Catalysis Today 176 (2011) 239–241

Contents lists available at ScienceDirect

Catalysis Today

journal homepage: www.elsevier.com/locate/cattod

Determining the characteristics of a Co-zeolite to be active for the selective catalytic reduction of NO_x with hydrocarbons

A.E. Palomares*, C. Franch, A. Corma

Instituto de Tecnología Química, Universidad Politécnica de Valencia, Camino de Vera s.n., 46022 Valencia, Spain

ARTICLE INFO

Article history:
Received 1 October 2010
Accepted 11 November 2010
Available online 31 January 2011

Keywords:
SCR
NO
Zeolites
Cobalt
Propane

ABSTRACT

The aim of this work is to study the activity, for the selective catalytic reduction (SCR) of NO_x with hydrocarbons, of different containing cobalt zeolites, with different typologies and compositions. It has been found that in order to obtain an active catalyst for this reaction is necessary that the zeolite presents an adequate topology: medium size pores, a Si/Al ratio of 8–30 and the absence of big cavities. The cobalt must be ion exchanged, because if the metal is in the zeolite framework the active sites are not accessible to the reactants. In addition for a commercial use of the catalyst, it has to be hydrothermically stable. New zeolite structures as ITQ27 and ITQ7 that present those characteristics have been ion exchanged with cobalt and they have been tested for the SCR of NO_x with propane, showing its potential as active catalysts for this reaction.

1. Introduction

Contrarily to what it occurs with other gas pollutants such as SO_2 or CO, the NO_x emissions are continuously increasing in the last years. Current regulations controlling such pollution are becoming more stringent and new processes to control these contaminants are imperative. Among the emission control technologies envisaged, the most widely applied methods are the selective catalytic reduction by NH_3 or urea [1,2] for stationary sources and the three way catalysts for the traditional stoichiometric gasoline engines mobile sources [3]. Another approach is the NO decomposition or the selective catalytic reduction of NO_x with hydrocarbons in the presence of O_2 [4–9]. Nevertheless the application of these systems requires an active catalyst in a wide range of operation conditions and during extended time periods. Main attention has been paid to the use of Cu/Co-ZSM5 or Cu/Co-beta as catalysts for this reaction; nevertheless these zeolites do not present enough hydrothermal stability for its commercial use, being necessary to find a more stable catalyst [8]. In addition no clear explanation has appeared about the reaction mechanism neither the reason why these zeolite structures are active. In this work we have prepared different containing cobalt microporous materials in order to determine the characteristics needed for an active catalyst in the propane SCR of NO_x. The activity in the reaction of some new zeolites with high hydrothermal stability, as ITQ7 and ITQ27, has been studied.

2. Experimental

The microporous materials studied were zeolites with different topologies. Zeolites MCM22, ITQ27, RHO, ITQ2 and ITQ7 were prepared in our laboratory according to [10–14], zeolites FAU, ZSM5 and BEA were commercial zeolites obtained from PQ Zeolites. The metal exchange of the acid zeolite was done in an aqueous solution containing $Co(CH_3COO)_2{\cdot}4H_2O$ with the adequate concentration to achieve the desired amount of metal on the zeolite, and with a solid/liquid ratio = 10 g L^{-1}. The exchange was carried out at 353 K under stirring for 24 h. After that, the zeolite was filtered and washed, and then calcined at 823 K for 3 h. A ZSM5 zeolite was prepared with cobalt in the framework, according to [15]. The composition of the samples was analyzed by atomic absorption and the results are shown in Table 1.

The activity tests were carried out in a fixed bed, quartz tubular reactor. In a typical experiment, 1 g of catalyst, as particles of 0.25–0.42 mm size, were introduced in the reactor and were 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 by NO, C_3H_8, variable quantities of oxygen and balanced with nitrogen. The NO_x present in the outlet gases was continuously analyzed by means of a chemiluminescence detector.

3. Results and discussion

The results obtained with the different containing cobalt zeolites are shown in Figs. 1–3. From these results, the zeolites may be

---

* Corresponding author. Tel.: +34 963879632; fax: +34 963877639.
E-mail address: apalomar@iqn.upv.es (A.E. Palomares).

0920-5861/$ – see front matter © 2011 Elsevier B.V. All rights reserved.
doi:10.1016/j.cattod.2010.11.092

Table 1
Chemical composition of the catalysts used.

Zeolites	Si/Al ratio	Co/Al ratio
ZSM5	25	0.7
ZSM5	17	(2.9 wt% Co in the zeolite structure)
BEA	15	0.64
BEA	50	0.78
FAU	14	0.61
MCM22	14	0.71
RHO	5	1.06
ITQ2	25	0.55
ITQ7	50	0.81
ITQ27	19	1.02

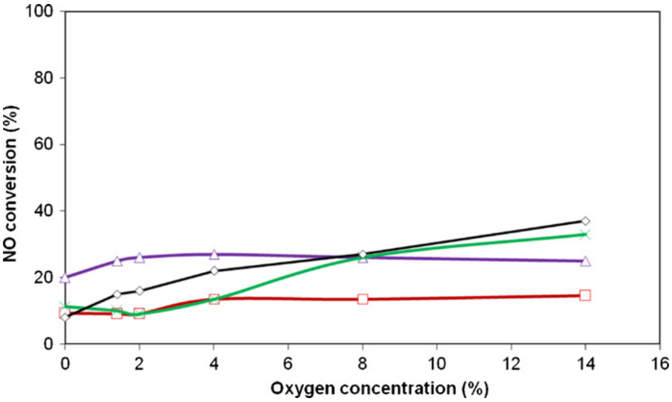

Fig. 1. NO_x conversion in C_3H_8-SCR on different Co/zeolites (△) ITQ-2, (□) ZSM5, with cobalt in the framework, (◇) RHO, (×) FAU, 850 ppm NO, 550 ppm C_3H_8, different oxygen concentrations, N_2 as effluent, $T = 723$ K.

divided in to three groups. The first group is formed by those zeolites that show a NO conversion lower than 30% at different oxygen concentrations (Fig. 1). Co-FAU, Co-RHO, Co-ITQ2 and ZSM5 with cobalt in the framework are included in this group. As it can be seen in Fig. 1, zeolites containing big cavities, as faujasite, present a low activity. It could be related with the segregation of the cobalt active sites in the zeolite cavities, forming cobalt oxide clusters that are not active for the NO reduction [16]. Another possible reason for the low activity of this zeolite is that the Co^{2+} sites of the Co-FAU are not able to form monodentate nitrates. These species, according to [17], will be the intermediates reduced by the hydrocarbons and its absence produces the catalyst low activity. The same reasons can be applied to the layered zeolites, as ITQ2, which show a similar catalytic behavior. Zeolites with small pores as RHO zeolite neither are adequate for the reaction; this is due to the size of the propane molecule compared with the 8 member ring pores of the zeolite. After the cobalt ion exchange, propane is not admitted in the zeolite pores and only the surface cobalt sites are active, resulting in a low active catalyst. Another zeolite characteristic that produces a non adequate catalyst is the presence of cobalt in the zeolite framework. The same behavior was observed with other zeolites containing tin in the framework [18], suggesting that the framework metal atoms are not active in the reaction. This result can be explained by taking into account that tetrahedrally coordinated framework cobalt is stable under reaction conditions and the cobalt centers cannot interact with the reactants.

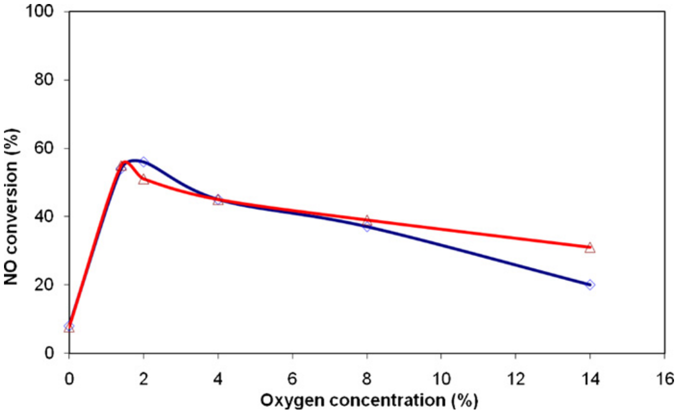

Fig. 2. NO_x conversion in C_3H_8-SCR on different Co/zeolites (△) BEA Si/Al = 50, (◇) MCM-22 Si/Al = 14, 850 ppm NO, 550 ppm C_3H_8, different oxygen concentrations, N_2 as effluent, $T = 723$ K.

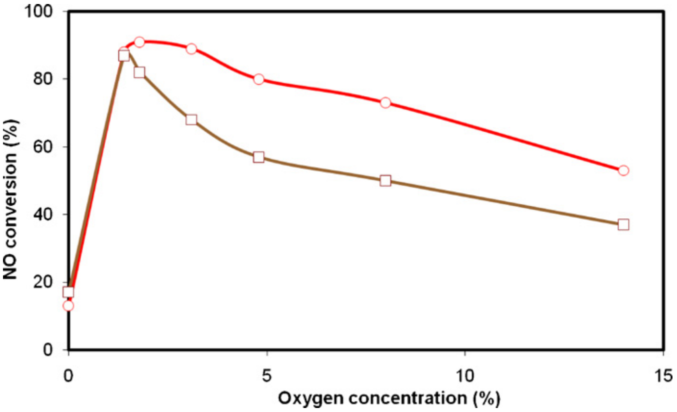

Fig. 3. NO_x conversion in C_3H_8-SCR on different Co/zeolites (○) BEA Si/Al = 25, (□) ZSM5 Si/Al = 15, 850 ppm NO, 550 ppm C_3H_8, different oxygen concentrations, N_2 as effluent, $T = 723$ K.

From these results we can conclude that non-adequate zeolites for the SCR of NO with propane are those that present a non-adequate topology: small channels, big cavities or laminar materials, and those zeolites where the cobalt is in the zeolite framework.

The second group of zeolites is those that show a NO conversion between 30 and 60% at different oxygen concentrations. The results obtained with these zeolites are shown in Fig. 2. Although, they are medium pore zeolites with 10 or 12 member rings and the cobalt is ion exchanged, they present medium size cavities as the MCM22 zeolite or the Si/Al ratio is very high as the BEA zeolite with a Si/Al ratio of 50. The presence of cavities, as it was discussed before, results in a less active catalyst and the high Si/Al ratio results in a zeolite with low cobalt content and in the absence of the neighboring sites that promote the adsorption and reaction of the reactants [19] diminishing the activity of the material.

The third group of zeolites is those clearly active for the SCR of NO with propane. They are zeolites with 10 or 12 member rings, without cavities, with the cobalt ion exchanged and with a Si/Al ratio between 8 and 35, as ZSM5 and BEA zeolites. These zeolites are active at high oxygen concentration and the results obtained are shown in Fig. 3. Nevertheless these zeolites present the problem of its hydrothermal stability and for this reason they cannot be used for a commercial purpose.

Recently new zeolites, as ITQ7 and ITQ 27, with a high hydrothermal stability have appeared. ITQ7 has a pore topology formed by a tridirectional system with 12 member rings similar to the structure of a beta zeolite. According to the results previously described, this zeolite presents the adequate topology to be active for the SCR of NO with propane when the cobalt is ion exchanged. Nevertheless this zeolite can only be synthesized with a Si/Al ratio of 50, for this reason this zeolite should be included in the second group of the

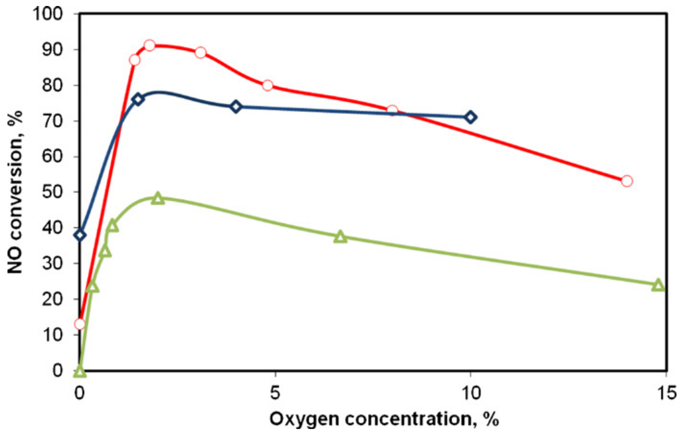

Fig. 4. NO_x conversion in C_3H_8-SCR on different Co/zeolites (○) BEA Si/Al = 25, (△) ITQ7 Si/Al = 50, (◊) ITQ27 Si/Al = 19, 850 ppm NO, 550 ppm C_3H_8, different oxygen concentrations, N_2 as effluent, T = 723 K.

zeolites that we established, with an expected conversion around 30–60%. In fact, as it can be observed in Fig. 4, this was the result obtained when using this zeolite for the propane SCR of NO. These results are very similar to those obtained with the BEA zeolite with a similar Si/Al ratio (Fig. 2).

On the other hand ITQ27 is a bidirectional zeolite with connected 12 member rings channels. It has a microporous volume of 0.21 cm^3/g, a microporous area of 434m^2/g and a porous diameter of 6.7 Å. It can be synthesized with a Si/Al ratio of 20 and the cobalt can be ion exchanged, for this reason it could be an adequate catalyst for the SCR of NO_x with propane. In Fig. 4 are shown the results obtained with the Co-ITQ27. It can be observed that they are very similar to those obtained with a cobalt ion exchanged beta zeolite with a similar Si/Al ratio. Nevertheless the main advantage of this zeolite is its hydrothermal stability. Contrarily to what it occurs with a BEA zeolite, after a hydrothermal treatment and in the presence of water the activity of the Co-ITQ27 is the same than that previously obtained before this treatment and in the absence of water. These results suggest that this material could be an interesting material for the SCR of NO with propane.

4. Conclusions

From this work we can conclude that in order to have an adequate zeolitic catalyst for the SCR of NO with propane it is necessary to have a medium pore zeolite with 10 or 12 member rings channels, without cavities, with the metal ion exchanged and with a Si/Al ratio between 8 and 35. In addition, for a commercial use, the zeolite should have a high hydrothermal stability. In this work we have shown that a new zeolite structure: ITQ 27 presents these characteristics and the catalytic results obtained confirm the adequacy of this zeolite for the SCR of NO_x with propane.

References

[1] R.M. Heck, Catal. Today 53 (1999) 519.
[2] T. Grzybek, J. Klinik, M. Motak, H. Papp, Catal. Today 137 (2008) 235.
[3] M.V. Twigg, Appl. Catal. B 70 (2007) 2.
[4] M. Iwamoto, Stud. Surf. Sci. Catal. 130A (2000) 23.
[5] A. Corma, V. Fornés, A.E. Palomares, Appl. Catal. B 11 (1997) 233.
[6] R. Burch, J.P. Breen, F.C. Meunier, Appl. Catal. B 246 (2002) 283.
[7] P. Pietrzyk, B. Gil, Z. Sojka, Catal. Today 126 (1–2) (2007) 103.
[8] R.J. Farrauto, R.M. Heck, Catal. Today 51 (1999) 351.
[9] T. Tabata, H. Ohtsuka, L.M.F. Sabatino, G. Bellussi, Micropor. Mesopor. Mater. 21 (1998) 517.
[10] A. Corma, C. Corell, J. Perez-Pariente, Zeolites 15 (1995) 2.
[11] D.L. Dorset, G.J. Kennedy, K.G. Strohmaier, M.J. Diaz-Cabanas, F. Rey, A. Corma, J. Am. Chem. Soc. 128 (2006) 8862.
[12] H.E. Robson, D.P. Shoemaker, R.A. Ogilvie, P.C. Manor, Adv. Chem. Ser. 121 (1973) 106.
[13] A. Corma, V. Fornés, S.B.C. Pergher, Th.L. Maesen, J.G. Buglass, Nature 396 (1997) 353.
[14] L. Villaescusa, M. Camblor, PCT/ES99/00401, 1999.
[15] E.M. Barea, V. Fornés, A. Corma, P. Bourges, E. Guillon, V.F. Puntes, Chem. Commun. (2004) 1974.
[16] H. Ohtsuka, T. Tabata, O. Okada, L.M.F. Sabatino, G. Bellussi, Catal. Lett. 44 (1997) 265.
[17] E. Ivanova, K. Hadjiivanov, D. Klissurski, M. Bevilacqua, T. Armaroli, G. Busca, Micropor. Mesopor. Mater. 46 (2001) 299.
[18] A.E. Palomares, F. Imbert, J.G. Prato, A. Corma, Appl. Catal. B 75 (2007) 88.
[19] H. Ohtsuka, T. Tabata, O. Okada, L.M.F. Sabatino, G. Bellussi, Catal. Today 42 (1998) 45.