SO₂ ADSORPTION ON TYPE Y ZEOLITE SYNTHESIZED FROM COAL FLY ASH

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Abstract: Ca- exchanged zeolite Y was prepared using coal combustion fly ash as a source of silica. This zeolite was characterized by chemical analysis, X-ray diffraction, N₂ adsorption and scanning electron microscopy. Its behaviour in SO₂ removal at 100°C, 0%-6% H₂O (v/v), 5% O₂ (v/v), 1000 ppmv SO₂ and spatial velocity of 1015 h⁻¹ was evaluated. The obtained results show that SO₂ removal capacity of fresh samples is high, decreasing to an almost constant value after some cycles of adsorption/desorption in absence of water in the gas stream. In presence of water the adsorption proceeds via H₂SO₄ formation, as the CaSO₄ detected in exhausted samples by XRD and FTIR analysis indicates. The formed H₂SO₄ produces a severe alteration in the zeolite structure that is responsible for its decreasing activity along several cycles adsorption-desorption.

Keywords: Fly Ash utilisation, adsorption, SO₂

1. INTRODUCTION

The increasing concern on the protection of the environment has influenced the design and operation of power plants, especially on the reduction of sulfur dioxide and nitrogen oxide emissions. Lime-based scrubbing is the post-combustion option currently used by utilities to reduce their SO₂ emissions (Liu et al., 2010; Srivastava et al., 2001). Although this flue gas desulfurization process has a number of advantages, it has also the serious drawback of generating a huge amount of solid wastes, which are also an environmental concern. Dry regenerative sorption processes based on the chemical reaction of SO₂ with a sorbent or catalyst is an interesting alternative for the control of SO₂ emissions because of their minimum waste disposal problems and their low energy requirements, since it avoids flue gas reheating. The sorbents are alumina or silica coated by a transition or alkaline earth metal precursor, activated carbon or charcoal, and to a lesser extent, zeolites. (Lin and Deng, 1988; Izquierdo et al., 2003; Demirbas, 2006).

Natural or synthetic zeolites are an important class of micro porous solids, which have been widely used as molecular sieve for gas separation. Some zeolites have also a good SO₂ adsorption capacity under several conditions and ability for regeneration (Cezarmarcu and Sandulescu, 2004; Deng and Lin, 1995; Gupta et al., 2004). Some zeolites can also adsorb simultaneously SO₂ and NO, in presence of water molecules (Kirschhock et al., 2004).

The use of coal fly ash as the base material in zeolite synthesis is attractive both economically
and environmentally, as fly ash represents about 60% of coal combustion products in coal-fired power plants (ECOBA, 2008; ACAA, 2009).

Research has been done in conversion of bulk fly ash into pure zeolite (Querol et al., 2002) by hydrothermal or fusion methods. However, direct conversion by hydrothermal method, produces heterogeneous zeolitic materials of low pore volume, and residual non-reacted fly ash components. The fusion method has the advantage of a higher purity of the final product, but the drawback of the high temperatures needed for the process (Chareonpanich et al., 2011). A two-stage procedure (Hollmann et al., 1999) enables to obtain pure-form zeolites by hydrothermal method using the fly ash as a source of Si. Moreover, high pore volume zeolites like A, X or Y can be obtained with this method.

Zeolite Y have channels of near circular cross section of 6 Å<d<9 Å, wide enough to adsorb SO2 molecules. Like other faujasite type zeolites, it has a low Si/Al ratio and therefore a hydrophilic character. This low Si/al ratio involves also a large population of cationic sites, which can act as adsorption centers.

Ion exchange is used for improvement of zeolites adsorption capability or catalytic activity. The ion exchange could modify pore volume or pore size, and promote changes in the zeolite lattice, which can influence the SO2 adsorption. Alkaline and alkaline-earth metal cations have been used for this purpose, but the SO2 adsorption improvement depends not only on the cation but also on the zeolite type and the adsorption conditions (temperature, and presence of other gases like water vapour, O2 or CO2) (Ivanova and Koumanova, 2009; Teraoka et al., 1997).

Water vapour in the flue gas can be preferentially adsorbed by zeolite Y because of its hydrophilic character, which can influence their SO2 adsorption capacity. Studies on SO2 adsorption in zeolites are mostly related to the adsorption of pure SO2, and very few studies on the SO2 adsorption in zeolites in presence of water or other gases can be found in the literature. In this context, this investigation was undertaken to determine and evaluate the SO2 abatement capacity at flue gas conditions (100ºC, 1000 ppmv SO2, 5% O2, 0- 6% H2O) of a calcium-exchanged zeolite Y obtained from coal fly ash by the two-stage method.

In the present paper, experimental procedures and materials are described in section 2, the obtained results are shown and discussed in section 3, and finally some conclusions are stated in section 4.

2. EXPERIMENTAL

2.1. Preparation of LYNa-FA zeolite.

Silica extraction. The SiO2 extraction from fly ash was carried out in a closed heated system using a 300 cc autoclave reactor with continuous stirring, and temperature and pressure controls (Parr 5500). The coal fly ash used was a class F from a pulverized coal power station from Escucha, Spain. Its chemical composition is given in Table 1. A 3.9 M NaOH solution and a ratio cc NaOH/g fly ash of 3.1 were used. The temperature and reaction time were 150ºC and 3.5 h respectively. After finishing the reaction time, the solution was separated from the mixture by filtration. In order to increase the Si content of the solution, a second SiO2 extraction was performed on fresh fly ash using the first extract as alkaline solution. In this way a final extract of chemical composition 5.3% SiO2, 4.4% Na2O, 0.3% K2O and 90.0% H2O was obtained.

Zeolite Y synthesis. The synthesized zeolite Y was ion-exchanged by calcium nitrate solution 0.1 N at 20ºC for 30 min. After being washed with deionized water, the sample was dried at room temperature. This sample was named LYCa-FA.
In order to prevent pressure drop in the reactor for SO2 removal, powdered LYCa-FA was shaped like small pellets of about 1.5 mm section and 4 mm length using a sodium silicate solution as binder (zeolite/agglomerant ratio =10 g zeolite:3.5 ml of sodium silicate). Pellets were dried at 108º for 14 h, cut in pieces of 3-5 mm long and cured in furnace at 600º during 1 h. After that, pellets were cooled slowly into the furnace. Zeolite LYCa-FA in the pellets showed a low structural affection after curing at 600º, as determined by XRD.

Table 2. Composition of different gels in synthesis of zeolite Y from fly ash extract

<table>
<thead>
<tr>
<th>Batch preparation</th>
<th>Coefficients for every oxide in gel composition</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Na2O</td>
</tr>
<tr>
<td>Seed gel</td>
<td>1.00</td>
</tr>
<tr>
<td>Feedstock gel</td>
<td>1.00</td>
</tr>
<tr>
<td>Overall gel</td>
<td>1.00</td>
</tr>
</tbody>
</table>

2.2.Characterization of zeolites

Zelite LYCa-FA was analyzed, by Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES) to obtain its calcium and sodium content: 5.14meq Ca2+/g and 0.84 meq Na+/g, which represents 10.3 % Ca and 1.9 % Na.

Both zeolites, LYNa-FA and LYCa-FA were also characterized by X Ray Diffraction (XRD), Scanning Electron Microscopy (SEM) and surface area measurement. XR diffractograms were obtained in an AXS D8 ADVANCE Bruker diffractometer, with a graphite monochromator, CuKα radiation (λ=1.5406 Å) and a NaI (TI) scintillation counter.

Table 2. Composition of different gels in synthesis of zeolite Y from fly ash extract

Table 1. Escucha fly ash composition obtained by Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES)

<table>
<thead>
<tr>
<th>% MxOy</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO2</td>
</tr>
<tr>
<td>Al2O3</td>
</tr>
<tr>
<td>CaO</td>
</tr>
<tr>
<td>Fe2O3</td>
</tr>
<tr>
<td>K2O</td>
</tr>
<tr>
<td>MgO</td>
</tr>
<tr>
<td>Na2O</td>
</tr>
<tr>
<td>TiO2</td>
</tr>
</tbody>
</table>

SEM images were obtained by a Hitachi S3400N equipped with EDX Röntec X Flash de Si (Li). Pellets were imbibed in epoxy resin and after polymerization, discs were polished to prepare longitudinal and transverse sections of pellets for further observation and analysis.

Surface areas of fresh and used zeolites were obtained applying BET equation to nitrogen adsorption isotherms at -196ºC. Isotherms were obtained in an apparatus ASAP 2020 from Micromeritics. Prior to the analysis, samples were outgassed at 250ºC up to a vacuum of 10⁻⁵ mm Hg.

Fresh zeolite and some of the samples resulting after SO2 cycles of adsorption/desorption experiments were also studied by FTIR spectroscopy in a Brucker Vertex 70 IRTF spectrometer using the technique of KBr disc (120 mg discs at 0.5 % sample concentration).

2.3. SO2 removal tests

An experimental installation built up for this purpose was used to test SO2 removal capacity of samples. A diagram of the installation is shown in Fig. 1. The installation consists of a fixed bed reactor, devices for the preparation of gas mixtures, temperature control and on-line analysis of the concentration of the gas stream. A flow of 25 ml/min of gas containing 1000 ppmv of SO2, 5% (v/v) O2 and Ar as balance is passed through a bed of sample at 100ºC of temperature. The reactor was provided with a bypass which allows the measurement of the concentration of each species before each experiment by mass spectrometry (MS). During the reaction the evolution of SO2, O2, and H2O were followed by mass spectrometry (MS).
The reaction results are described in terms of SO$_2$ adsorption: C/C$_0$, being C the concentration of SO$_2$ at a time t and C$_0$ the initial concentration of SO$_2$, measured when the gas stream is bypassed the reactor, before starting an experiment.

Desorption of exhausted samples after adsorption experiments was conducted at 500 °C of temperature and a flow of 25 ml/min of Ar. Time used for regeneration was variable depending on the evolution of SO$_2$, considering the final point when the concentration was below 30 ppmv SO$_2$.

3. RESULTS AND DISCUSSION

3.1. Characterization of samples

Zeolites LYNa-FA and LYCa-FA presented XRD patterns of Faujasites (Linde Type Y) with peak intensities and values of 2θ very similar for both materials (see Fig. 2).

Chemical analysis by total dissolution of sample in HF and ICP-OES showed the chemical stoichiometry $K_{0.2} Na_{1.2} Al_{1.2} Si_{1.9}$ for zeolite LYNa-FA. The presence of K in the structure is due to the existence of that element in alkaline extract of fly ash. LYNa-FA (Si/Al=1.6) could be considered as medium-silica Linde Type Y.

The theoretical chemical composition of this zeolite is Na$_2$ Al$_2$ Si$_5$ O$_{14}$·10 H$_2$O.

Chemical analysis of the calcium-exchanged zeolite (LYCa-FA) led to the following stoichiometry $Na_{0.2} Ca_{0.4} Al Si_{23}$, which show that some exchange positions occupied initially by Na in original zeolite cannot be exchanged by Ca in the conditions of zeolite LYCa-FA preparation.

XRD pattern of that zeolite presents minor modifications compared to XRD pattern of zeolite LYNa-FA: peaks at 2θ=6.30, 15.70, 23.65 and 31.40° presented small shift (≤0.15°) towards lower values and intensity ratios for those peaks are slightly different in both zeolites suggesting small structural modifications in channels.

Study by SEM (see Fig. 3) showed that LYNa-FA zeolite has the typical octahedral crystals of Faujasites (Figure 3a) crystal size ≤2 μm). The distribution of Ca/Na in LYCa-FA pellets (Figure 3b) was determined by EDS, and the atomic element ratios obtained were the following: Si/Na=7.2, Al/Na=2.2 and Ca/Na=1.1, while the values calculated according the composition of mixture in pellets are Si/Na=7.2, Al/Na=2.8 and Ca/Na=1.1. So then, this good agreement suggests an adequate mixture of components in filling material.
3.2. SO$_2$ removal test

Breakthrough curves of zeolite LYCa-FA are given in Figure 4. Breakthrough curve named LYCa-FA fresh corresponds to the experiment carried out with fresh zeolite. Breakthrough curve named HTT corresponds to the experiment carried out with the zeolite previously treated at 500ºC for 1h in a flow of Ar. Breakthrough curves named 1 to 5 correspond to adsorption/desorption experiments. Thus cycle 1 is the curve obtained for the SO$_2$ adsorption on desorbed zeolite LYCa-FA fresh, cycle 2 is the curve obtained for the SO$_2$ adsorption on desorbed sample after cycle 1, and the same up to cycle 5.

![Fig. 3. SEM microphotographs of zeolite LYNa-FA (a); pelletized zeolite LYCa-FA(b)](image)

![Fig. 4. Breakthrough curves of LYCA-FA fresh, cycles 1 to 5 and thermally treated zeolite (HTT) in absence of water in the gas stream. (25 cc/min, 100ºC, 5% O$_2$, 1000ppmv SO$_2$, Ar as balance)](image)

All the breakthrough curves in Fig. 4 show typical S-shaped profiles, indicating a strong adsorption of SO$_2$ onto the samples. However, fresh sample exhibit a less steepness curve and a higher breakthrough time compared with those experiments where zeolite has undergone a previous heat treatment or adsorption/desorption cycle. This fact can be explained in terms of the water content of fresh zeolite. In presence of water the SO$_2$ adsorption proceeds according a different mechanism, probably via H$_2$SO$_4$ formation (Garcia-Martinez et al., 2002; Kirschhock et al., 2004; Laniecki et al., 1987).

In order to test the influence of water content in the fresh sample on SO$_2$ adsorption, fresh zeolite was heated up to 500ºC of temperature and a total flow of 25 ml/min of Ar during 1 h, simulating temperature, flow and time used during a desorption of experiment, previously to an SO$_2$ adsorption experiment. As can be seen in Fig. 4, the breakthrough curve obtained with HTT sample is very similar to curve corresponding to experiment carried out with sample after first desorption experiment.

Further adsorption cycles give similar breakthrough curves as well as SO$_2$ removal capacity, expressed as amount of SO$_2$ removed at breakthrough point of 50% (see Table 3). This fact is indicative of the thermal and chemical stability of the zeolite along the cycles in absence of water in the gas stream.

Because of the time taken, to be exhausted is different for each experiment, and to compare the amount removed in an experiment, the values given in Table 3 correspond to the amount of SO$_2$ removed when 50% of breakthrough is achieved.
The main difference in breakthrough curves is found between experiments carried out with fresh sample and desorbed samples. This difference could correspond to the presence of water in the fresh sample, because in presence of water SO$_2$ is converted to H$_2$SO$_4$ and this acid could form Ca salts. Therefore the difference found between fresh and regenerated samples can be due to two different facts: a part of SO$_2$ removed is not evolved during desorption or the H$_2$SO$_4$ could dealuminate the zeolite, modifying partially its structure and consequently decreasing its surface area.

In order to confirm these last points, experiments were conducted on LYCa-FA introducing water in the gas stream in a concentration of 6%, at the same reaction conditions as in experiments without water.

The breakthrough curves obtained are depicted in Fig. 5 and Fig. 6. As can be seen from the experiments shown in Fig. 5 the best performance of the zeolite LYCa-FA is obtained when water is introduced and no roll-up effect due to water is observed as it can be found described in the literature (Mello and Mladen, 2002). Moreover, the steepness of the curves are similar to that obtained for fresh sample in absence water in the gas stream shown in Fig. 4, indicating a similar SO$_2$ removal mechanism, but in presence of water, the breakthrough time and total SO$_2$ removal capacity (see Table 3) of fresh sample is much higher.

The mechanism of SO$_2$ adsorption by the zeolite in presence of water is confirmed in the experiments shown in Fig. 6, where the breakthrough curves of LYCa-FA fresh and further adsorption-desorption cycles are represented.

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![Table 3. SO$_2$ removal capacity of LYCAFA in presence and absence of water in the gas stream](image)

<table>
<thead>
<tr>
<th>0% water experiments</th>
<th>mg SO$_2$ removed/g sample (50% breakthrough)</th>
<th>6% water experiments</th>
<th>mg SO$_2$ removed/g sample (50% breakthrough)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LYCa-FA fresh</td>
<td>6.9</td>
<td>LYCa-FA fresh</td>
<td>21.9</td>
</tr>
<tr>
<td>LYCa-FA HTT</td>
<td>1.8</td>
<td>LYCa-FA Cycle 1</td>
<td>4.5</td>
</tr>
<tr>
<td>LYCa-FA Cycle 1</td>
<td>1.9</td>
<td>LYCa-FA Cycle 2</td>
<td>2.4</td>
</tr>
<tr>
<td>LYCa-FA Cycle 2</td>
<td>2.2</td>
<td>LYCa-FA Cycle 3</td>
<td>1.6</td>
</tr>
<tr>
<td>LYCa-FA Cycle 3</td>
<td>2.2</td>
<td>LYCa-FA Cycle 4</td>
<td>0.9</td>
</tr>
<tr>
<td>LYCa-FA Cycle 4</td>
<td>2.2</td>
<td>LYCa-FA Cycle 5</td>
<td>0.7</td>
</tr>
<tr>
<td>LYCa-FA Cycle 5</td>
<td>2.2</td>
<td>LYCa-FA Cycle 5W</td>
<td></td>
</tr>
<tr>
<td>LYCa-FA Cycle 5W</td>
<td>16.2</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

![Fig. 5. Breakthrough curves obtained for LYCa-FA fresh and LYCa-FA cycle 5 in absence of water in gas stream and for LYCa-FA cycle 5W in presence of 6% water (25 cc/min, 100°C, 5% O$_2$, 1000ppmv SO$_2$, Ar as balance)](image)

As expected, the SO$_2$ adsorption capacity of fresh sample is much higher than that of the same sample in absence of water, and also higher than the LYCa-FA cycle 5 in presence of water (LYCa-FA cycle 5W), because the latter has lost its own structural water, which also plays a positive role in the SO$_2$ adsorption, as demonstrated the experiments shown in Fig. 4.

In fact, the sum of adsorbed amount of SO$_2$ by LYCa-FA cycle 5W (16.2 mg) and LYCa-FA fresh in absence of water in the gas stream (6.9 mg) fits quite well to the amount of SO$_2$ adsorbed by LYCa-FA fresh in presence of water in the gas stream (21.9 mg).

On the other hand, it can be observed in Fig. 6 a noticeable decrease in SO$_2$ removal capacity of LYCa-FA after several cycles adsorption-desorption in presence of water in the gas stream. This decrease can be attributed to the
dealumination of zeolite caused by the formed H2SO4, which partially destroys the zeolite structure. This point is confirmed by the decrease in BET surface and pore volume (see Table 4) and also by XRD and FTIR studies.

Fig. 6. Breakthrough curves of LYCA-FA fresh, cycles 1 to 5 in presence of 6% water in the gas stream. (25 cc/min, 100ºC, 5% O2, 1000ppmv SO2, Ar as balance).

Table 4. BET surface areas and pore volume of pelletized fresh and used zeolites

<table>
<thead>
<tr>
<th>Sample</th>
<th>S BET (m²/g)</th>
<th>Vp/p0=0.99 (cm³/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LYCa-FA</td>
<td>426</td>
<td>0.37</td>
</tr>
<tr>
<td>LYCa-FA(after cycle 5)</td>
<td>235</td>
<td>0.25</td>
</tr>
<tr>
<td>LYCa-FA(after cycle 5W)</td>
<td>288</td>
<td>0.32</td>
</tr>
</tbody>
</table>

Fig. 7. XRD of (1) LYCa-FA after several cycles of SO2 adsorption in presence of water, (2) LYCa-FA after SO2 adsorption in absence of water and (3) LYCa-FA fresh

Diffractograms of several samples are depicted in Fig. 7. XRD pattern of sample LYCa-FA after SO2 adsorption in absence of water in gas stream presents minor modifications with regards to XRD pattern of fresh zeolite excepting for the intensity of peak at 2θ=6.30º. This result suggests a modification in the size of channels, but no structural modification of the zeolite. This fact agrees with the decrease of the surface area (see Table 2) and with the lower SO2 removal capacity exhibited during cycle 5 (see Table 3) compared with fresh zeolite.

XRD pattern of sample LYCa-FA after several cycles of adsorption-desorption in presence of 6% water presents important differences from pattern corresponding to fresh zeolite. Lower intensities and disappearance of some peaks suggest important structural modifications, which could be due to acid formation. The appearance of peaks at 2θ = 19 º, 28.2 º and 38.5º, corresponding to CaSO4, confirms the formation of H2SO4.

No significant changes are observed in FTIR spectrum of LYCa-FA after SO2 adsorption in absence of water with regards to fresh sorbent LYCa-FA, as can be seen in Fig.8. However, some changes in spectrum of LYCa-FA after SO2 adsorption in presence of H2O can be appreciated: new small peaks appear at 1385, 680 and 600 cm⁻¹ and a strong absorption about 1140 (shoulder) that overlaps with strong adsorption in 1200-1100 region related to the Si-O bond vibrations in zeolite structure.

These new FTIR bands are related to presence of sulfates (Gadsden, 1975): small peak at 1385 cm⁻¹ is associated to asymmetric stretching vibration of S=O (Sohn et al., 2001), stronger absorption about 1140 cm⁻¹ corresponds to asymmetric stretch of S-O and small peaks which appear at 680 and 600 cm⁻¹ correspond to asymmetric bending vibration of S-O (Lane, 2007), these last absorptions being characteristic of anhydrous CaSO4.
4. CONCLUSIONS

A Calcium-exchanged zeolite type Y was obtained from coal fly ash by the two-stage method, using fly-ash as source of silica. This zeolite showed a stoichiometry \( Na_{0.2} Ca_{0.4} Al Si_{2.3} \), and the typical octahedral crystals of Faujasites. The \( SO_2 \) adsorption capacity of this zeolite at simulated flue gas conditions was high, and very dependent on the presence of water (both structural as well as in the gas stream). The different steepness of the breakthrough curves suggests different mechanisms for \( SO_2 \) adsorption in presence or in absence of water. In presence of water the adsorption proceeds via \( H_2SO_4 \) formation, as demonstrates the presence of \( CaSO_4 \), determined by XRD and FTIR analysis of exhausted samples. The formed \( H_2SO_4 \) produces a severe alteration in the zeolite structure that is responsible for its decreasing activity along several cycles adsorption-desorption.

ACKNOWLEDGEMENTS

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**Fig. 8. FTIR spectra of (1) LYCa-FA fresh, (2) LYCa-FA after \( SO_2 \) adsorption in absence of water and (3) LYCa-FA after several cycles of \( SO_2 \) adsorption in presence of water.**
chemically modified with salt solutions. 
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