

## Fe–Ce–ZSM-5 a new catalyst of outstanding properties in the selective catalytic reduction of NO with NH<sub>3</sub>

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**A Fe–Ce–ZSM-5 catalyst elaborated from a new synthesis route exhibits very high NO conversion (75–100%) in the selective catalytic reduction of NO by NH<sub>3</sub> in a wide temperature window (523–823 K), even in the presence of H<sub>2</sub>O and SO<sub>2</sub>.**

Nitrogen oxides emitted from mobile and stationary sources have been a major source of air pollution. Up to now the most efficient control technology to remove NO from stationary sources is the selective catalytic reduction (SCR) of NO by ammonia ( $4\text{NO} + 4\text{NH}_3 + \text{O}_2 \rightarrow 4\text{N}_2 + 6\text{H}_2\text{O}$ ).<sup>1</sup> Recently, there has been high interest in adapting this technology to mobile diesel engines in order to achieve impending emission standards. The most efficient SCR catalysts show optimum performance in a narrow temperature window while the automotive application of this process calls for a high NO<sub>x</sub> removal over a temperature range of 423–823 K. In this context there are continuing efforts to develop new highly active and selective catalysts for the reduction of NO to N<sub>2</sub> over a broader temperature window that are stable in the presence of SO<sub>2</sub> and water. Fe-overexchanged zeolite catalysts have been found to be attractive candidates for SCR reactions.<sup>2–4</sup> Ma and Grünert<sup>2</sup> and Sun *et al.*<sup>3</sup> reported the preparation of an overexchanged Fe-ZSM-5 catalyst by sublimation of FeCl<sub>3</sub> into H-ZSM-5; the catalyst showed NO conversions close to 80% (GHSV ≈ 300 000 h<sup>-1</sup>–360 000 h<sup>-1</sup>) in the temperature range 623–823 K and was stable in the presence of water vapor and SO<sub>2</sub>. Long and Yang<sup>4</sup> reported a Fe-ZSM-5 catalyst prepared by the ion exchange method showing nearly 100% NO conversion within the range 673–773 K; the addition of small amount of cerium increased the catalyst activity for temperatures above 773 K. Zeolites containing cerium were also found to be active catalysts for this process.<sup>5</sup> Unfortunately, for all these catalysts the NO conversion was very low below 600 K. We want to report here outstanding catalytic performances for the SCR of NO with ammonia over a new Fe-Ce-ZSM-5 catalyst; high NO conversion values (≥ 75%) were obtained within a much broader temperature window (523–823 K) under a high gas hourly space velocity (GHSV) of 332 000 h<sup>-1</sup>. Its catalytic activity remains stable when SO<sub>2</sub> and H<sub>2</sub>O were introduced in the feed. With an NO conversion value close to 90% at 563 K (N<sub>2</sub> selectivity > 99%) the new catalyst is more active than overexchanged Fe-ZSM-5 catalyst prepared by FeCl<sub>3</sub> sublimation method.<sup>2,3</sup>

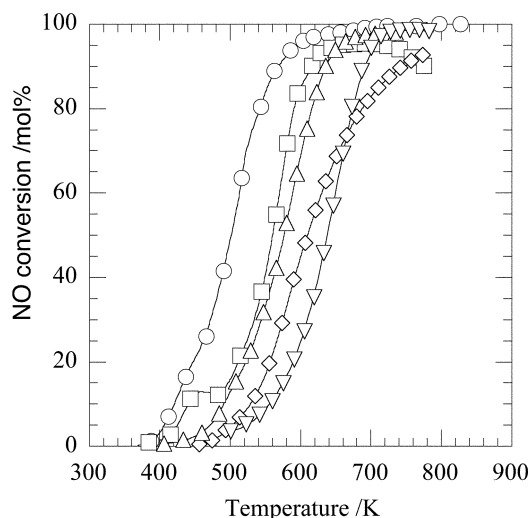
This new Fe-Ce-ZSM-5 catalyst was prepared in the organic phase by improving a previously reported method;<sup>6</sup> the parent zeolite material NH<sub>4</sub>-ZSM-5 (Si/Al = 16.4) supplied by Zeolyst International Company was used in its H<sup>+</sup> form. Iron and cerium were introduced into zeolite by using a solution of iron acetylacetonate and cerium nitrate dissolved in acetonitrile. Characterised by a higher dipole moment than water and a high dielectric constant, CH<sub>3</sub>CN is able to provide a tuned interaction medium inside the small pores of H-ZSM-5. 150 mL of an organic solution of iron and cerium (in the desired molar ratio) was added slowly during an 8 hour period over 3 g of zeolite dispersed in 40 mL of acetonitrile, at 443 K, with strong stirring in a refluxing flask. The triphasic reaction medium and the high temperature value were chosen in order to facilitate specific interactions between the cations and the zeolite framework inside the pores. The resulting product was aged for 48 hours at 393 K, the solvent evaporated and the material dried at 383 K overnight. Before the catalytic tests the samples were calcined at 723 K for 3 hours under a stream of

helium and oxygen. Temperature programmed reduction (TPR) by H<sub>2</sub>/Ar (3/97) was carried out by using a Micromeritics AutoChem 2910 apparatus with TCD detection. Details about the conditions used during TPR experiment are given elsewhere.<sup>7</sup> The catalytic experiments are performed at atmospheric pressure with a conventional fixed-bed flow reactor. The typical reaction conditions are as follows: 20 mg of sample (0.025 mL), 2000 ppm NO, 2000 ppm NH<sub>3</sub> and 3% O<sub>2</sub> in helium, balance He, 138.3 mL·min<sup>-1</sup> total flow rate and a GHSV = 332 000 h<sup>-1</sup>. The effluent composition was monitored continuously by sampling on line to a quadrupole mass spectrometer (Pfeiffer vacuum Omnistar equipped with channeltron and Faraday detectors 0–200 amu). Nine masses characteristic of NO (30), NO<sub>2</sub> (30,46), N<sub>2</sub>O (28,30,44), NH<sub>3</sub> (16,17), H<sub>2</sub>O (17,18), O<sub>2</sub> (16,32) were followed.

The compositions of the catalysts as determined by ICP analysis are given in Table 1. The conversion of NO as a function of temperature is reported in Fig. 1 for the different samples. For comparison, the catalytic behavior of an overexchanged Fe-ZSM-5 catalyst (CVD-Z), prepared according to the FeCl<sub>3</sub> sublimation procedure,<sup>8</sup> is also reported. The CVD-Z and Fe(3.9)-Z which contain the same Fe amount, exhibit similar trends for NO conversion with light-off temperature (50% NO conversion) at *ca.* 570 K. However, Fe(3.9)-Z demonstrates better performances with

**Table 1** Chemical composition of the samples

Sample	Composition (wt%)		Fe, Ce loading	
	Fe	Ce	Al	(mmol·gcat <sup>-1</sup> )
Fe(1.9)-Z	1.9	—	1.9	0.35
Fe(3.9)-Z	3.9	—	1.7	0.70
CVD-Z	3.9	—	2.1	0.8
Fe(1.6)Ce(2.5)-Z	1.6	2.5	1.9	0.5
Ce(3.9)-Z	—	3.9	1.9	0.3



**Fig. 1** NO conversion as a function of temperature, (—○—) Fe(1.6)Ce(2.5)-Z, (—□—) CVD-Z, (—△—) Fe(3.9)-Z, (—◇—) Ce(3.9)-Z and (—▽—) Fe(1.6)-Z.

full NO conversion above 623 K. It is noteworthy that only trace amounts of  $N_2O$  were detected below 673 K. At lower Fe content, Fe(1.9)-Z, the NO conversion profile is shifted to higher temperatures with light-off at about 623 K. For Ce(3.9)-Z the light-off occurs at 640 K. The presence of both Ce and Fe species in Fe(1.6)Ce(2.5)-Z sample has a strong positive influence on the catalyst activity with light-off at ca. 500 K and NO conversions over 90% above 563 K. These results demonstrate that the joint action of cerium and iron gives rise to a highly active catalyst for the process of SCR of NO by ammonia. It should be underlined that the NO selectivity to  $N_2$  is only slightly below 100% above 723 K. The TPR tool may provide useful information regarding the nature of Fe and/or Ce active species. In Fig. 2, large  $H_2$  consumption peaks between 473–1073 K are observed for the TPR profiles of Fe(1.9)-Z, Ce(3.9)-Z and Fe(1.6)Ce(2.5)-Z. For Fe(1.9)-Z the peak maximum occurs at 633 K and the hydrogen consumption ( $H_2/Fe$ , mol/mol) is 0.44; From similar TPR patterns and  $H_2$  consumption at  $T \leq 770$  K, it was proposed that Fe species in Fe-ZSM-5 and Fe-beta zeolite are composed of “Fe-oxo” cations of low nuclearity, with Fe–O–Fe bridges, which reduce from  $Fe^{III}$  to  $Fe^{II}$  upon TPR treatment.<sup>7–10</sup> The TPR profile of Ce-ZSM-5 presents a broad peak with a maximum at ca. 763 K pointing out that Ce species in zeolite are more difficult to reduce than Fe; the  $H_2/Ce$  ratio of ca. 0.5 corresponds to the reduction of  $Ce^{IV}$  to  $Ce^{III}$ . The TPR profile of the Fe(1.6)Ce(2.5)-Z shows that Fe and Ce species are in close interaction because they are simultaneously reduced and thus Fe makes the reduction of Ce much faster. The TPR trace presents a maximum at 663 K and a  $H_2/(Fe + Ce)$  ratio of 0.55 agrees quite well with the reduction of  $Fe^{III}$  to  $Fe^{II}$  and of  $Ce^{IV}$  to  $Ce^{III}$ . These observations (TPR trace and  $H_2/(Fe + Ce)$  value) are strong indications that Fe and Ce could be together in the same “Fe,Ce-oxo” cations with possibly Fe–O–Ce bridges. We further studied the effect of  $H_2O$  and  $SO_2$  on the SCR activity of Fe(1.6)Ce(2.5)-Z (Fig. 3). Before adding  $SO_2$  and water the SCR reaction had been

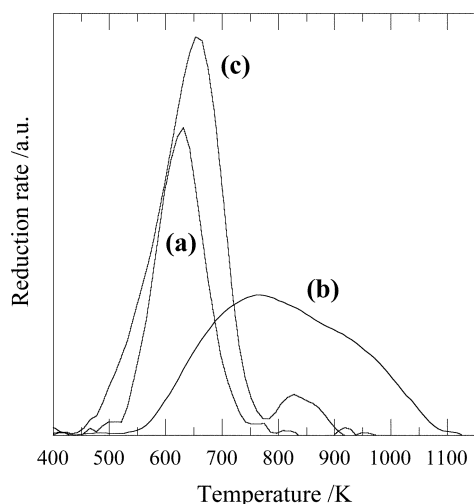


Fig. 2 TPR profiles of Fe(1.9)-Z (a), Ce(3.9)-Z (b), Fe(1.6)Ce(2.5)-Z (c).

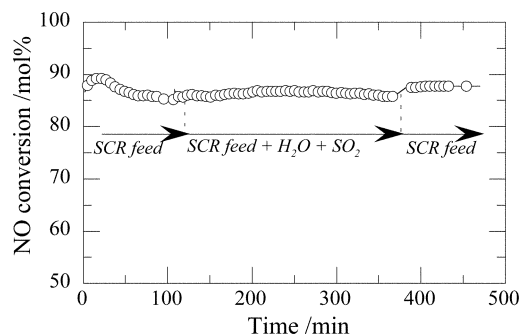


Fig. 3 NO conversion as a function of time at 573 K on Fe(1.6)Ce(2.5)-Z catalyst.

stabilized for 100 minute at 573 K. Upon switching to a  $H_2O$ ,  $SO_2$ -containing feed (2.0%  $H_2O$  and 25 ppm  $SO_2$ ), the NO conversion remains stable ( $\approx 90\%$ ) for 8 h. After removing the water vapor and  $SO_2$  a barely detectable increase of the conversion is observed.

In conclusion the new Fe-Ce-ZSM-5 catalyst exhibits outstanding performance for the selective catalytic reduction of NO when ammonia is used as a reductant. NO conversions maintains above 75% in a wide temperature window (523–823 K) with a GHSV of  $332\,000\ h^{-1}$ ; the catalytic activity is stable in the presence of water vapor and  $SO_2$ . It is assumed that the special preparation method is able to promote specific iron–cerium interactions within the zeolite framework. The facility of the catalyst preparation makes it attractive for industrial application. Optimization of the catalyst formulation (*i.e.* the ratio Fe/Ce) is under way in our laboratory.

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