ELSEVIER

Catalysis Today 75 (2002) 367–371

CATALYSIS TODAY

www.elsevier.com/locate/cattod

A new active zeolite structure for the selective catalytic reduction (SCR) of nitrogen oxides: ITQ7 zeolite
The influence of NO_2 on this reaction

Antonio E. Palomares [a], J.G. Prato [b], A. Corma [b],*

[a] Departmento de Ingeniería Química y Nuclear, Universidad Politecnica de Valencia, Avenida de los Naranjos s/n, 46022 Valencia, Spain
[b] Instituto de Tecnologia Quimica, UPV-CSIC, Universidad Politecnica de Valencia, Avenida de los Naranjos s/n, 46022 Valencia, Spain

---

Abstract

The activity of a new zeolite material, ITQ7, has been studied for the selective catalytic reduction (SCR) of NO. The pore topology of this material is similar to the structure of a beta zeolite, with a tridirectional system with 12-member rings. ITQ7 exchanged with copper or cobalt shows a catalytic behaviour very similar to a beta zeolite exchanged with copper or cobalt, probably due to its similar structure. The presence of oxygen, water, sulphur dioxide and NO_2 has been studied, obtaining the best results at low oxygen concentration and in the absence of water and SO_2. Nevertheless if NO_2 is present in the reaction mixture, the maximum activity of the catalyst shifts towards higher oxygen concentration. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Zeolites; ITQ7; Selective catalytic reduction; NO; Propane; NO_2

---

1. Introduction

Contrary to what occurs with other gas pollutants such as SO_2 or CO, NO_x emissions are increasing in the last few years. They come mainly from the automotive engines' exhaust gases and their control has become an urgent necessity. Among the commercial emission control systems actually applied, the most important methods are the selective catalytic reduction (SCR) by NH_3 for stationary sources and the three-way catalysts for mobile sources. But these systems cannot be applied to the new engines with better fuel efficiency, the lean burn engines, which operates with an excess of oxygen over the stoichiometric ratio [1–3].

Since the former work of Iwamoto et al. [4] about the possibilities of using Cu-ZSM5 as an active catalyst for the SCR of NO in the presence of oxygen and using hydrocarbons as a reducing agent, large and medium pore zeolite structures exchanged with different cations have been studied [5–8]. So far the best results are achieved with metal exchanged Cu or Co ZSM5 or beta zeolites. Nevertheless the reason why these zeolite structures are active in the NO removal is still a matter of discussion. Recently a new zeolite structure named IM5 has also shown interesting results in this reaction [9]. Its structure is still unknown but it has been suggested that it may be formed by either 10 MR crossing pores or 10 MR pores with lobes close to the structure of ZSM5 [10]. In this work, the activity of another new zeolite structure, ITQ7, has been studied. This zeolite has a pore topology formed by a tridirectional system with 12-member ring similar to the structure of beta zeolite, suggesting that ITQ7 can also be an active catalyst for the

---

* Corresponding author. Tel.: +34-6-387-7800;
fax: +34-6-387-7809.
E-mail address: acorma@itq.upv.es (A. Corma).

PII: S0920-5861(02)00066-4

SCR of NO. The activity of this zeolite when metal exchanged with copper or cobalt has been compared with that of a beta zeolite and the influence of the addition of oxygen, water, sulphur dioxide and NO_2 to the feed stream has been studied.

2. Experimental

ITQ7 synthesised in our laboratory as described in [11] and beta zeolites obtained from PQ zeolites have been used as starting materials. The zeolites were metal exchanged with copper or cobalt according to [8] and the composition of the samples was analysed by atomic absorption. The chemical analysis shows that ITQ7 zeolite has a Si/Al molar ratio of 50. The Co/Al molar ratio of the ITQ7 metal exchanged with cobalt is 0.78 and the Cu/Al ratio of the sample when exchanged with copper is 1.2. The activity of these samples was compared with that of beta zeolites with similar Si/Al ratio and similar copper or cobalt content.

Activity tests were carried out in a fixed bed quartz tubular reactor 2.2 cm in diameter and 53 cm in length. In a typical experiment, 1 g of a zeolite catalyst, as particles of 0.25–0.42 mm in size, was introduced in the reactor and was heated up to 350 °C under nitrogen flow. At this temperature the flow was maintained for 6 h. After that, the desired reaction temperature was set and the reaction feed admitted. This consists of 650 ml min^{-1} of a mixture composed of 600 ppm of NO, 380 ppm of C_3H_8, variable quantities of oxygen and balanced with nitrogen. The NO_x present in the outlet gases from the reactor was continuously analysed by means of a chemiluminescence detector model Rosemount 951 A. The presence of N_2O was detected by gas chromatography with a 5 A molecular sieve column used to separate oxygen, nitrogen and carbon monoxide and a Poraplot Q column for the separation of carbon dioxide and hydrocarbons. The surface areas of catalysts were obtained in an ASAP 2000 apparatus, using the BET method from the nitrogen adsorption isotherms at 77 K. X-ray diffraction (XRD) patterns were collected using a Phillips X'Pert-MPD diffractometer provided with a graphite monochromator, operating at 40 kV and 20 mA and employing nickel-filtered Cu Kα radiation ($\lambda = 0.1542$ nm).

3. Results and discussion

The catalysts tested have areas higher than 300 m^2/g, without a significant decrease in the area

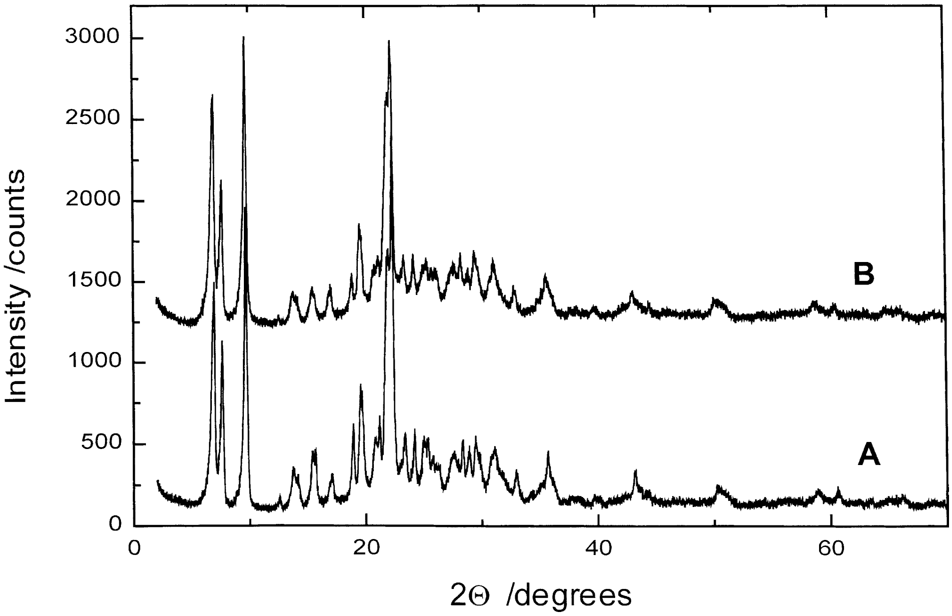

Fig. 1. XRD patterns of the ITQ7 zeolite as-synthesised (A) and after Cu ion exchange (B).

after the metal exchange. Fig. 1 shows the XRD patterns of the ITQ7 zeolite as-synthesised (A) and after copper exchange (B). The ion-exchanged samples have crystallinities between 80 and 90% with respect to the crystallinity of the parent zeolite, indicating that the catalyst lattice was practically undisturbed after exchange with copper and that although the sample is over-exchanged, metal oxide crystals were not detected. Similar results were obtained when the zeolite was metal exchanged with cobalt.

In a preliminary experiment the stability of the catalysts was studied by carrying out the NO_x reduction at 623 K in the presence of 1.5% oxygen. No significant changes in activity were observed at least during the 2-hour duration of the experiment and this allowed us to perform several experiments with the same catalyst sample. The formation of N_2O in these reactions was very low, then the consideration that all the NO_x is converted into N_2 is assumed. The stability of the catalyst was checked by repeating the experiment at the end of the last run, under the experimental conditions which gives a maximum in conversion.

The influence of the reaction conditions on the catalytic activity was studied for the ITQ7 and compared with that of a beta zeolite with a similar Si/Al ratio and exchanged with the metal at a similar level. The maximum activity for either copper or cobalt metal exchanged ITQ7 was achieved around 723 K, observing a strong increase in the conversion when the temperature goes from 623 to 723 K. At temperatures higher than 823 K, the conversion decreased as a consequence of the higher activation energy of the competing reaction, i.e., the oxidation of propane, which produces a depletion of the reductor with the corresponding decrease in the efficiency of NO_x reduction. Nevertheless, it should be pointed out that an increase in reaction temperature does not cause a permanent loss in catalyst activity. The results obtained with the zeolite exchanged with copper show some differences when compared with previous works [12] of metal exchanged beta or ZSM5 copper, which usually shows maximum activity at 623 K. This is due to the high silicon content of the ITQ7 zeolite. It has been observed that when the Si/Al ratio of the zeolite is higher than 30, the temperature of maximum activity shifts towards higher temperatures, probably due to a change in the coordination of the active centres or to the occurrence of different reaction paths.

Fig. 2 shows the influence of the oxygen concentration on the SCR of NO with propane at 723 K. ITQ7 exchanged with copper shows a very low conversion if no oxygen is present, however the activity increases rapidly after adding small quantities of O_2 and a peak of maximum activity is obtained with oxygen content around 0.5–1%. A further increase in the oxygen concentration results in the decrease of the activity. Similar results were obtained with copper beta zeolite, as we can expect considering the similarities in the structure. Some differences can be observed when cobalt instead of copper is the metal exchanged. The maximum conversion obtained with this sample is lower, but ITQ7 exchanged with cobalt presents the maximum activity at higher oxygen concentration (around 1.5–2.5% oxygen) and it seems to be more active in a wider range of operation conditions, probably due to additional stabilisation of the catalyst because of the presence of cobalt in the zeolite.

From a practical point of view, it is necessary to study the influence of potential catalyst poisons such as water and SO_2. As it can be seen in Fig. 3, the presence of 2.5% water does not result in an important decrease of the activity at 723 K. This behaviour is similar to that showed by beta zeolites, although at low oxygen concentration, the activity of the ITQ7 is higher than that of beta zeolite. Under these conditions, the deactivation is not irreversible, and after regeneration of the catalyst, it recovers the original activity.

The influence of different SO_2 concentrations was also studied, observing that the presence of 20 ppm of SO_2 does not affect the activity of the sample, but a negative effect appears at SO_2 concentration higher than 60 ppm, decreasing the activity of the catalyst about to 25% of the original conversion. Similar results were obtained with beta zeolites, although when cobalt is metal exchanged on the zeolite, beta zeolites show a slightly higher resistance to the poisoning by SO_2 than Co-ITQ7.

Nevertheless it is our goal to show that if small quantities of NO_2 are added in the feed stream, the dependence of the conversion with the oxygen content changes substantially (Fig. 4), shifting the maximum activity of the catalyst towards higher oxygen concentration. As it can be observed, when 30 ppm of NO_2 are added to the reactor, the maximum activity of the catalyst exchanged with copper appears

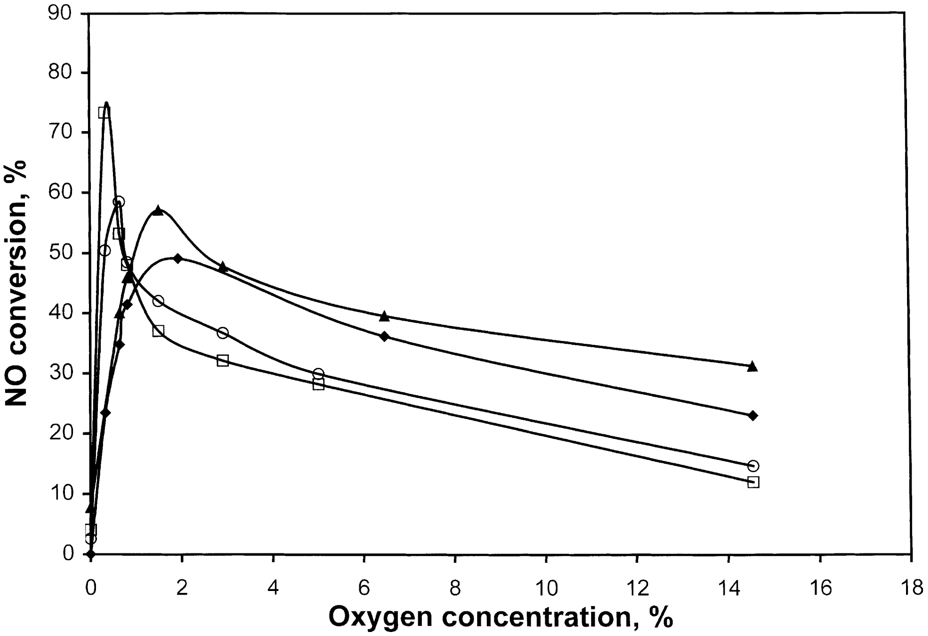

Fig. 2. Influence of the metal exchanged on the zeolite, under different oxygen concentrations, in the SCR of NO with propane. (○) beta-Cu, (□) ITQ7-Cu, (▲) beta-Co, (◆) ITQ7-Co, $T = 723$ K.

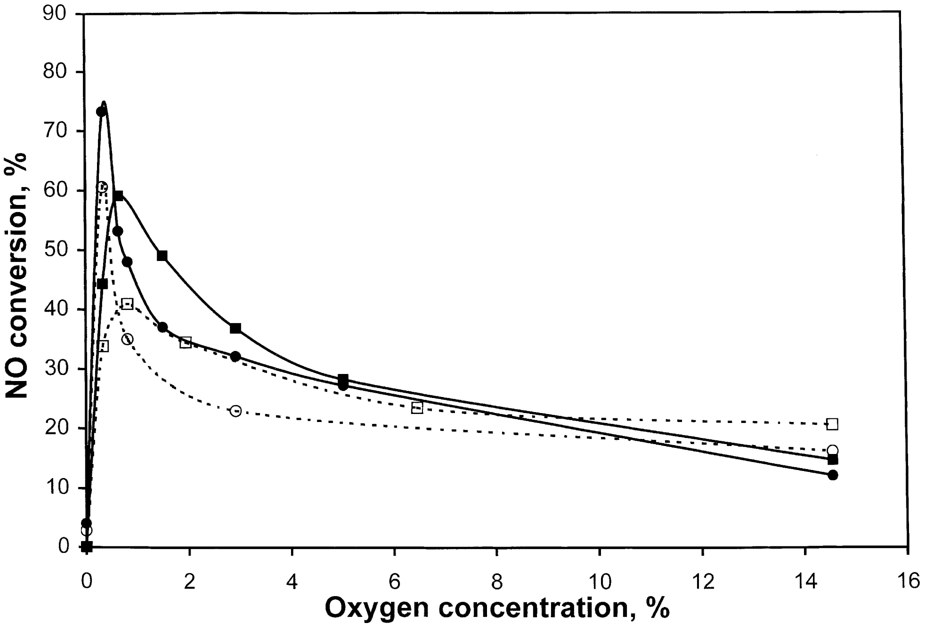

Fig. 3. Influence of water in the SCR of NO with propane: (●) ITQ7-Cu, fresh catalyst, (○) ITQ7-Cu, with water, (■) beta-Cu, fresh catalyst, (□) beta-Cu, with water, 2.5% water, $T = 723$ K.

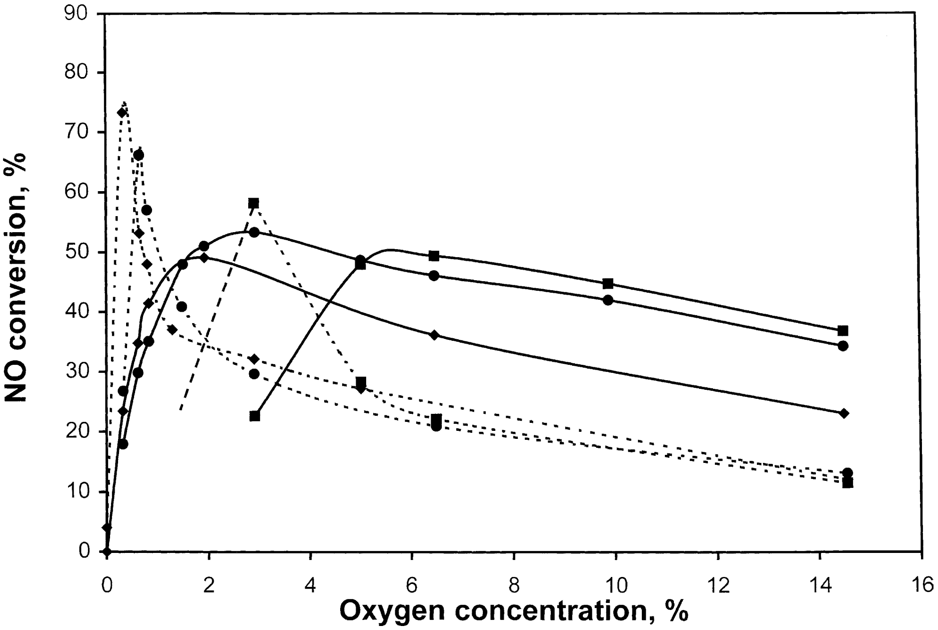

Fig. 4. Influence of NO_2 in the SCR of NO with propane. (- - -) ITQ7-Cu, (—) ITQ7-Co, (◆) 0 ppm NO_2, (●) 3.5 ppm NO_2, (■) 31.8 ppm NO_2.

at an oxygen concentration of 2–4%, while for ITQ7 exchanged with cobalt, the maximum activity appears when an oxygen concentration of 6–8% is introduced in the reaction system. A similar situation is observed with copper and cobalt beta, where this shift is even broader, suggesting that the presence of NO_2 can be a determinant for achieving high activities at high oxygen concentration. The nature of this effect has to be related to the mechanism of the reaction and although we still do not have a clear image of what is occurring, it seems that the presence of NO_2 either preserves the active centres of the catalyst from being poisoned by the oxygen or protects the hydrocarbon from being burnt by the oxygen. Further studies are in play in order to understand the exact nature of this effect.

From the study of this material we can conclude that ITQ7 when exchanged with copper or cobalt is an active catalyst for the SCR of NO with propane, obtaining similar conversion as other active catalysts with high Si/Al ratio like beta zeolite, probably due to its similar structure and the presence of similar active sites. It has also been observed that the presence of NO_2 in the feed results in an increase of the overall rate of reduction of NO_x and simultaneously reduces its dependence on the oxygen concentration. These results might be related to the reaction mechanism and opens new possibilities for the SCR of NO under lean burn conditions.

References

[1] F.P. Boer, L.L. Hegedus, T.R. Gouber, K.P. Zak, Chem. Technol. (May 1990) 312.
[2] A. Fritz, V. Pitchon, Appl. Catal. B 13 (1997) 1.
[3] R.J. Ferrauto, R.M. Heck, Catal. Today 51 (1999) 351.
[4] M. Iwamoto, H. Yahiro, S. Shundo, Y. Yu-u, N. Mizuno, Shokubai (Catalyst) 32 (1990) 430.
[5] M. Iwamoto, Stud. Surf. Sci. Catal. 130A (2000) 23.
[6] Y. Traa, B. Burger, J. Weitkamp, Micropor. Mesopor. Mat. 30 (1999) 3.
[7] G. Centi, F. Fazzini, A. Galli, Res. Chem. Intermediat. 24 (1998) 541.
[8] A. Corma, A. Palomares, V. Fornes, Res. Chem. Intermediat. 24 (1998) 613.
[9] A.E. Palomares, F. Marquez, S. Valencia, A. Corma, J. Mol. Catal. 162 (2000) 175.
[10] A. Corma, A. Chica, J.M. Guil, F.J. Llopis, G. Mabilon, J.A. Perdigón-Melón, S. Valencia, J. Catal. 189 (2000) 382.
[11] L. Villaescusa, M. Camblor, PCT/ES99/00401, 1999.
[12] A. Corma, A.E. Palomares, V. Fornes, Appl. Catal. B 11 (1997) 233.