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No removal in the selective catalitic reduction process over Cu and Fe exchanged type Y zeolites synthesized from coal fly ash

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ABSTRACT

The nitric oxide (NO) removal capacity of ion-exchanged zeolite Y obtained from coal combustion fly ash was evaluated in this work. Zeolite Y was exchanged either with Cu^{2+} or Fe^{2+} to obtain two different catalysts for the selective catalytic reduction of NOx from flue gas.

The selective catalytic reduction experiments were carried out at temperatures ranging from 50°C to 350°C, water content 0% and 5% and 5% O_2. In the absence of water, a total conversion of NO is obtained at 200°C for both zeolites, but important differences were found between zeolites LY-Cu and LY-Fe in the reduction of NO at temperatures lower than 200°C, and especially in the presence of water, that could be attributed to the different temperatures at which active species Cu^{2+} and Fe^{3+} are available for both ion-exchanged zeolites at the studied conditions. The greater surface area of zeolite LY-Cu can also contribute to its higher activity.

KEYWORDS
Coal fly ash; NO; selective catalytic reduction; zeolite

1. Introduction

The two oxides of nitrogen identified as important pollutants in the lower atmosphere are nitric oxide (NO) and nitrogen dioxide (NO_2), jointly referred to as NO_X. NOx are formed during the combustion of fossil fuels. NOx and the pollutants formed from NOx in the atmosphere can be transported over long distances. This means that problems associated with NOx are not confined to areas where NOx are emitted.

NOx react with other substances in the air to form acids, making rainwater acidic. Moreover, the chemical interaction in the atmosphere of nitrogen oxides, hydrocarbons, and oxygen under bright sunlight produces two secondary pollutants, leading to the formation of photochemical smog (the so-called ground level ozone) (Smith, 1980).

The increasing knowledge of pollution problems arising from NO_X has led to the introduction of stringent regulations in the developed countries since the 1990s, encouraging the development of low-NOx combustion techniques.

The International Energy Outlook projects an increase in global electricity generation by 2.2% per year (EIA, 2013). The burning of fossil fuels by power plants will continue to play a key role in energy production in many industrial and developing countries for decades to come. Because of this, NOx emissions associated with fossil fuel power generation are still an important issue.

Despite the fact that flue gas treatment results in relatively high investment and operational costs than combustion control, this method has become indispensable to meet the ever increasing stringent regulations.

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Selective catalytic reduction (SCR) is the only flue gas denitrification technique so far extensively studied, successfully commercialized and applied on a large scale (Hjalmarsson, 1990). The basic principle of SCR is the reduction of NOx to N_2 and H_2O by the reaction of NOx and reducing agents as ammonia (NH_3) within a catalyst bed. However, in tail-end position, the reactor is placed at the final flue gas cleaning stage where the temperature of the flue gas is too low for the catalytic reaction and therefore it has to be raised to a higher temperature at which the catalyst is effective. Noble metals, metal oxides, zeolites, and different types of carbons are used as the catalysts for SCR. However, most catalysts have low conversion of NOx at lower temperatures.

Zeolites can operate at lower temperatures than that corresponding to commercial catalysts based on vanadium and, in this context, present research work focuses on catalysts based on ion-exchanged zeolite partially synthesized from coal fly ash for SCR of NOx. The comparison of Cu and Fe exchanged over the same zeolite and tested on the same operating conditions can give valuable information about their feasibility as NO reduction catalysts. Moreover, few research works can be found in the literature concerning SCR of NO in the presence of water vapor using zeolite fly-ash-based catalysts.

2. Experimental

2.1. *Preparation of materials*

Coal fly ash was used as silicon source for the preparation of zeolite Y. The composition of the alkaline extract was as follows: 27.93 g Si/l, 36.61 g Na/l, and 0.08 g Al/l.

Zeolite Y was prepared according to verified recipe of International Zeolite Association (Robson and Lillerud, 2001). Adapting the theoretical molar ratios to the alkaline extract from fly ash, the resulting molar ratios are 4.99, 0.51, 0.10, 9.97, and 0.02, respectively. Zeolite thus obtained was referred as LY-Na.

The preparation of the acidic form of zeolite Y was carried out by replacing Na^+ in LY-Na with NH_4^+ and further calcination. This acidic form of the zeolite was labeled LY-H Cu- and Fe-exchanged zeolite Y were prepared at room temperature for 30 min, using an ion concentration of 0.05 M for Cu^{2+} and 0.01 for Fe^{2+}, keeping pH below 4.5 and 6.5, respectively. The exchanged zeolites were named LY-Cu and LY-Fe. LY-Fe (II) was subsequently converted into the definitive LY-Fe (III) by air heating (550°C, 6 h).

2.2. *Characterization of materials*

Zeolites were characterized by X-ray diffraction (XRD).

Diffractograms were obtained in an AXS D8 ADVANCE Bruker diffractometer, with a graphite monochromator.

The obtained zeolites were analyzed in an SEM (scanning electron microscopy) installation (Hitachi S3400N) coupled with energy dispersive X-ray spectrometry (EDS). Average chemical composition of the synthesized zeolites was calculated from EDS analyses in every sample.

Surface area of pelletized zeolites was obtained by applying BET (Brunauer, Emmet, Teller) equation to nitrogen adsorption isotherms at −196°C. Isotherms were obtained in an apparatus ASAP 2020 from Micromeritics. Prior to the analysis, samples were outgassed 1 h at 90°C and further at 250°C up to a vacuum of 10^{-5} mm Hg.

2.3. *NO removal tests*

An experimental installation was used to test the NO removal capacity of the zeolites under SCR conditions. The installation consists of a fixed-bed reactor and devices for the preparation of gas mixtures, temperature control, and online analysis of the concentration of the gas stream.

A flow of gas containing 1,000 ppmv NO, 5% (v/v) O_2, 1,100 ppmv NH_3, 0–5% H_2O and Ar as the balance is passed through a bed of zeolite at different temperatures. The reactor was provided with a bypass which allows the measurement of the NO concentration before each experiment. The concentration of NO, NO_2, N_2O and N_2, NH_3, O_2 and H_2O are monitorized online using a mass spectrometer calibrated for each gas. The reaction results are described in terms of NO conversion as

$$\%\text{NOconversion} = (\text{NO}_{\text{in}} - \text{NO}_{\text{out}}) \times 100/\text{NO}_{\text{in}}.$$

The selectivity of the reaction is calculated by

$$\%\text{Selectivity to } N_2 = N_{2\text{out}} \times 100/(N_{2\text{out}} + N_2O_{\text{out}})$$

No N_2O was detected at the outlet of the reactor once the steady state was reached.

In the presence of O_2, and at the studied conditions, 90–100 ppm of the inlet NO is oxidized to NO_2. The concentration of this NO_2 was followed also by mass spectrometry. More details of the experimental procedure are given in Izquierdo and Rubio (2008).

3. Results and discussion

The obtained sodium zeolite Y (LY-Na) shows typical crystal shapes (see Figure 1) of Faujasite family.

Stoichiometry obtained from inductively coupled plasma atomic emission spectroscopy and SEM–EDS for LY-H and metal-exchanged zeolites is shown in Table 1. It can be observed that total Na in LY-Na cannot be removed in the used exchange conditions. Some acidic sites are maintained after exchanging with Cu^{2+} or Fe^{2+}.

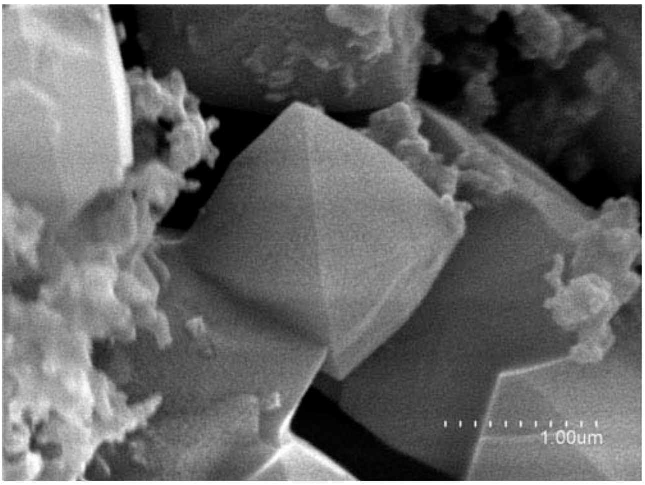

Figure 1. SEM photomicrography of zeolite LY-Na.

Table 1. Calculated stoichiometry for studied zeolites.

Material	Stoichiometry
LY-H	$(H_3O^+)_{0.4}$ $Na_{0.6}$ Al $Si_{2.4}$ $O_{6.8}\cdot$ 2.4 H_2O
LY-Cu	$(H_3O^+)_{0.2}$ $Na_{0.2}$ $Cu_{0.3}$ Al $Si_{2.3}$ $O_{6.6}\cdot$ 3.8 H_2O
LY-Fe	$(H_3O^+)_{0.2}$ $Na_{0.2}$ $Fe_{0.2}$ Al $Si_{2.3}$ $O_{6.6}\cdot$ 2.4 H_2O

X-ray diffractograms for the three materials are shown in Figure 2. 2Θ for the strongest reflection is shifted toward slightly lower values (6.3° for LY-H, 6.25° for LY-Cu, and 6.2° for LY-Fe) suggesting small enlarging of 12-ring channel zeolite after metal exchanges.

Surface areas and pore volume of the pelletized zeolites are reported in Table 2.

Cu-exchanged zeolite LY-Cu shows the highest surface area and micropore volume. However, the mesopore (diameter 2–50 nm) volume of Fe-exchanged zeolite LY-Fe is slightly higher. This indicates more structural defects in the intracrystalline pores for this zeolite, since ideal zeolite Y consists of sodalite cages with 7.4 Å diameter assembled to form larger supercages with a 12 Å diameter (Song et al., 2005).

The NO conversion profiles for SCR of NO by NH_3 in the absence of water vapor on samples LY-Cu and LY-Fe are presented in Figure 3. After a short initial period of time, steady state is achieved. In steady state, no emissions of N_2O are detected, and the selectivity to N_2 is 100%. At low reaction temperatures, the time needed to reach the steady state is higher than at high temperatures.

NO conversion values at the steady state for samples LY-H, LY-Cu, and LY-Fe in the presence or absence of water vapor in the inlet gas stream are reported in Figure 4. Negligible NO conversion occurred on the zeolite LY-H sample both in the presence or absence of water vapor.

In the absence of water, at low temperatures (below 200°C), low-NO conversion values are obtained, but NO conversion for sample LY-Cu is higher than that for LY-Fe. At higher temperatures, both zeolites can reach near 100% conversion. This fact can indicate that active species are available at different temperatures for both ion-exchanged zeolites (Berthomieu and Delahay, 2006; Kumar et al., 2006). For Cu ion-exchanged Y zeolite, the catalytic activity comes from the upkeep of the redox cycle at temperatures in the range of 200–210°C. On the contrary, at low temperatures the kinetic of the redox cycle Fe^{2+}/Fe^{3+} is slow and it is more difficult for the oxygen to reoxidize ferrous ions.

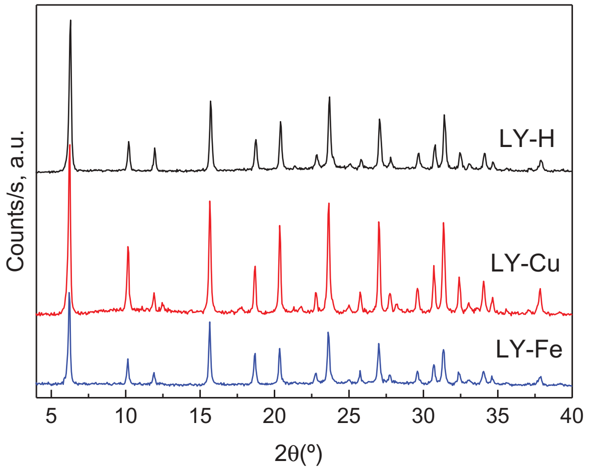

Figure 2. XRD diffractograms of the acidic form and metal-exchanged zeolite Y.

Table 2. Surface area and pore volume of the studied zeolites.

Material	`S_{BET} m²/g	V_p (at $p/p0$=0,995) cm³/g	$V_{micropore}$ cm³/g	$V_{mesopore}$ cm³/g
LY-H	402	0.25	0.18	0.05
LY-Cu	536	0.36	0.24	0.06
LY-Fe	182	0.17	0.06	0.09

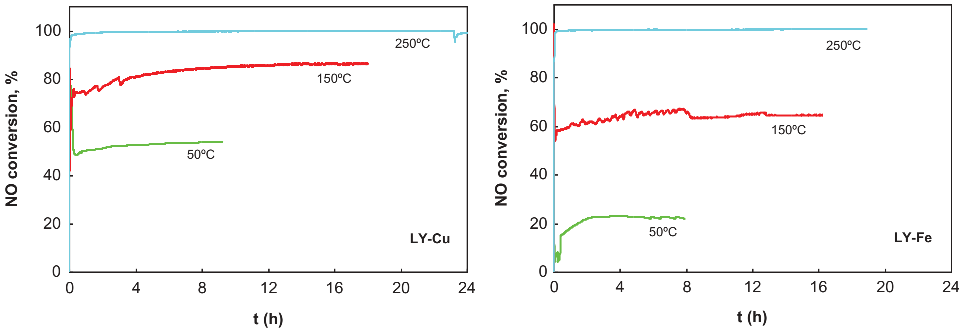

Figure 3. NO conversion curves for zeolites LY-Cu and LY-Fe. Experimental conditions as follows: 1,000 ppmv NO, 1,100 ppmv NH_3, 5% (v/v) O_2, 0% H_2O Ar as balance.

As an alternative for commercial vanadium-based SCR catalysts, temperature is an important issue, because of the possibility to avoid the reheating of the exhaust gases at tail-end position and because the N_2O formation is minimal at lower temperatures. But other important issue is the presence of water in the gaseous stream. Water vapor can influence negatively the activity of metal-exchanged zeolite catalysts due to the competition with reactant molecules for the surface active sites and to the capillary condensation of water.

In the present work, a concentration of 5% of water vapor was added to the simulated exhaust gas to study the behavior of the zeolites. NO conversions at steady state for the three zeolites studied are shown in Figure 4b. As it was expected, zeolite LY-Fe exhibits a decrease in NO conversion at temperatures below 200°C. At higher temperatures, maximum NO conversion are reached indicating that the increase in the kinetics of the redox cycle can compensate the water interaction.

On the contrary, maximum NO conversion is already reached at 100°C on zeolite LY-Cu. The overall reaction (1), where water is a product of the reaction, was suggested to apply to Cu-zeolite catalysts and Cu-faujasite zeolites (Komatsu et al., 1994; Kieger et al., 1999):

$$4NO + 4NH_3 + O_2 \leftrightarrow 4N_2 + 6H_2O \qquad (1)$$

Because it has been claimed that oxidation of Cu^+ to Cu^{2+} (the most active species) below 325°C temperature is due to NO + O_2, the presence of water vapor in the gas stream can displace the

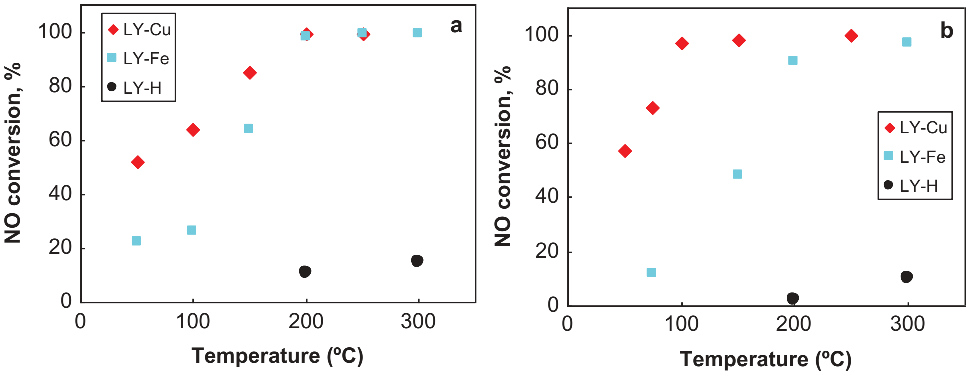

Figure 4. NO conversion at steady state. (a) 1,000 ppmv NO, 1,100 ppmv NH_3, 5% (v/v) O_2, 0% H_2O and Ar as balance. (b) 1,000 ppmv NO, 1,100 ppmv NH_3, 5% (v/v) O_2, 5% H_2O and Ar as balance.

equilibrium of the reaction (1), increasing the concentration of NO + O_2 on the neighboring of the Cu cations, favoring the oxidation of Cu^+ and increasing the amount of active sites.

In summary, the differences found between zeolites LY-Cu and LY-Fe in the reduction of NO at temperatures lower than 200°C, and especially in the presence of water, can be attributed to the different temperatures at which active species Cu^{2+} and $Fe^{3+}$are available for both ion-exchanged zeolites. The greater surface area of zeolite LY-Cu can also contribute to its higher activity at the studied conditions.

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