CO_2 adsorption on ceria impregnated

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Ce 담지 NaZSM-5의 이산화타소 흡착 특성

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Abstract

NaZSM 5 was synthesized in an alkaline medium and impregnated with cerium oxide by wet method using cerium nitrate as the source for cerium. There TGA results shows decomposition of nitrate at 200°C. The ceria impregnated ZSM 5 materials were designated as NaZSM 5 (X) where X is the percent ceria impregnated (3, 5, 7, 11, 19%). They were characterized by XRD, SEM, EDAX, BET techniques. XRD analysis showed decrease in intensity of the patterns with the increase in the ceria loading but crystallization of ceria to larger size is evident for 11 and 19% loading. The surface area and pore volume decreased with increase in ceria loading. The maximum adsorption capacity of NaZSM 5 (5%) is 100.2 mg/g of sorbent. The ceria impregnated NaZSM 5's were found to be regenerable, selective and recyclable.

1. Introduction

Much attention has been recently given to control the rise in CO_2 level in the atmosphere, a major green gas which causes global warming. The raise in the use of fossils fuel contributes to the increase in the CO_2 level [1,2]. Research is focused in developing various technologies to capture and separate the emission of CO_2 from industries [3,4]. Adsorption and desorption of CO_2 has been extensively studied using organic amines, amine dendrimers, amine functionalized silica and mesoporous materials [5 14]. Alkali and alkaline earth metal oxides supported porous materials and carbons have also been examined for the same process [15,16]. As the alkali and alkaline earth metal oxide forms readily carbonate with CO_2 they are convenient for adsorption desorption studies. In comparison to such oxides, transition metal and rare earth metal oxides are advantageous for adsorption and desorption of CO_2 as such oxides do not form carbonates. But they can adsorb CO_2 by nucleophilic interaction of their oxidic sites with the positively charged carbon dioxide carbon. Taking into consideration of this view in the present study NaZSM 5 was synthesized in an alkaline medium and impregnated with cerium oxides by wet method using cerium nitrate as the source for cerium.

2. Experimental

2.1. Synthesis of NaZSM-5 and ceria impregnated ZSM-5.

The Na form ZSM 5 was synthesized as per the reported procedure [17]. Appropriate amount of TEOS was mixed with 65 g of deionized water. In order to maintain
pH 1 few drops of sulfuric acid was slowly added to the above mixture under vigorous stirring and the stirring was continued for 20 h at 30°C. Then

calculated amount of TPABr and $Al_2(SO_4)_3 \cdot 18H_2O$ were added to the above mixture. After 10 mins of stirring, the hydrogel with pH of 10 was obtained by adding 1.62 g NaOH. The final molar composition of the synthesis gel was $8.8Na_2O:40SiO_2:\ 1Al_2O_3:3.9TPABr:1600H_2O$. The crystallization was carried out at 180 °C for 3 days in the static oven. The crystallized product was recovered by filtration, washed repeatedly with water, dried at 100 °C and calcined at 500 °C in air. The obtained material is designated as NaZSM 5. The ceria impregnated ZSM 5's with varying ceria loading were prepared by wet impregnation of 5g of NaZSM 5 with ethanolic solution of cerium nitrate. The mixture was stirred and vacuum dried to remove ethanol. The obtained material is finally calcined in air at 550 °C for 10 h. The materials obtained were designated as NaZSM 5 (X) where X is the percent ceria impregnated (3, 5, 7, 11 and 19%).

2.2 Catalyst characterization

Powder X ray diffraction pattern (XRD) were recorded using a with Cu Kα radiation (λ=0.154 nm). The diffraction data were recorded in the 2Θ range of 5 to 40° at 0.02° steps size and 1 s step time. The nitrogen adsorption desorption isotherms were measured at 77K on a Micromeritics ASAP 2010 volumetric adsorption analyzer. Prior to each adsorption measurement the samples were evacuated at 100 °C under vacuum ($p<10^{-5}$ mbar) in the degas port. The surface area was determined from the linear part of the Brunauer, Emmett and Teller (BET) equation. The pore volume was calculated using the BET plot from the amount of nitrogen gas adsorbed at the last adsorption point (P/P_0 = 0.95). TGA analyses were carried out in N_2 atmosphere at a flow rate of 20 ml/ min, on SCINCO thermal gravimeter N 1000 Thermo gravimetric analyzer, by heating 10 mg of the sample from 25 to 800 °C in steps of 10°C/min. The morphologies of the samples were studied by scanning electron microscopy (SEM) after gold coating using a FEI Quanta 200 instrument operating at 30 keV equipped with an energy dispersive X ray analysis (EDAX) detector.

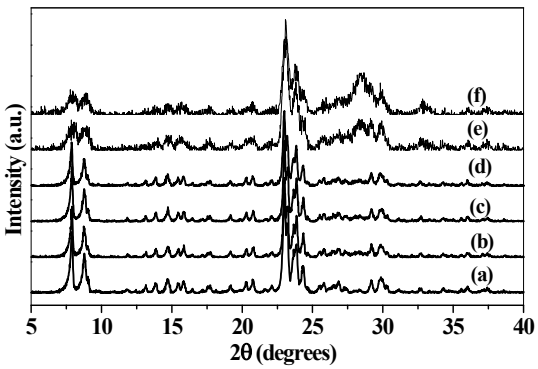
2.3. CO_2 adsorption

CO_2 adsorption desorption measurements for synthesized materials were performed using a thermo gravimetric analyzer. A sample weight of ca. 10 mg was loaded into an alumina sample pan in a TG unit (SCINCO thermal gravimeter N 1000) and tested for CO_2 adsorption desorption performances. The initial activation of the samples was carried out at 200 °C for 1 h in nitrogen atmosphere. The adsorption and desorption runs were conducted using high purity CO_2 (99.999%) gas and N_2 flow, respectively. The adsorption runs were conducted at 25, 50 and 75 °C under atmospheric condition and desorption at 200 °C. Both the gases, CO_2 and N_2, were passed through an automatic valve, assisted with a timer for continuous adsorption and desorption profile.

3. Results and discussion

3.1. XRD analysis

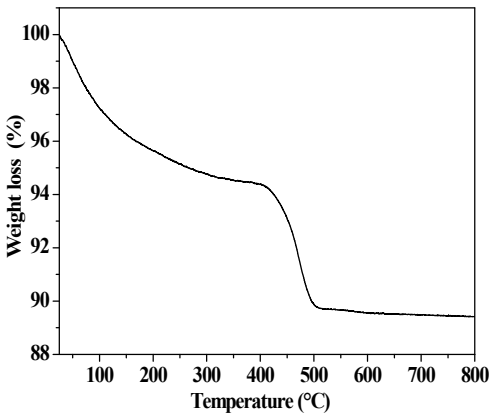
The powder diffraction patterns of the NaZSM 5 and the ceria impregnated samples are presented in Fig.1. The spectra carry the characteristic patterns for ZSM 5. The intensity of the patterns decreased with the increase in the ceria loading but crystallization of ceria to larger size is evident for 11 and 19% loading. It was confirmed by broadening of XRD pattern close to 28° (2Θ). Pure ceria gives its intense pattern at 28° (2Θ) is due to (111). Similar broadening of the signal at the same 2Θ value was also reported by Sugi et al [18]. But they reported broadening at 20% loading. But in this study broadening started at 11% loading. Hence ceria particles might be finely divided and not having enough dimension to produce their characteristic patterns.



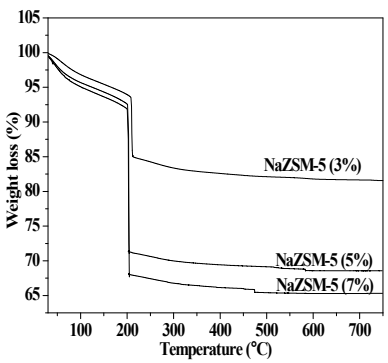
[Fig. 1] XRD patterns of (a) NaZSM-5, (b) NaZSM-5 (3%), (c) NaZSM-5 (5%), (d) NaZSM-5 (7%), (e) NaZSM-5 (11%) and (f) NaZSM-5 (19%).

3.2. TGA

The TG curve of the as synthesized Na ZSM 5 (Fig.2a) shows two stages of weight loss. The initial weight loss is attributed to the physisorbed water while the loss at around 400 450°C is due to the decomposition of the occluded template. The cerium impregnated samples when subjected to TG analysis revealed a sharp weight loss at 200°C corresponds to the decomposition of the nitrate.



(a)



(b)

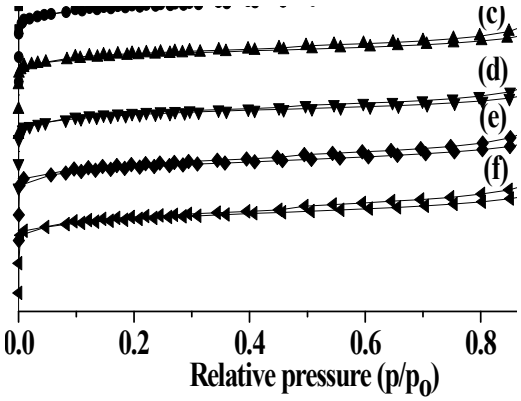
[Fig.2] Thermograms of (a) as-synthesized NaZSM-5 and (b) NaZSM-5 (3,5 and 7%)

3.3. BET

The N_2 adsorption and desorption isotherms are depicted in Fig. 3. The isotherms are of type 1 confirming the characteristic microporosity nature of the ZSM 5. The surface area and the pore volume are tabulated in table 1. The surface area and pore volume decreased with increase upon ceria loading. The decrease was also not uniform for the ceria impregnated samples. Such a random distribution of surface area and pore volume for ceria impregnated ZSM 5 has already been reported by Sugi et al [18]. Hence ceria might be impregnated within the pores of ZSM 5. It is also verified from SEM analysis.

3.4. SEM

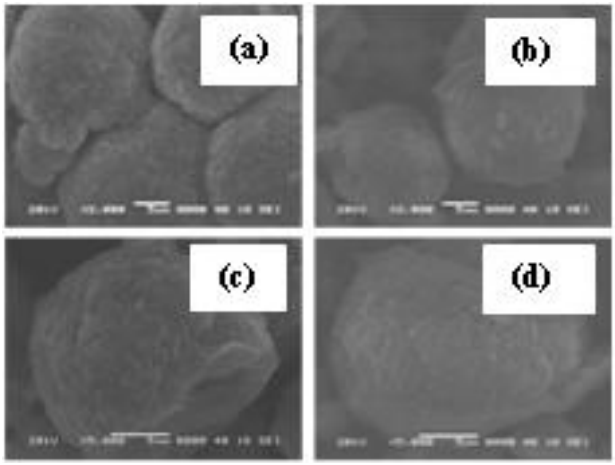
The SEM pictures of the synthesized samples are shown in Fig. 4. The small sized ZSM 5 crystals assemble to form large spherical particles. The SEM picture of the ceria impregnated samples did not show any evidence for separate crystals for cerium. The presence of cerium is evidenced from the EDAX analysis (Figure not shown)



[Fig. 3] N2 adsorption-desorption isotherms of (a) NaZSM-5, (b) NaZSM-5 (3%), (c) NaZSM-5 (5%), (d) NaZSM-5 (7%), (e) NaZSM-5 (11%) and (f) NaZSM-5 (19%).

Table 1. Textural properties of the synthesized materials

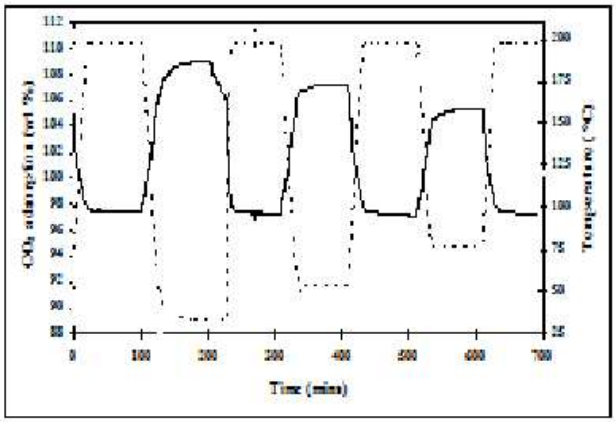
Catalysts	Surface area (m^2/g)	Pore volume (cm^3/g)
NaZSM-5	377.20	0.219
NaZSM-5 (3%)	344.19	0.212
NaZSM-5 (5%)	303.32	0.211
NaZSM-5 (7%)	320.27	0.208
NaZSM-5 (11%)	330.02	0.209
NaZSM-5 (19%)	334.40	0.204



[Fig. 4] SEM images of (a) NaZSM-5,, (b) NaZSM-5 (3%), (c) NaZSM-5 (5%), (d) NaZSM-5 (7%)

3.5. CO_2-TGA

CO_2 and the adsorption/desorption profiles of the synthesized materials (at 25, 50 and 75 °C) were depicted in Fig. 5. The maximum adsorption capacity of NaZSM 5 (5%) was found to be 100.2 mg/g of sorbent. The high adsorption capacity over ceria impregnated NaZSM 5 are due to statistically favored CO_2 chemisorption on ceria due to reduced Ce^{3+} sites [19]. An increase in adsorption was observed from NaZSM 5 (3%) to NaZSM 5 (5%) but a decrease for NaZSM 5 (7 and 11%). The decrease in CO_2 adsorption of NaZSM 5 (7 and 11 %) (Table 2) is due to reduced diffusivity of CO_2 into the pores as it is confirmed by decrease in pore volume of NaZSM 5 (7 and 11%). The CO_2 adsorption over all ceria impregnated NaZSM 5 decreases at 50 and 75 °C due to the less reactivity between CO_2 and ceria sites. The kinetic energy of CO_2 molecules is increased at 50 and 75 °C and hence CO_2 molecules are not available for the reaction with ceria sites.



[Fig. 5] CO_2 adsorption/desorption profile of NaZSM-5(5%)

Table 2. CO_2 adsorption capacity over ceria impregnated NaZSM-5

Catalysts	Adsorption capacity (mg/g)
NaZSM-5 (3%)	95.2
NaZSM-5 (5%)	100.2
NaZSM-5 (7%)	98.1
NaZSM-5 (11%)	97.3
NaZSM-5 (19%)	97.1

Adsorption temperature: 25 °C; Desorption temperature: 200 °C; feed gas CO_2 concentration: 99.99%

4. Conclusions

Ceria impregnated NaZSM 5 was synthesized by wet impregnation method. The XRD patterns revealed the high crystallinity of the synthesized samples and carried the characteristic patterns of the ceria at higher loadings. The decrease in surface area and pore volume confirmed the impregnation of ceria inside the pores. The NaZSM 5 (5%) showed a maximum adsorption capacity of 100.2 mg/g of the sorbent. Hence, from this study it is concluded that ceria impregnated any porous material could be treated as novel materials for CO_2 adsorption desorption.

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