

Very active CeO₂-zeolite catalysts for NO_x reduction with NH₃

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Selective catalytic reduction of NO with NH₃ over high weight percentage CeO₂-zeolites showed excellent NO_x conversions at very high space velocities under simulated exhaust gas conditions in the presence of H₂O.

Selective catalytic reduction (SCR) of NO with NH₃ is an indispensable technology in NO_x (NO + NO₂) emission control. The temperatures associated with exhaust gases vary widely and are often in the range 350–550 °C, where commercial V₂O₅/TiO₂¹ systems are not efficient. Recent studies have focussed on the use of Fe-ZSM-5^{2,3} catalysts because of their activity and stability. Ce³⁺ ion exchanged zeolites were found to be active for NO_x reduction using NH₃.⁴ The CeO₂-zeolite systems prepared by physical mixing and co-precipitation methods were studied in the SCR with hydrocarbon reductants.^{5–7} The CeO₂-zeolite catalyst systems did not receive attention using NH₃ as a reductant. We found that, CeO₂ in the presence of small amount of H-zeolite showed excellent SCR activity with NH₃. In this paper, preliminary results on the SCR of NO with NH₃ under simulated exhaust gas conditions over high weight percentage CeO₂-zeolite catalysts, prepared by simple physical mixing are presented. NO_x conversions of > 85% are observed over a broad temperature range at very high space velocities. A synergistic effect was found between an intimately mixed oxidation component and the proton exchanged zeolite. The presence of water vapour enhanced the NO_x conversions above 450 °C.

H-BEA (Si/Al = 11, Uetikon), H-MOR (Si/Al = 10, Zeolyst), Na-ZSM-5 (Si/Al = 11) and K-FER (Si/Al = 9.2) (TOSOH, Japan), were used in the present study. Na⁺ and K⁺ forms of the zeolites were converted to the H-form. The required amount of CeO₂ (75 and 50 wt%, surface area = 128 m² g⁻¹) and zeolite were thoroughly mixed in a mortar and calcined at 600 °C for 5 h. The catalysts (0.3 g, sieve fraction 300–500 μm) were screened for SCR of NO_x and the oxidation of NH₃ and NO in a tubular quartz reactor (5 mm internal diameter) between 300 and 600 °C. The gas hourly space velocity (GHSV) was 5 × 10⁵ h⁻¹, based on the catalyst bulk density of 1 g cm⁻³. The SCR synthetic exhaust gas mixture contained 1000 ppm NO, 1000 ppm NH₃, 10 vol% O₂, 9 vol% H₂O (when used) and balance N₂. NH₃ and water were removed by placing phosphoric acid and water traps before some analysers. The concentration of NO_x, N₂O and NH₃ were monitored with a chemiluminescence detector, gas chromatography and by a microwave analyser (MIPAN) respectively. The NO_x conversion was calculated after 1 h of time on stream at each reaction temperature. The materials were characterised by chemical analysis, N₂ adsorption, NH₃-TPD and SEM.

Fig. 1 shows the conversion of NO_x and NH₃ at different reaction temperatures over 75 wt% CeO₂, physically mixed with 25 wt% of the zeolites H-BEA, H-MOR, H-ZSM-5 and H-FER. All the catalysts tested with simulated exhaust gases having excess H₂O and at high space velocities, in general showed excellent NO_x conversions with NH₃ between 300 and 600 °C. In the reaction temperature range 350–550 °C, NO_x conversions exceeding 80% are observed over all the catalysts. N₂O formation was negligible (max. 9 ppm) over the catalysts studied. The activity of the 75 wt% CeO₂-H-zeolite catalysts is

similar to the most active Fe-ZSM-5 catalysts reported in the literature.^{2,3} The NH₃ conversions followed the same trend as that of NO_x below 350 °C. Above 350 °C, 100% of NH₃ is converted over all the catalysts which rules out NH₃ slip under the SCR conditions. Among the catalysts tested the highest conversions are observed over 75 wt% CeO₂-H-BEA at 300, 350 and at 600 °C. The structure and acidity of the zeolites did not have a significant influence on NO_x conversion under the reaction conditions used. In spite of the relatively lower amount and the strength of acidity of H-BEA, observed from NH₃-TPD, 75 wt% CeO₂-H-BEA resulted in a better NO_x reduction performance. SEM micrographs revealed that the crystallite size of H-BEA is smaller than that of other zeolites used. The large external surface area (145 m² g⁻¹) of zeolite beta, highest among the zeolites studied, could lead to improved mixing of the two solids and also to the accessibility of the reactants/intermediates to the acidic sites. It is known that the SCR reaction mainly takes place near the pore entrances of the zeolites.⁸ Though Brønsted acidity is necessary for SCR to achieve high conversions, smaller crystallites could expose relatively more pore openings to the reactants, which results in enhanced NO_x conversions. It was not possible to compare the catalysts in the temperature region 400–550 °C due to the high NO_x conversions (> 85%). At 600 °C the NO_x conversion decreased over all the catalysts due to extensive oxidation of NH₃ to N₂ and NO_x, which can be seen from the direct oxidation of NH₃ (examples in Table 1). Enhancement in the NO_x conversion was reported when the feed contained a particular NO/NO₂ ratio (1:1).⁸ Under the reaction conditions, CeO₂ increases the concentration of NO₂ in the simulated exhaust gas mixture, which further reacts with the NH₃ activated over zeolites leading to higher conversions. Irrespective of the zeolites used all the catalysts showed similar NO conversions to NO₂ with a maximum at 450 °C (Fig. 1) which also explains similar conversion trends of NO_x in SCR over the catalysts.

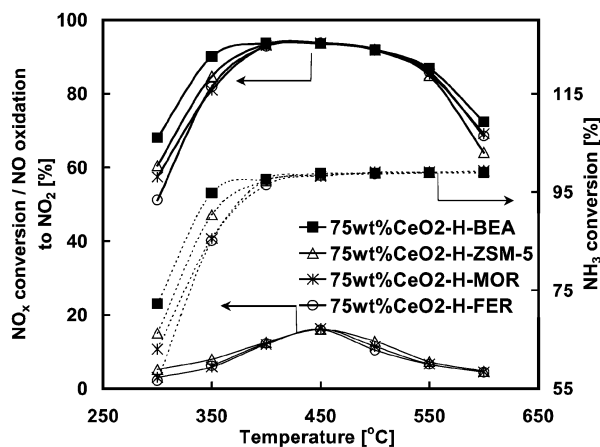


Fig. 1 Conversion of NO_x and NH₃ in SCR (1000 ppm NO, 1000 ppm NH₃, 10 vol% O₂ and 9 vol% H₂O balance N₂) and oxidation of NO to NO₂ (1000 ppm NO, 2 vol% O₂ balance N₂). GHSV = 5 × 10⁵ h⁻¹.

Table 1 NH₃ oxidation over CeO₂-zeolite catalysts

Catalyst ^a	Reaction temperature/°C	Conversion of NH ₃ (%)	Selectivity to NO _x (%)
75 wt% CeO ₂ -H-MOR	600	100	19.6
75 wt% CeO ₂ -H-BEA	600	100	17.5
50 wt% CeO ₂ -H-BEA	600	100	13.3
75 wt% CeO ₂ -H-BEA	600/wet	96	3.2
75 wt% CeO ₂ -Na-ZSM-5	550	100	64.6
CeO ₂	550	100	75.4

^a Reaction conditions: 1000 ppm NH₃, 10 vol% O₂, balance N₂. GHSV = 5 × 10⁵ h⁻¹. Wet = in the presence of 9 vol% H₂O in the above feed.

Fig. 2 presents the NO_x conversion vs. temperature over CeO₂, 50 and 75 wt% CeO₂-H-BEA, H-BEA and over a catalyst having CeO₂ (75 wt%) as the top bed and H-BEA (25 wt%) as the bottom bed separated by quartz wool. No appreciable NO_x conversion is observed over CeO₂ (13%) and H-BEA (20%). 20 ppm of N₂O was observed over CeO₂ at 500 and 550 °C. By decreasing the CeO₂ content from 75 to 50 wt%, a decrease in NO_x conversion at 300 and 350 °C is observed over CeO₂-H-BEA catalysts. The NO_x conversions remained >85% over both the catalysts between 350 and 550 °C. A small improvement in the NO_x conversion over 50 wt% CeO₂-H-BEA at 600 °C could be expected as seen from Fig. 2, due to the lower CeO₂ content and decreased direct NH₃ oxidation to NO_x (Table 1).

Fig. 2 also gives the NO_x conversion over 75 wt% CeO₂-H-BEA tested in the presence and absence of water. NO_x conversions remained similar and high up to 450 °C under both conditions. In the absence of water in the feed, NO_x conversion decreased from 90 to 34% when the reaction temperature was increased from 450 to 600 °C. When water is present in the simulated exhaust gas mixture, a relatively small decrease in NO_x conversion, from 93% at 450 °C to 72% at 600 °C is observed. Similar results were obtained over 75 wt% CeO₂-H-ZSM-5 (Fig. 3). Water did not affect the conversion of NO to NO₂ significantly (Fig. 2). Screening the 75 wt% CeO₂-H-BEA catalyst for NH₃ oxidation at 600 °C showed 100 and 96% NH₃ conversion in the absence and presence of water, respectively (Table 1). The selectivity to NO_x is high in the absence of water (17.5%) compared with the NO_x selectivity in the presence of water (3.2%). Oxidation of NH₃ to N₂ generally proceeds in two steps.⁹ First, a part of NH₃ is oxidised to NO_x and subsequently NO_x is reduced with unconverted NH₃ in the presence of acidic sites to N₂. If extensive oxidation of NH₃ to NO_x takes place, which is the case in the absence of H₂O, less NH₃ will be available for further reduction, and thus decreases the overall NO_x conversion. The improved NO_x conversions in the

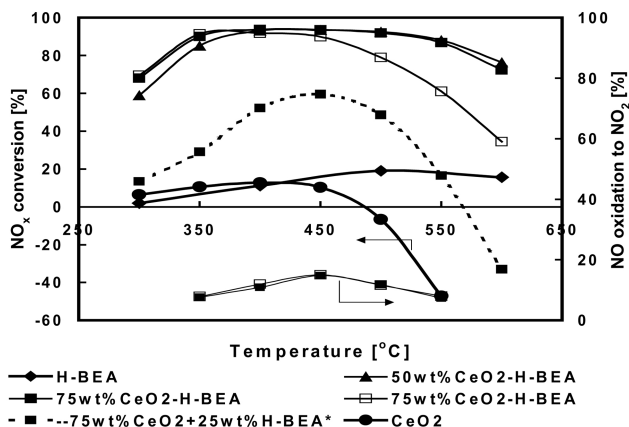


Fig. 2 NO_x conversion over CeO₂-H-BEA catalysts in SCR and in NO oxidation to NO₂ (reaction conditions as in Fig. 1). Filled symbols in the presence of 9 vol% H₂O, open symbols in the absence of H₂O. *CeO₂ (0.225 g, top bed) + H-BEA (0.075 g, bottom bed). GHSV = 5 × 10⁵ h⁻¹.

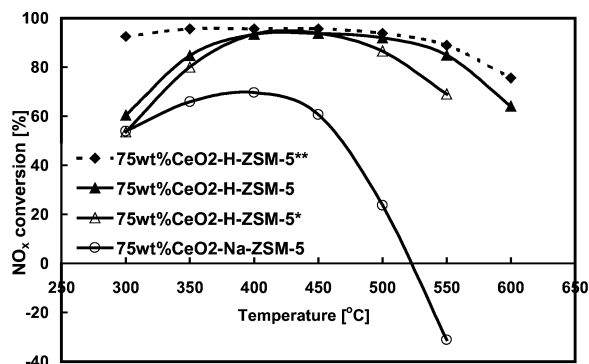


Fig. 3 NO_x conversion over CeO₂-ZSM-5 catalysts. Filled symbols in the presence of 9 vol% H₂O, open symbols in the absence of water, GHSV = 5 × 10⁵ h⁻¹ (*This catalyst was aged at 600 °C, **GHSV = 2 × 10⁵ h⁻¹, 500–800 μm particles, reactor internal diameter 7 mm).

presence of water are therefore due to strong suppression of the direct oxidation of NH₃ over CeO₂. The catalyst having separate beds of CeO₂ and H-BEA, resulted in a lower NO_x conversions at all reaction temperatures. The NO_x conversion of >45% (14 ppm N₂O at 600 °C) is observed in a narrow temperature range. This clearly shows that the diffusion of reaction intermediates between oxidation and acidic sites is most effective when both the components are in intimate contact due to synergetic effect.

A synergetic effect between the acidic sites of zeolite and the oxidation component is further evident from Fig. 3. When the Na-form of the zeolite is used, over the resulting 75 wt% CeO₂-Na-ZSM-5 catalyst, the NO_x conversion (<65%) at all the reaction temperatures is inferior to that of 75 wt% CeO₂-H-ZSM-5 under the same conditions. In the absence of Brønsted acidic sites, due to extensive oxidation of unadsorbed NH₃ to NO_x, which is seen from the selectivity of NO_x in direct oxidation of NH₃ over CeO₂ and 75 wt% CeO₂-Na-ZSM-5 (Table 1), the NO_x conversions were even negative above 500 °C. Due to preferential adsorption of NH₃ over Brønsted acid sites in 75 wt% CeO₂-H-zeolite catalyst, its direct oxidation over CeO₂ to NO_x decreases resulting in superior NO_x conversions. This is evident from the broad temperature range where >80% NO_x conversions are maintained over 75 wt% CeO₂-H-ZSM-5 in the absence of water in the feed. The NO_x conversions at 300 and 350 °C can be further improved by decreasing the space velocity (Fig. 3). The catalysts tested at a space velocity of 2 × 10⁵ h⁻¹, in the presence of water showed conversions of >80% in the whole temperature range tested (300–600 °C).

In conclusion, the high weight percentage CeO₂-H-zeolite composite mixtures are excellent selective catalytic reduction catalysts with NH₃ as a reductant. NO_x conversions above 85% are obtained over a broad temperature range (350–550 °C) and at high space velocities (5 × 10⁵ h⁻¹). The synergetic effect between the intimately mixed CeO₂ and the zeolite Brønsted acidity is responsible for superior NO_x conversions.

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