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Study of sulfur dioxide adsorption on Y zeolite

IOAN-CEZAR MARCU and IOAN SĂNDULESCU *

Department of Chemical Technology and Catalysis, Faculty of Chemistry, University of Bucharest, Bd. Regina Elisabeta No. 4-12, 030018 Bucharest, Romania (e-mail: isandulescu@chem.unibuc.ro)

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Abstract: Sulfur dioxide adsorptive properties of Y zeolite, the structure of which was confirmed by XRD, were investigated at temperatures within the 25–200 ºC range and sulfur dioxide concentrations between 0.9 to 6 % (vol./vol.). It was found that this sorbent possesses a relatively high adsorption capacity. The Y zeolite did not lose its activity during 20 adsorption-desorption-regeneration cycles. The manner in which sulfur dioxide is adsorbed on Y type zeolite was also investigated by analyzing the sample with and without adsorbed SO_2, using IR spectroscopy, as well as total and Lewis acidity measurements. The sulfur dioxide molecule is probably adsorbed by hydrogen bonding to one or two conveniently positioned surface hydroxyl groups.

Keywords: sulfur dioxide, adsorption, Y zeolite, desulfurization.

INTRODUCTION

Air pollution airising from the emission of sulfur dioxide resulting from combustion in boilers, furnaces and engines has increasingly been recognized as a problem. Dry regenerative sorption processes based on the chemical reaction of SO_2 with a sorbent/catalyst[1–6] or adsorption of SO_2 on solids,[7–25] have attracted increasing attention for SO_2 removal because these methods possess several advantages over conventional wet-scrubbing processes. Among the dry processes, the adsorption process offers an alternative and promising way for the control of SO_2 emissions because of the minimum energy requirements for the regeneration of the adsorbent, relatively simple design as compared with a chemical reactor and minimum waste disposal problems.

A large variety of adsorbents have been tested for SO_2 adsorption,[7–25] among these, natural or synthetic zeolites[7–20] seem to have the highest activity. It should, however, be pointed out that the major advantage of using zeolites is the possibility of their successive regeneration. Despite a large number of studies, the application of zeolites in air pollution control has just begun to emerge.[20]

In this article, the study sulfur dioxide adsorption on Y type zeolite is reported. The goal was to obtain information about some factors which can influence the adsorption capacity and about the adsorption mechanism.

* Corresponding author.

EXPERIMENTAL

The zeolite sample was supplied by INCERP Ploieşti, Romania. The structure of the Y zeolite was identified by XRD (Brüker D5005, CuK_{α}) measurements and the surface area was determined by the BET method using nitrogen adsorption.

The SO_2 adsorption was carried out in a fixed bed, down-flow tube reactor using 2.6 g (5 cm^3) of zeolite in the temperature range 25–200 ºC, as described elsewhere.[15] The feeding gas was a synthetic mixture of nitrogen and sulfur dioxide. The flow rates were controlled by fine needle valves and were measured by capillary flow meters. The zeolite was thermally pretreated for one hour at 120 ºC, followed by one hour at 400 ºC in a nitrogen stream. The adsorption was performed until the concentration of sulfur dioxide in the effluent gas was equal to that in the feed gas. The SO_2 was desorbed thermally (400 ºC) in a nitrogen stream and the adsorbed quantity of sulfur dioxide was established by iodometric titration: the sulfur dioxide was bubbled through an iodine solution and the excess of iodine titrated with a sodium thiosulfate solution. The adsorbent regeneration was carried out in a nitrogen stream for 30 min at 400 ºC.

The infrared spectra in the range of 400–400 cm^{-1} were recorded on a SPECORD 75 spectrometer using the KBr technique. Pyridine and ethyl acetate were used as probe molecules for IR measurements of the total acidity and Lewis acidity, respectively.

RESULTS AND DISCUSSION

The X-ray diffraction pattern displayed in Fig. 1 confirms that the sample was a well-crystallized Y zeolite. The specific surface area of the sample was 387 m^2/g.

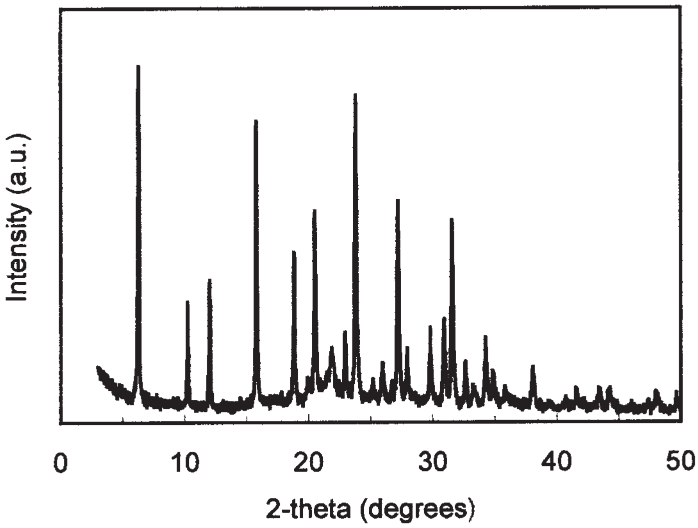

Fig. 1. X-Ray diffraction patterns of the Y zeolite used as adsorbent.

Adsorption measurements

The effect of the temperature on the adsorption capacity of the zeolite is shown in Fig. 2. The sulfur dioxide concentration in nitrogen was 1.85 % (vol./vol.) and the gas flow rate was 135 ml/min. The adsorption capacity is expressed as mg SO_2 adsorbed per gram of zeolite.

A diminution of the adsorption capacity with increasing temperature was noted. The zeolite maintains high adsorption capacity values over the temperature range 100–150 ºC but its adsorption capacity value becomes zero above 200 ºC. The high values of zeolite adsorption capacity at low temperature are assumed to be the result of both physical ad-

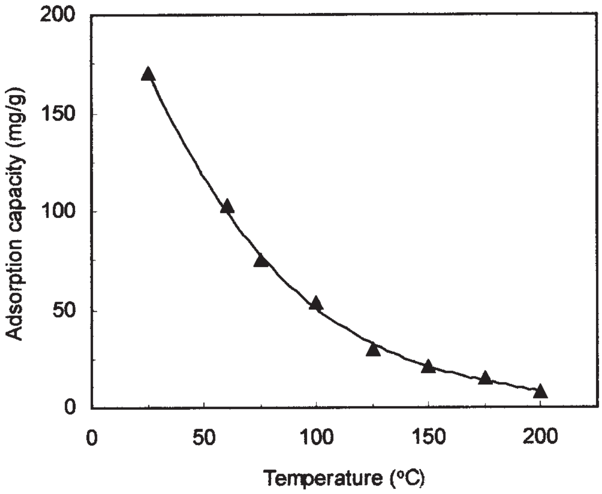

Fig. 2. Effect of temperature on the adsorption capacity of the Y zeolite (SO_2 concentration in N_2: 1.85 % (vol./vol.), gas flow rate: 135 ml/min).

sorption and chemisorption, the former being predominant under the employed conditions.[11,16]

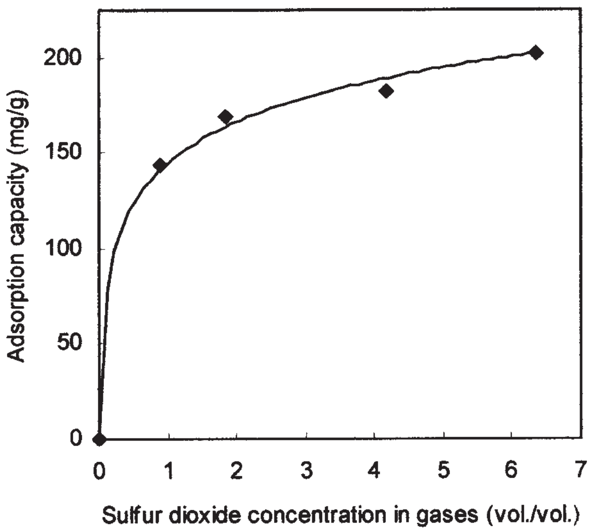

Fig. 3. Adsorption isotherm for SO_2 on the Y zeolite at 25 °C (gas flow rate: 135 ml/min).

Figure 3 shows the adsorption isotherm of Y zeolite obtained at 25 °C when the sulfur dioxide content in the feed gas was varied from 0.9 to 6 % (vol./vol.), maintaining the total flow rate constant at 135 ml/min. The slope of this isotherm changes dramatically at low concentrations but afterwards the adsorption capacity increases only slightly with concentration. Other authors[11–13] also mentioned an increase of adsorption capacity with increasing concentration of sulfur dioxide in the gases. This behavior could be accounted for by an accumulation of sulfur dioxide in the condensed state.[11]

As be seen in Fig. 4, the activity of the Y zeolite do not alter significantly during 20 adsorption-desorption-regeneration cycles operated under identical experimental conditions, *i.e.*, 25 ºC, 1.85 % SO_2 in N_2, gas flow 135 ml/min and in the absence of water vapors for the adsorption step, and 400 ºC in N_2 flow for desorption-regeneration. Some zeolites have not lost their activity even after more than 2000 such cycles carried out under industrial conditions.[17] However, it is possible that the activity of this adsorbent may change in the presence of water vapors and at higher temperatures.

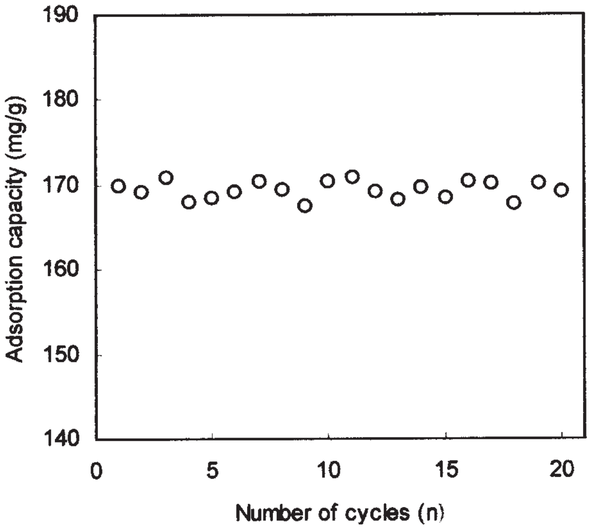

Fig. 4. Influence of the number *n* of adsorption-thermal regeneration cycles on the adsorption capacity of the Y zeolite (adsorption conditions: 25 ºC, 1.85 % SO_2 in N_2, gas flow rate 135 ml/min, desorption-regeneration conditions: 400 ºC, in a N_2 flow).

IR spectroscopy studies

In order to obtain some information about the adsorption mechanism on Y zeolite, the sulfur dioxide adsorption was investigated using IR spectroscopy. The most striking feature of the SO_2 spectrum is a pair of absorption bands representing SO vibrations. These occur in the gas phase at 1360 (ν_3) and 1151 cm^{-1} (ν_1) and are also found in the spectrum of SO_2 adsorbed at room temperature and low pressure at 1330 and 1140 cm^{-1}, values similar to those observed for liquid SO_2.[26]

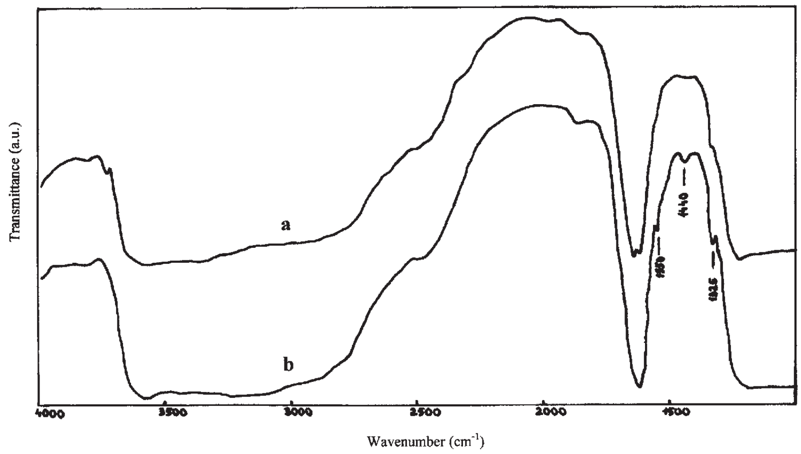

Fig. 5. IR Spectra of Y zeolite without (a) and with (b) adsorbed SO_2.

The IR spectra of Y zeolite with and without adsorbed sulfur dioxide are shown in Fig. 5. An absorption band at 1325 cm^{-1}, corresponding to adsorbed SO_2, can be easily seen. The accompanying band at 1150 cm^{-1} is not visible because of the background absorption of the zeolite in this region. A pair of absorption bands at 1440 and 1550 cm^{-1} that might be the ν_3 and ν_1 vibrations of perturbed SO_2 molecules can also be seen.[26] Hence, the spectrum shows two forms of adsorbed sulfur dioxide, physisorbed and chemisorbed.

Deo *et al.*[26] suggested that SO_2 adsorption results in the disappearance of the high frequency OH vibration and the appearance of a broad band at 3500 cm^{-1} due to hydrogen-bonded OH. Obviously the SO_2 is adsorbed by hydrogen bonding to surface hydroxyl groups. This fact was not visible in the present study because of the background absorption of the zeolite in this region of the spectrum.

Acidity studies

The total acidity of the sample with and without adsorbed sulfur dioxide was determined. The results obtained are presented in Table I. It can be seen that the total acidity of the sample increased four times when sulfur dioxide was adsorbed.

TABLE I. Total and Lewis acidity of Y zeolite, with and without adsorbed SO_2

Sample	Total acidity/mmol g^{-1}	Lewis acidity/mmol g^{-1}
Y	0.36	under the limit of detection
Y + SO_2	1.32	1.02

It is known that sulfur dioxide is a middle Lewis acid with the S atom being the acceptor site. We considered that the Lewis acidity is responsible for the increase of the total acidity of the sample containing SO_2 and so the Lewis acidity of samples with and without

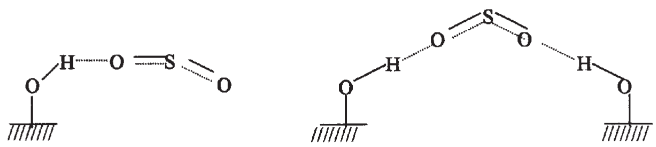

Fig. 6. Sulfur dioxide adsorption mechanism on Y type zeolites.

SO_2 were measured using ethyl acetate as a probe molecule. The results obtained are presented in Table I. In the case of the sample without SO_2, no Lewis acidity was detected, while the sample with adsorbed SO_2 showed significant Lewis acidity.

These observations lead to the conclusion that the adsorbed sulfur dioxide is responsible for the increase in the Lewis acidity of the samples. This, in correlation with the results obtained by IR spectroscopy, allows the supposition that the sulfur dioxide molecules are adsorbed by hydrogen bonding to one or two conveniently positioned surface hydroxyl groups, as shown in Fig. 6.

This type of proposed mechanism explains the IR bands corresponding to the interaction of SO_2 with OH groups[26] and the variation of the total acidity and the large increase of the Lewis acidity.

CONCLUSIONS

Y zeolite possesses good sulfur dioxide adsorptive properties and its activity remains constant during 20 adsorption-desorption-regeneration cycles. It is interesting to note that the values of the adsorption capacity for Y zeolite are higher than those for other zeolites presented in the literature.[12,13,17]

The adsorption temperature and sulfur dioxide concentration in gases are key factors which exert major effects upon the adsorption capacity, which diminishes with increasing temperature and with decreasing sulfur dioxide concentration in the gases.

The IR and the acidity measurements on samples with and without adsorbed sulfur dioxide showed that the SO_2 molecules are probably adsorbed by hydrogen bonding to one or two conveniently positioned surface hydroxyl groups.

ИЗВОД

ПРОУЧАВАЊЕ АДСОРПЦИЈЕ СУМПОР-ДИОКСИДА НА Y ЗЕОЛИТУ

IOAN-CEZAR MARCU и IOAN SĂNDULESCU

Department of Chemical Technology and Catalysis, Faculty of Chemistry, University of Bucharest, Bd. Regina Elisabeta No. 4-12, Bucharest – 03 Romania

Проучване су карактеристике адсорпције сумпор-диоксида на Y зеолиту помоћу рендгенске дифракције у области концентрације 0,9 – 6 % (v/v) и температурном опсегу 25 – 200 ºC. Показано је да сорбент има релативно висок апсорпциони капацитет. Y зеолит није изгубио своју активност ни после 20 адсорпционо-десорпционо-регенеративних циклуса. Начин адсорпције сумпор-диоксида на Y зеолиту проучаван је упоређењем зеолита са и без адсорбованог сумпор-диоксида инфрацрвеном спектроскопијом као и одређивањем Lewis-ове киселости. Молекули сумпор-диоксида су вероватно адсорбовани водоничним везама за једну од погодно постављених хидроксилних група.

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