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# Selective catalytic reduction of NO by alcohols on Co- and Fe-Siβ catalysts

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## Abstract

Co–Siβ and Fe–Siβ catalysts prepared by a two-step post-synthesis method were characterised by EPR, diffuse reflectance UV–vis, XRD and $N_2$-physisorption. Iron and cobalt ions are present as isolated lattice tetrahedral $Co^{II}$ and $Fe^{III}$ species for low metal contents (0.7 and 0.9 wt.%, respectively). For higher iron content, $FeO_x$ oligomers appear. Zeolites with isolated $Co^{II}$ and $Fe^{III}$ species are active in selective catalytic reduction of NO with ethanol. On $FeO_x$ oligomers the oxidation of NO to $NO_2$ starts to dominate in the selective catalytic reduction of NO with ethanol at the temperatures higher than 700 K.

*Keywords:* Dealuminated beta zeolite; Siβ; Silanol; Cobalt; Iron; XRD; EPR; Diffuse reflectance UV–vis; NO reduction; SCR; Oxide

## 1. Introduction

Microporous materials containing transition metal ions have been much studied because of their potential application in catalytic oxidation of hydrocarbons or reduction of NO [1–4]. There has been many reports on selective catalytic reduction (SCR) of $NO_x$ by hydrocarbons in presence of oxygen over zeolites [3–6]. Alcohols such as methanol or ethanol have been found to act also as reducing agents [7,8].

In this paper, we have investigated the role of ethanol, as reducing agents, and of isolated lattice tetrahedral $Co^{II}$ and $Fe^{III}$ species in the SCR reaction on Co–Siβ and Fe–Siβ zeolites prepared by a two-step post-synthesis method which consists first of creating vacant T-sites by dealumination of β-zeolite with nitric acid, and then impregnating the resulting Siβ with aqueous $Co(NO_3)_2$ and $Fe(NO_3)_3$ solutions, respectively.

Co and Fe-containing zeolites have been characterised both at the macroscopic (chemical analysis, BET, XRD) and molecular (DR UV–vis, EPR) levels. Co (0.7 wt.%) Siβ and Fe (0, 9 and 3.6 wt.%) Siβ have been chosen as catalysts.

## 2. Experimental

A tetraethylammonium β (TEAβ) zeolite (Si/Al = 11) from RIPP (China) was dealuminated by treatment with a 13 mol $L^{-1}$ $HNO_3$ solution for 4 h at 353 K with stirring, as described earlier [9–11]. The resulting dealuminated Siβ zeolite (Si/Al > 1300) with vacant T sites was recovered by centrifugation, washed with distilled water and dried overnight at 353 K.

Then, in order to introduce Co and Fe ions in vacant T sites Siβ zeolite was impregnated in air by an aqueous $Co(NO_3)_2\cdot 6H_2O$ and $Fe(NO_3)_3\cdot 9H_2O$ solution. First, 2 g of Siβ were stirred for 24 h at 298 K in excess solvent using 200 ml of $Co(NO_3)_2\cdot 6H_2O$ ($1.2 \times 10^{-3}$ mol $L^{-1}$) or 100 ml of $Fe(NO_3)_3\cdot 9H_2O$ (0.9 or 3.6 mol $L^{-1}$) aqueous solution. Then, the suspensions (pH 2.4 or 2.3, respectively) were stirred for 2 h in air at 353 K until complete evaporation of water. The solid was then washed three times with distilled water and dried in air at 353 K overnight. The samples Co–Siβ with 0.7 Co wt.% and Fe–Siβ with 0.9 and 3.6 Fe wt.% are labeled $Co_{0.7}$Siβ, $Fe_{0.9}$Siβ and $Fe_{3.6}$Siβ, respectively.

Nitrogen adsorption–desorption isotherms were obtained at 77 K using a Micromeritics ASAP 2010 apparatus [12]. Powder X-ray diffractograms were recorded on a Siemens D5000 using

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the Cu K$\alpha$ radiation ($\lambda = 154.05$ pm). EPR spectra were recorded at 298 and 77 K on a Bruker ESP 300 computerised spectrometer at 9.3 GHz (X band) with a 100 kHz field modulation and a 10 G modulation amplitude.

Diffuse reflectance UV–vis (DR UV–vis) spectra were recorded on a Cary 5E spectrometer equipped with an integrator and a double monochromator.

The activity of catalysts in the SCR of NO with ethanol was measured in a conventional flow reactor coupled to a gas chromatograph. The composition of the feed was following: 1000 ppm NO, 1000 ppm ethanol, 2 vol.% $O_2$ with a catalyst volume 1 ml and GHSV 10,000 $h^{-1}$.

Before calalytic test the samples were heated up to 523 K in oxygen/helium mixture and then NO and ethanol vapour streams were switched on. In standard conditions 2 h catalytic runs in 523–623 K and 1 h runs in higher reaction temperatures were chosen ($NO_x$ and $CO_x$ concentrations at the reactor outlet were continuously monitored for checking if the pseudo steady-state conditions were established).

Reaction temperatures were enhaced every 50 K intervals up to 773 K, and then lowered in the same manner to 473 K. In the case of histeresis loop of NO conversion or product selectivities the heating sequence was repeated to obtaining the real steady-state reaction conditions in whole reaction temperature region.

## 3. Results and discussion

### 3.1. Characterization at the macroscopic level

The porosity and crystallinity of Si$\beta$ zeolite are preserved after its impregnation by $Co(NO_3)_2$ or $Fe(NO_3)_3$ solutions, drying and calcination. Si$\beta$, $Co_{0.7}$Si$\beta$, $Fe_{0.9}$Si$\beta$ and $Fe_{3.6}$Si$\beta$ present similar XRD patterns which do not show any evidence of extra lattice crystalline compounds or long-range amorphization of the zeolite. A change of the position of the narrow main diffraction peak around 22–23° is generally taken as evidence of lattice contraction/expansion of the $\beta$ structure [13,14]. The significant decrease of the $2\theta$ value of this after introduction of Co or Fe ions indicates some expansion of the $\beta$ structure and suggests that the latter are incorporated into lattice [13,14] and thus tetracoordinated.

### 3.2. Characterization at the molecular level: nature and environment of Co and Fe

As synthesized, the blue $Co_{0.7}$Si$\beta$ sample exhibits three UV–vis bands at about 537, 590 and 647 nm (Fig. 1) assigned to isolated tetrahedral Co species and attributed to $^4A_2 \rightarrow {}^4T_1$ ($^4$P), $^4A_2 \rightarrow {}^4T_1$ ($^4$F) and $^4A_2 \rightarrow {}^4T_2$ transitions, in line with earlier studies on Co-MFI and CoAPO-5 [15,16]. Exposure of $Co_{0.7}$Si$\beta$ to moist air does not lead to change of the coordination of $Co^{II}$ ions from tetrahedral to octahedral symmetry: the color of this sample remains blue and there is no UV–vis band at about 500 nm characteristic of $Co^{II}$ in octahedral symmetry ($3d^7$ configuration), in line with earlier report on Co-MFI zeolite [15,17]. The absence of a broad band above 500 nm, typical of $CoO_x$ oligomers [15], suggests that the latter are not present in $Co_{0.7}$Si$\beta$. The broad band around 289 nm is difficult to assign although it may be likely associated with oxygen-to-metal charge transfer (CT) transition [18], the oxidation state or coordination cobalt can not be ascertained.

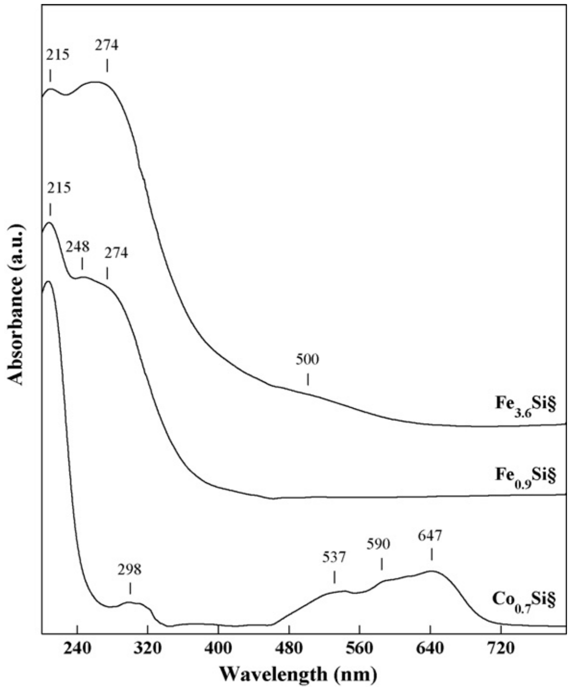

Fig. 1. DR UV–vis spectra of $Co_{0.7}$Si$\beta$, $Fe_{0.9}$Si$\beta$ and $Fe_{3.6}$Si$\beta$ samples. Spectra recorded at room temperature with Si$\beta$ as reference.

$Fe_{0.9}$Si$\beta$ exhibits bands at 215 and 248 nm assigned to isolated tetrahedral $Fe^{III}$ species involved in oxygen $Fe^{III}$ CT transitions while the band at 274 nm is associated to oxygen-to-octahedral $Fe^{III}$ CT transition, in line with earlier results

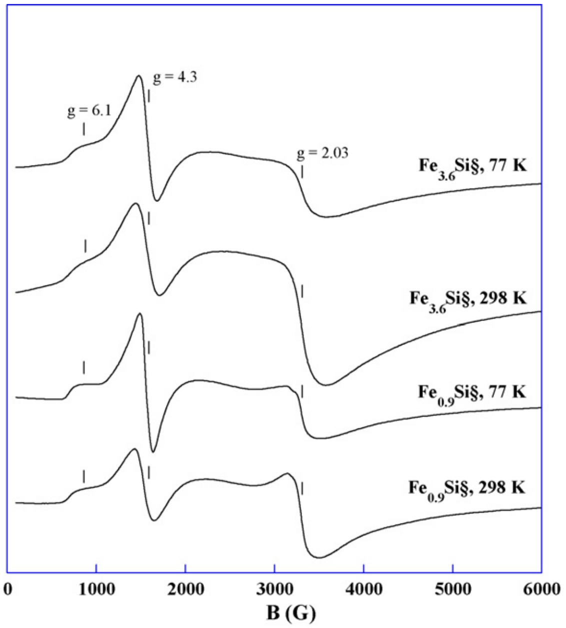

Fig. 2. EPR spectra (X-band) of $Fe_{0.9}$Si$\beta$ and $Fe_{3.6}$Si$\beta$ samples registered at 298 and 77 K.

[19,20]. For $Fe_{3.6}Si\beta$, a broad band at about 500 nm is assigned to FeOx oligomers, as proposed earlier [19].

The EPR spectra of $Fe_{0.9}Si\beta$ and $Fe_{3.6}Si\beta$ show three signals at $g = 6.1$, 4.3 and 2.03 (Fig. 2). The signal at $g = 4.3$ is assigned to tetrahedral lattice $Fe^{III}$ ions, the signal at $g = 6.1$ to isolated $Fe^{III}$ ions in higher coordination and the line at $g = 2.03$ to isolated $Fe^{III}$ ions or $FeO_x$ oligomers, as proposed earlier [6].

### 3.3. Catalytical properties

When ethanol is used as a reducing agent, the NO conversion and selectivity towards $N_2$ are very high on $Co_{0.7}Si\beta$ and $Fe_{0.9}Si\beta$ over a wide temperature range.

Fig. 3 presents the results obtained with $Co_{0.7}Si\beta$. A wide temperature range with selectivity towards $N_2$ exceeding 95% is observed for relatively high NO conversion level (from 20 to 75%). Above 623 K, the NO conversion (Fig. 3A) and the selectivity towards $N_2$ decrease while $NO_2$ is detected (Fig. 3B).

Figs. 4A and 5A show the NO conversion and Figs. 4B and 5B selectivities toward $N_2$ and $NO_2$ as a function of temperature reaction for $Fe_{0.9}Si\beta$ and $Fe_{3.6}Si\beta$ samples, respectively. $Fe_{0.9}Si\beta$ exhibits a very high selectivity towards $N_2$ in SCR of NO (over 95%) in a temperature window much wider (from 548 to 773 K) than in the case of $Co_{0.7}Si\beta$. $Fe_{3.6}Si\beta$ exhibits a very high selectivity towards $N_2$ in SCR of NO in the low temperature region (473–623 K) (Fig. 5B). However, at higher temperature selectivity towards $N_2$ substantially decreases at the expense of $NO_2$ formation. The different catalytic properties of $Fe_{0.9}Si\beta$ and $Fe_{3.6}Si\beta$ may be due to the different nature of iron species: the latter catalyst, apart from isolated $Fe^{III}$ ions also contains $FeO_x$ oligomers.

Apart from the promissive activity of lattice tetrahedral $Co^{II}$ and $Fe^{III}$ species in SCR of NO towards $N_2$, the ethanol oxidation on the investigated samples was rather not selective: the substantial amounts of ethylene, organic intermediates and carbon monoxide were observed up to 623 K or higher reaction temperatures. It was checked that organic intermediates formed during reaction contain only small amounts of nitrogen containing compounds (mainly acetonitrile).

We suggest that decreasing of the selectivity towards $N_2$ at higher temperature is related to the depletion of organic mild oxidation product in the reaction zone. On the basis of experimental evidences we can assumne that the first step of SCR reaction is oxidation of NO to $NO_2$. Then $NO_2$ reacts with ethanol molecule forming the active organic intermediates.

However, we have yet not enough experimental evidences to distinguish if $N_2$ may be formed in the consecutive reactions between NO and organic intermediates in the gaseous or adsorbed state [21,22] or in the course of NO dissociattive adsorption on the reduced catalyst surface and further

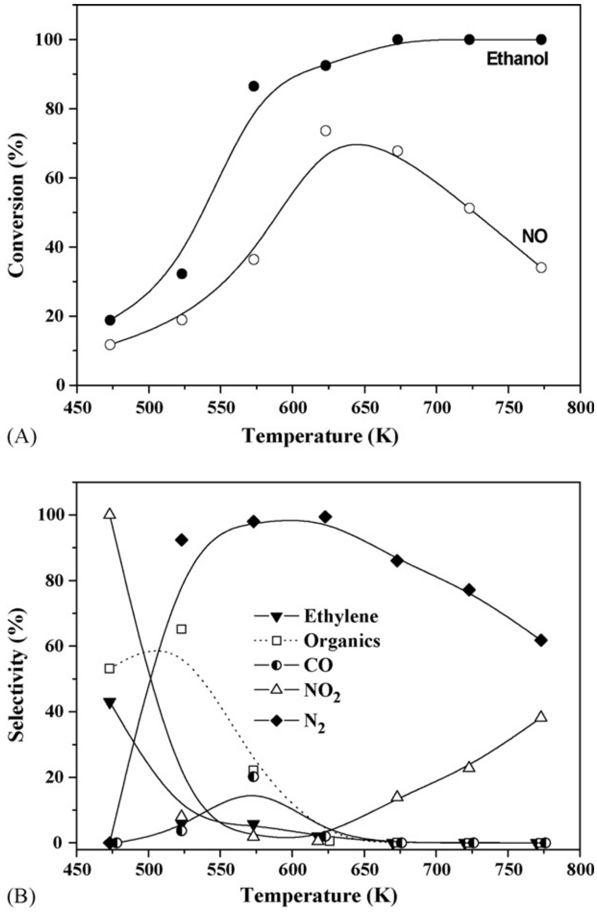

Fig. 3. Temperature reaction dependence of (A) ethanol and NO conversion and (B) product selectivities in SCR of NO with ethanol on $Co_{0.7}Si\beta$ catalyst.

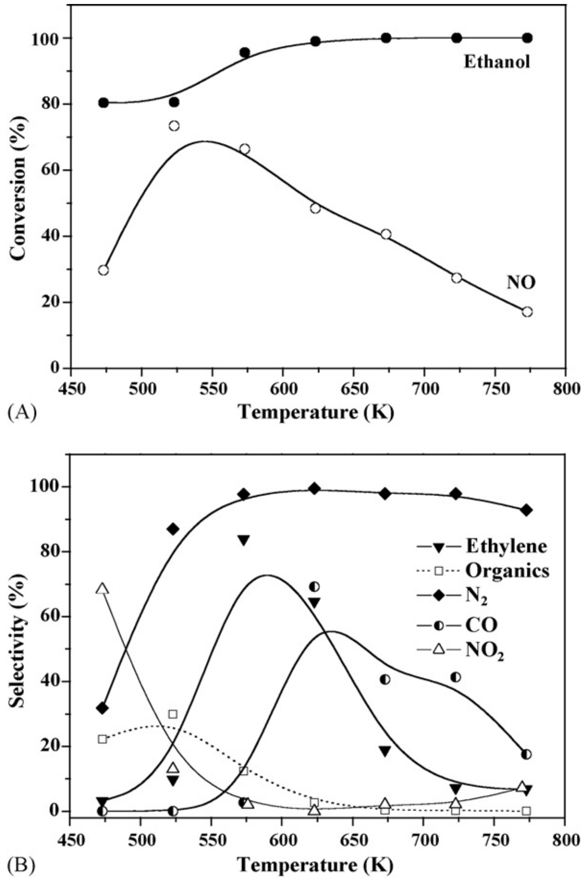

Fig. 4. Temperature reaction dependence of (A) ethanol and NO conversion and (B) product selectivities in SCR of NO with ethanol on $Fe_{0.9}Si\beta$ catalyst.

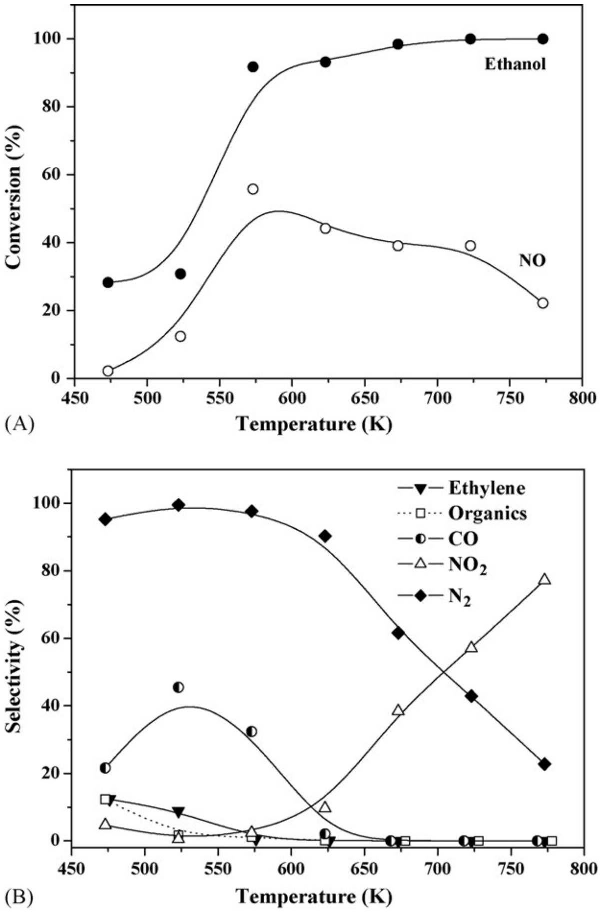

Fig. 5. Temperature reaction dependence of (A) ethanol and NO conversion and (B) product selectivities in SCR of NO with ethanol on $Fe_{3.6}Si\beta$ catalyst.

recombination of two atomic N adsorbed species to give rise to the formation of molecular $N_2$. In the latter case $NO_2$ serves as active intermediates and acts as reductant of adsorbed oxygen species left from NO decomposition to $N_2$ allowing to restore of the catalytic sites according to Djéga-Mariadassou model [23,24].

## 4. Conclusions

The aim of this work is to study the role of ethanol, as reducing agent, and of isolated lattice tetrahedral $Co^{II}$ and $Fe^{III}$ species in the SCR of NO on Co–Siβ and Fe–Siβ zeolites prepared by a two-step post-synthesis method.

As shown by UV–vis and EPR, upon impregnation of Siβ, prepared by dealumination to generate vacant T sites, Co or Fe are introduced from aqueous $Co(NO_3)_2 \cdot 6H_2O$ or $Fe(NO_3)_3 \cdot 9H_2O$ solution as isolated tetrahedral $Co^{II}$ or $Fe^{III}$ species respectively for low metal contents (0.7 and 0.9 wt.%, respectively). For higher iron content (3.6 wt.%) $FeO_x$ oligomers appear on the surface of Siβ zeolite.

Zeolites with isolated tetrahedral $Co^{II}$ and $Fe^{III}$ species are active and selective towards $N_2$ in the SCR of NO with ethanol. When $FeO_x$ oligomers appear, the oxidation of NO to $NO_2$ starts to dominate in the SCR of NO with ethanol at temperature above 700 K.

Further studies are underway to complement the description of the Co and Fe sites present in Co–Siβ and Fe–Siβ zeolites, particularly with EPR and Mössbauer spectroscopies.

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