-doped TiO_2 supports have been characterized by N_2 adsorption/desorption technique. When the molar ratio of Zr/Ti is less than 0.1, the supports exhibit large S_{BET} , pore diameter and pore volume. With the rise of Zr/Ti ratio, the S_{BET} , pore diameter and pore volume decrease gradually. Compared with these supports, the material of $\text{TiO}_2(\text{Zr}_{0.125})$ displays little S_{BET} , pore diameter and pore volume. The results may be caused by the introduction of Zr species in the framework of TiO_2 . When the molar ratio of Zr/Ti is large than 0.1, new product of ZrO_2 may be dispersed on the surface [36]. Therefore, the S_{BET} , pore diameter and pore volume decreased rapidly and $\text{TiO}_2(\text{Zr}_{0.1})$ is selected as the support in this paper. In addition, the total pore volume decreases but the microporous volume increases with the increase of Zr and TEPA content. The radius of Zr is larger than Ti. With the doping of Zr, a part of Ti atoms are replaced by

Zr species. In addition, the loading of TEPA in the pore channels is beneficial to the further decline of pore volume and the formation of micropores. Therefore, there is an enhancement for the microporous volume and a reduction for the total volume.

$\text{TiO}_2(\text{Zr}_{0.1})$ shows type IV adsorption-desorption curve with a hysteresis loop. Besides, the pore diameter is within 2–40 nm and the pore volume is about $0.261 \text{ cm}^3/\text{g}$. The results suggest that the Zr-doped support is a mesoporous material. Similar to the previous work [22, 31], the S_{BET} , V_p and d_p decrease rapidly with the rise of TEPA content as a result of the pore filling of TEPA. However, all of the pore diameters are within 2–50 nm. Consequently, both of $\text{TiO}_2(\text{Zr}_{0.1})$ and the modifiers of $\text{TEPA}(n)/\text{TiO}_2(\text{Zr}_{0.1})$ synthesized in this work are mesoporous materials.

3.1.6. Thermogravimetric analysis (TGA)

Fig. S2 displays the TGA profiles of $\text{TiO}_2(\text{Zr}_{0.1})$ and $\text{TEPA}(n)/\text{TiO}_2(\text{Zr}_{0.1})$. There is little weight loss over TiO_2 and $\text{TiO}_2(\text{Zr}_{0.1})$, indicating that the support is stable before 600°C . Compared with $\text{TiO}_2(\text{Zr}_{0.1})$, the modifiers exhibit lower thermal stability as a result of the decomposition of TEPA. Similar to the previous work reported by Kuwahara [26], the decomposition temperature of $\text{TEPA}(n)/\text{TiO}_2(\text{Zr}_{0.1})$ is about 180°C , which is 27°C higher than that of $\text{TEPA}(40)/\text{TiO}_2$ without Zr species. In addition, the thermal-stability of $\text{TEPA}(n)/\text{TiO}_2(\text{Zr}_{0.1})$ is also higher than the traditional adsorbents synthesized by loading amines on SiO_2 [25, 26], which

is attributed to the condensation bond between Zr and N species. The TGA results suggest that Zr species in the framework has a positive influence on the thermal stability of TEPA immobilized TEPA/TiO₂(Zr_{0.1}).

With the rise of TEPA/TiO₂(Zr_{0.1}) mass ratio, there is an increase of TEPA weight loss. For TEPA(25)/TiO₂(Zr_{0.1}), TEPA(30)/TiO₂(Zr_{0.1}), TEPA(35)/TiO₂(Zr_{0.1}), TEPA(40)/TiO₂(Zr_{0.1}), TEPA(45)/TiO₂(Zr_{0.1}) and TEPA(50)/TiO₂(Zr_{0.1}), the weight loss of TEPA are 7.83, 8.18, 8.9, 9.35, 13.15 and 13.77%, respectively. There is a significant jump in weight loss between TEPA(40)/TiO₂(Zr_{0.1}) and TEPA(45)/TiO₂(Zr_{0.1}), which may be associated with the viscosity of TEPA. When the mass ratio of TEPA/TiO₂(Zr_{0.1}) is large than 40%, TEPA is excess and could not be dispersed well in the solution. These TEPA molecules coats on the surface of the support. These molecules could not be removed at low temperature. Therefore, the jump is observed. In addition, there is a difference between the theoretical load and the actual load. This phenomenon could be explained by the pore structure of TiO₂(Zr_{0.1}), the content of Zr, and the intermolecular repulsion of TEPA. First, TiO₂(Zr_N) is a mesoporous material. However, the pore volume is too small to accommodate all the TEPA molecules. Besides, the content of Zr is limited. The number of acidic sites will decline rapidly with the reaction between Zr and TEPA, leading to the decrement of the attraction between the support and TEPA. Finally, TEPA in the pore channels have an intermolecular repulsion to that outside the pore. Therefore, some TEPA could not get access to the pore channels. Based on these, the difference is observed.

3.1.7. Scanning electron microscope (SEM), Transmission electron microscope (TEM) and Energy dispersion spectrum (EDS)

Scanning electron microscope (SEM) and transmission electron microscope (TEM) of TiO₂(Zr_{0.1}) and TEPA(40)/TiO₂(Zr_{0.1}) are used to characterize the morphology and the influence of TEPA. As seen, 1) The SEM images of TiO₂(Zr_{0.1}) and the modifier tell us that they are composed of lots of big particles (Fig. S3). 2) The EDS result show that Ti, Zr, O and C are detected on TiO₂(Zr_{0.1}). The appearance of C species is related to the physically adsorbed CO₂. Except from Ti, Zr, O and C, N species is also detected on TEPA(40)/TiO₂(Zr_{0.1}), which is associated with the loading of TEPA (Fig. S3). 3) In the TEM images of TiO₂(Zr_{0.1}) and TEPA(40)/TiO₂(Zr_{0.1}), a number of big particles are observed (Fig. S4). For TiO₂(Zr_{0.1}), Ti, Zr and O atoms are detected in the mapping images (Fig. S5). Compared with TiO₂(Zr_{0.1}), C and N species are also observed (Fig. S6). Based on these, we confirm that TEPA is successfully grafted on the support.

Combined with the characterization results and the information in the previous work [22], a possible route for the synthesis of TEPA(n)/TiO₂(Zr_{0.1}) could be deduced as displayed in Fig. S7. Zr species are introduced to the framework of TiO₂ via the formation of Ti-O-Zr bond. Then, TEPA is grafted on the surface of TiO₂(Zr_N) through the coordination between N and Zr species.

3.2. CO₂ Adsorption

3.2.1. Effect of adsorption time and TEPA amount

Fig. 5 reveals the adsorption capacity of TEPA(n)/TiO₂(Zr_{0.1}) at 75°C as a function of adsorption time. One can see that 1) all of the adsorbents accomplish CO₂ adsorption within 3 min; 2) compare

Fig. 5. CO₂ uptake of TiO₂, TiO₂(Zr_{0.1}) and TEPA(n)/TiO₂(Zr_{0.1}) as a function of adsorption time.

with TiO₂ and TiO₂(Zr_{0.1}), the modifiers achieve the saturated adsorption capacity within a longer adsorption time, which is related to the reaction between CO₂ and -NH₂ groups [22, 31]. 3) the capacity of TEPA(n)/TiO₂(Zr_{0.1}) increases with the adsorption time and then keep stable. The phenomenon is similar to the previous work reported by Zhang [37], which can be explained by the consumption of affinity sites over the TEPA-functionalized adsorbents. As seen in Table S2, the pore diameters of TEPA grafted adsorbents are large enough for the diffusion of CO₂ which kinetic diameter is only 0.33 nm [25, 38]. With the extension of adsorption time, more and more CO₂ are introduced to the adsorption system to react with the basic sites. After 3 min, most of the affinity sites are spent for CO₂ adsorption. Therefore, there is no significant increase for the adsorption capacity. 4) the capacities of TEPA(n)/TiO₂(Zr_{0.1}) are larger than the support of TiO₂(Zr_{0.1}) alone, suggesting that TEPA is a good candidate for the enhancement of CO₂ adsorption capacity. The phenomenon is similar to that reported by Xu [31], which is attributed to the chemical reaction between -NH₂ groups and CO₂ molecules. 5) the capacity increases first and then declines with the rise of TEPA content. When TEPA weight percentage is 40wt%, the maximum adsorption capacity of 113.1 mg/g is achieved. Similar to the previous work reported by Xu [31], the optimal adsorption capacity is higher than that of pure TEPA, indicating that the support exhibits a synergetic effect on CO₂ adsorption. With the rise of TEPA amount, more and more basic sites coming from -NH₂ groups are introduced to the support. When the amount is larger than 40wt%, TEPA is excess. In this situation, the adsorption capacity decreases with the rise of TEPA loading, which could be explained by a more marked pore occlusion and a reduced accessibility of CO₂ towards the amine active sites [31].

3.2.2. Effect of adsorption temperature

The influence of adsorption temperature must be taken into consideration based on the great effect on CO₂ adsorption. For instance, polyethylenimine (PEI) functionalized Zr-SBA-15 exhibited the optimized adsorption capacity at 75°C [26]. In this work, the effect of adsorption temperature on TEPA(n)/TiO₂(Zr_{0.1}) was investigated

and the results are revealed in Fig. 6. For all of the TEPA modified adsorbents, the adsorption capacity decreases with the rise of adsorption temperature. According to the previous work [31], physical adsorption and chemical adsorption occur simultaneously on organic amines occluded solid adsorbents. With the increase of temperature, the chemical adsorption equilibrium shifts to the reverse direction, leading to the decrease of chemical adsorption capacity. Moreover, the physical adsorption capacity decreases with the rise of temperature as a result of the exothermic nature on the surface of porous materials [31, 39]. Therefore, the adsorption capacity decreases with the rise of temperature.

Except adsorption conditions, the tested method has a great effect on CO₂ adsorption. In the previous work [22, 25, 31], CO₂ adsorption was performed using TG analysis technique. In this way, CO₂ adsorption is controlled by the diffusion of gas molecules at low temperature, leading to a poor adsorption capacity. With the rise of adsorption temperature, more and more CO₂ molecules react with amines, resulting in the enhancement of CO₂ adsorption capacity. When the temperature is higher than the optimal point, the adsorption is dominated by the thermodynamic process. In this situation, the capacity decreases with the temperature on account of the exothermic chemical reaction between CO₂ and amines. Therefore, CO₂ adsorption capacity is low at low temperature. In this study, the adsorption performance was estimated by the breakthrough experiment. Under this condition, gas molecules are easier to get access to the pore channels and react with amines. Based on these, both of the physical and chemical adsorption capacities decrease rapidly with the rise of temperature. Therefore, CO₂ adsorption capacity is high at low temperature.

N₂ adsorption of the pristine TiO₂ (Fig. S1) is highest among all samples but the CO₂ adsorption is lowest (Fig. 6). The phenomenon is associated with the reasons as follows: 1) N₂ could be adsorbed in the pore channels of TiO₂ and TEPA-functionalized adsorbents, which is associated to the physical adsorption. The pore volume is beneficial to N₂ adsorption. Compared with TiO₂, TEPA(n)/TiO₂(Zr_{0.1}) has less pore volumes because of the filling of TEPA

molecules. Moreover, the volumes decrease rapidly with the increase of TEPA loading. Therefore, the adsorption capacity of N₂ on the pristine TiO₂ is higher than the modifiers. 2) Similar to N₂ adsorption, CO₂ could also be adsorbed on TiO₂ on account of physical adsorption. However, the mechanism of CO₂ adsorption on TEPA(n)/TiO₂(Zr_{0.1}) is different from this. Before TEPA loading, physical adsorption occurs on TiO₂(Zr_{0.1}) and the adsorption capacity of 40.3 mg/g is achieved. After the modification, TEPA could be used as basic sites to afford the chemical adsorption of CO₂. Over TEPA(n)/TiO₂(Zr_{0.1}), amino groups originating from TEPA react with CO₂ molecules, resulting in a positive effect on CO₂ adsorption. Compared with TiO₂, TEPA(n)/TiO₂(Zr_{0.1}) has a high content of TEPA. Consequently, the CO₂ adsorption is higher than that on TiO₂.

3.2.3. Effect of gas flow rate

Fig. 7 displays the adsorption capacity of TEPA(40)/TiO₂(Zr_{0.1}) with the rise of gas flow rate. The breakthrough time decreases with the rise of CO₂ flow rate because of the decline of contact time between CO₂ molecules and basic sites [22, 40]. When the flow rate is less than 20 mL/min, the adsorption capacity increases rapidly as the rise of flow rate and the maximum amount of 131.1 mg/g is achieved. When the flow rate is large than 20 mL/min, a decrement of adsorption capacity is observed. Before the optimal flow rate, the adsorption process over TEPA(40)/TiO₂(Zr_{0.1}) is controlled by the diffusion of CO₂ molecules [22]. With the rise of CO₂ flow rate, more and more gas molecules get access to the pore channels and react with the affinity sites, leading to the enhancement of adsorption capacity. When CO₂ flow rate is beyond the optimal value, CO₂ adsorption is dominated by the contact time and the change of mass transfer zone [22, 40-42]. With the rise of CO₂ flow rate, the contact time between N species and CO₂ molecules decreases and the mass transfer zone over TEPA(40)/TiO₂(Zr_{0.1}) increases rapidly. Therefore, the capacity decreases with further rise of flow rate.

CO₂ adsorption performance over TEPA(40)/TiO₂(Zr_{0.1}), traditional amine-decorated metal oxides and Zr-doped molecular sieves is displayed in Table S3. After the doping of Zr, amine immobilized

Fig. 6. CO₂ adsorption capacity TiO₂(Zr_{0.1}) and TEPA(n)/TiO₂(Zr_{0.1}) as a function of adsorption temperature. (Conditions: t = 6 min, adsorbate = 5% CO₂, flow rate = 10 mL/min)

Fig. 7. CO₂ adsorption capacity of TEPA(40)/TiO₂(Zr_{0.1}) as a function of gas flow rates.

TiO₂(Zr_{0.1}) displays a larger adsorption capacity and N utilization. Compared with amine modified Zr-doped molecular sieves and TiO₂ [22, 25, 26, 41-47], TEPA(40)/TiO₂(Zr_{0.1}) exhibits a larger amine utilization. Amine utilization is calculated according to the equation of (1), where q_e and q_0 are the saturated adsorption capacity of the modifiers and the supports, M_1 and M_2 are the molecular weight of amine and CO₂, W_A is the mass of amine per gram of adsorbent.

$$\eta = \frac{(q_e - q_0) \times M_1}{W_A \times M_2 \times 500} \quad (1)$$

3.2.4. Recyclability performance

In practical application of CO₂ adsorption, the cyclic adsorption-desorption performance should be considered as one of the most significant factors [12, 15, 17, 19, 20, 22, 25, 26]. In the present study, the cyclical adsorption performance of TEPA(40)/TiO₂(Zr_{0.1}) at 30°C and 75°C was tested and the results are presented in Fig. 8. As seen, the capacities keep stable at 30°C and 75°C, demonstrating that TEPA(40)/TiO₂(Zr_{0.1}) is a good candidate for CO₂ adsorption.

Fig. 8. Cyclical adsorption performance of TEPA(40)/TiO₂(Zr_{0.1}) at 30°C and 75°C (Conditions: $t = 6$ min, 5% CO₂ in a stream of 10 mL/min flow rate).

3.2.5. CO₂ adsorption mechanism

According to the previous work [22], IR experiment could be used for the investigation of CO₂ adsorption mechanism over organic amine modified materials. In this study, TEPA(40)/TiO₂(Zr_{0.1}) before and after CO₂ adsorption were used to afford the task and the results are illustrated in Fig. S8. After the adsorption, CO₂ molecules were adsorbed on the surface, leading to the formation of carbamate [22, 48]. Consequently, C-O, C=O and C-N bonds may be detected. In the image of (B), the peaks at 1,305 and 1,576 cm⁻¹ are observed which are assigned to C-O bonds in -COO⁻. Besides, the peaks at 1,408 and 1,527 cm⁻¹ ascribed to the formation of C-N bonds are also detected. In addition, no peak assigned to HCOO₃⁻ is observed. The similar results are also achieved on TEPA modified TiO₂. In the image of (D), the peaks at: 1) 1,298 and 1,573 cm⁻¹ assigned to C-O bonds in -COO⁻; 2) at 1,408 cm⁻¹ is ascribed to

the formation of C-N bonds; 3) at 1,498 cm⁻¹ is attributed to N-H bonds. The phenomenon is similar to the previous work reported by Yang [22] and Liao [48], suggesting that there is a chemical adsorption on the TEPA decorated TiO₂ and TiO₂(Zr_{0.1}).

In this study, an adsorption capacity of 40.3 mg/g is obtained over TiO₂(Zr_{0.1}) without TEPA, suggesting that a physical adsorption occurs on TiO₂(Zr_{0.1}). After the modification with TEPA, amino groups react with CO₂ molecules, leading to the formation of C-N bond and -COO⁻ species. Therefore, we speculate that physical adsorption and chemical adsorption exist simultaneously over TEPA immobilized TiO₂(Zr_{0.1}). The adsorption mechanism was displayed in Fig. S9.

4. Conclusions

Zr-doped metal oxide of TiO₂(Zr_N) was first synthesized and optimized by adjusting Zr/Ti molar ratio. The optimal support of TiO₂(Zr_{0.1}) was functionalized with TEPA and tested for CO₂ adsorption. Over the modifiers, TEPA molecules are immobilized on the surface through the coordination between N and Zr species. TEPA treated adsorbents display good thermal stability when the temperature is lower than 180°C. Moreover, the adsorbents exhibit good CO₂ adsorption performance in a stream of 5% CO₂ concentration. With the rise of TEPA/TiO₂(Zr_{0.1}) weight ratio, there is an improvement for the adsorption capacity. The similar phenomenon is also observed with the extension of adsorption time and CO₂ flow rate. At 75°C, the maximum adsorption capacity of 113.1 mg/g is achieved for TEPA(40)/TiO₂(Zr_{0.1}) in a stream of 10 mL/min. After 20 cycles of adsorption-desorption, the adsorption capacity keep stable.

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Author Contributions

F.M. (Associate Professor) conducted all the experiments and wrote the manuscript. L.J. (Ph.D student) completed literature consultation. G.W. (Professor) revised the manuscript.

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