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Coated bifunctional catalysts for NO_x SCR with C_3H_6 Part I: water-enhanced activity

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Abstract

Bifunctional catalysts comprising metal-exchange zeolites coated by metal oxides have been prepared and shown to be active catalysts for the selective catalytic reduction of NO_x with propylene. Characterization of the materials by various means shows that oxide nano-particles adhere to the external surface of the zeolite and create a fine permeable coating which does not block the zeolite pores. When ceria is used, the combination of phases lowers the maximum activity temperature of the deNOx reaction as much as 150 °C relative to the metal-zeolite only. In addition, a unique activity enhancement in the presence of water is observed. These effects are observed in different zeolite systems to various degrees indicating that the nature of the exchanged metal or zeolite framework is not critical. In particular, CeO_2/Cu-ZSM-5 displays a maximum of activity at a temperature as low as 250 °C. The benefits of low temperature and water-enhanced activity obtained by the coating technique exceed those displayed by other bifunctional materials combining cerium and zeolites through different approaches.

Keywords: Cu-ZSM-5; CeO_2; Lean-burn; deNOx; Low temperature; Propylene

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1. Introduction

Strict governmental regulations on NO_x emissions over the last decade have driven several advances in NO_x abatement technology. The current industrial solution under excess oxygen conditions is the use of ammonia for the selective catalytic reduction of NO_x (NH_3-SCR). While this method is effective at reducing NO_x emissions, ammonia storage, transportation, slippage and equipment corrosion are of concern.

An alternative method is the use of a light hydrocarbon, such as propene, propane, or methane, instead of the ammonia, as the reductant during the catalytic reduction of NO_x (HC-SCR). Hydrocarbons can be provided from the fuel source, thus adding no new storage, transportation or corrosion concerns. At the same time, hydrocarbons can be easily oxidized to CO_2 and water by current catalytic devices or flares.

A large body of catalysts has been found to work for HC-SCR. The use of metal-exchange zeolites, such as Cu-ZSM-5, has been identified as a potential technology for the abatement of nitrogen oxides from emission streams [1]. One drawback of these catalysts is that they generally exhibited poor activity in the presence of water. This deactivation has been attributed to the competitive adsorption of water on the active metal sites and to the modification of the sites caused by it. The long-term hydrothermal instability of the catalyst has been attributed to active metal agglomeration and to the dealumination of the zeolite [2,3].

Numerous studies in the literature have looked at ways of understanding the water instability displayed by zeolite base catalysts as well as at devising new catalysts to improve the deNOx activity under wet conditions. One approach has been building some bifunctional activity into the zeolite using multiple metal sites. There have been reports that co-exchanging rare-earth metal ions into Cu-ZSM-5 yield some stability to the catalyst towards water [4]. However, these bifunctional materials tend to have lower activity and selectivity than the corresponding monometallic zeolite.

Since the mid-1990s different groups have reported the successful use of mixtures of metal-exchanged zeolites

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and easily-reducible oxides. For example, Yokoyama and Misono reported that mechanically mixed Ce-ZSM-5 and Mn_2O_3 are active for NO reduction by propene even though the individual components are not very active for the same reaction [5]. Recently, Krishna et al. reported that physical mixtures of CeO_2 and H-ferrierite possess high activity for HC-SCR regardless of the presence of water in the feed [6]. To improve the long-term water stability different groups have co-added rare-earth metals such as Ce and La, followed by calcination to form nano-sized particles of the oxides inside the zeolite pores [7]. While these methods do lead to water stability, they do not achieve the desired activity improvements for the HC-SCR reaction.

In this work, we report novel bifunctional catalysts with superior response to water under deNOx conditions. By externally coating active zeolite-based catalysts with metal oxide fine particles, an improvement in the activity and selectivity of the catalyst is observed upon the introduction of water in the feed. In addition, the synergy of the coating with the catalyst decreases the HC-SCR temperature range by about 150 °C.

2. Experimental

2.1. Materials

Ammonium forms of different zeolite frameworks (BEA, FAU, FER, MFI, and MOR) with various Si/Al ratios (10–140) were provided by Zeolyst International. To obtain their H-forms, zeolites were calcined at 550 °C for 4 h in a static furnace. Transition metals (Ag, Co, Cu) were ion-exchanged into the zeolite according to commonly used literature procedures. For instance, to obtain a 60% exchanged Cu-ZSM-5 sample (following the commonly used nomenclature where 100% exchanged stands for one Cu ion per every two Al sites), hereafter referred as Cu(60)-ZSM-5, 100 mL of a 0.015 M $Cu(NO_3)_2{\cdot}2.5H_2O$ (99.99%, Aldrich) solution were stirred vigorously with 10 g of H-ZSM-5 ($Si/Al = 25$) for 2 h before adjusting dropwise the pH to 8 using a 0.8 M NH_4OH (30%, AR, Mallinkrodt) solution while stirring. The slurry was kept under stirring for an additional 24 h period. The solid was filtered, rinsed with water and dried at 100 °C. Samples were calcined for 4 h at 450–500 °C. The number of exchange steps performed and/or the concentration of the metal solution was modified in order to achieve different metal loadings.

Metal oxides (CeO_2, MoO_3, ZrO_2) were added to the metal exchanged zeolite by incipient wetness impregnation of a nanoparticle sol. For instance, to prepare a 24% CeO_2/Cu(60)-ZSM-5 catalyst, where 24% stands for the added weight of ceria, 1.2 mL of CeO_2 sol (20%, Nyacol, 20 nm, acetate stabilized) were impregnated on 1.0 g of Cu-ZSM-5 under constant mechanical mixing. After drying at 100 °C, the solid sample was calcined at 500 °C for 4 h. Additional impregnations or a diluted sol were used to achieve higher or lower loadings respectively.

2.2. Characterization

X-ray diffraction (XRD) patterns were collected between 5 and 50 °C at a scan rate of 0.08°/min on a Siemens D-5000 diffractometer using Cu Kα radiation at 40 kV and 20 mA.

Nitrogen physisorption was measured on a Micromeritics ASAP 2010 instrument to determine the catalysts surface area. The BET method was used.

Images from field emission scanning electron microscopy (FESEM) were obtained on a Hitachi-S-4700 instrument equipped with two secondary electron (SE) detectors and a backscattered electron (BSE) detector. To avoid charging, catalyst crystals were suspended on ethanol and dispersed on a holey carbon-coated copper grid (SPI Supplies, Mesh 400).

Energy dispersive X-ray microanalysis (EDX) was performed on a Vantage System instrument. Mapping was performed with 128 × 128 pixel resolution. Catalyst samples were scattered on carbon tape on top of aluminum stubs.

Transmission electron microscopy (TEM) was performed on a Phillips CM120 instrument operating at 120 kV, equipped with a CCD camera. The samples were also mounted on holey carbon-coated copper grids.

2.3. Catalytic activity

A microscale plug flow reactor was used to test the catalyst activity. Pure He (99.995%) and the gas mixtures 5% O_2 in He, 5% NO in He, and 3% C_3H_6 in He were obtained from AGA in Certified Grade. Gas flow rates were controlled using Brooks 5860E mass flow controllers to achieve a nominal gas concentration of 2% O_2, 1000 ppm NO and 1000 ppm C_3H_6, balance He at 100 cm^3/min. Water was introduced, when used, through a syringe pump to achieve 10% by volume in the reactant feed; all lines after water introduction were heat traced until vented to prevent condensation. The sample mass was typically 150 mg, diluted up to 2 g using SiC (Electro Abrasive, 40 mesh, 350 μm particle size) in order to increase the size of the bed and avoid heat transfer effects. The temperature of the catalyst was monitored by a thermocouple inserted in the catalyst bed and controlled using an Omega CN9000 temperature controller. A clam-shell furnace was used to maintain reaction temperatures between 150 and 600 °C.

The use of two analytical instruments allowed the monitoring of all common products of HC-SCR reactions. The NO and NO_2 concentrations were monitored on-line with a California Analytical Instruments Model 400-HCLD Chemiluminescence NO/NOx analyzer. An internal heated pump prevented water condensation inside the instrument. An on-line MTI MicroGC 200 equipped with a thermal conductivity detector (TCD) and two chromatographic columns was used to analyze the other components of the effluent gas stream. N_2, O_2 and CO were separated on a Molecular Sieve 5A column (10 m) while a PoraPLOT U column (4 m) was used for CO_2, N_2O, hydrocarbons and water.

Pretreatment of the catalysts included heating the samples in situ at 500 °C under pure He for 1 h followed by 2 h at 250 °C under the reaction feed in order to approach pseudo-steady-state conditions. Every point measurements was taken after 15 min stabilization and at least three points were taken at each temperature.

3. Results

3.1. Characterization

X-ray diffraction patterns of a representative catalyst (Fig. 1) show that there is no substantial change in the zeolite structure due to the addition of the oxide. Broad peaks attributed to CeO_2 can be observed in CeO_2/Cu-ZSM-5, indicating that bulk (as opposed to surface or intrazeolitic) nanocrystalline ceria is present in the system as well.

The location of the ceria particles on the bifunctional samples was confirmed using electron microscopy. SEM photographs of the native Cu-ZSM-5 and the bifunctional catalyst prepared from it are shown in Fig. 2a and b. There is clear evidence of small particles coating the surface of the zeolite crystals in the case of the bifunctional sample. Fig. 2c and d shows TEM images of the same materials. The added particles of around 2–10 nm fully cover the surface of the crystals in the bifunctional sample.

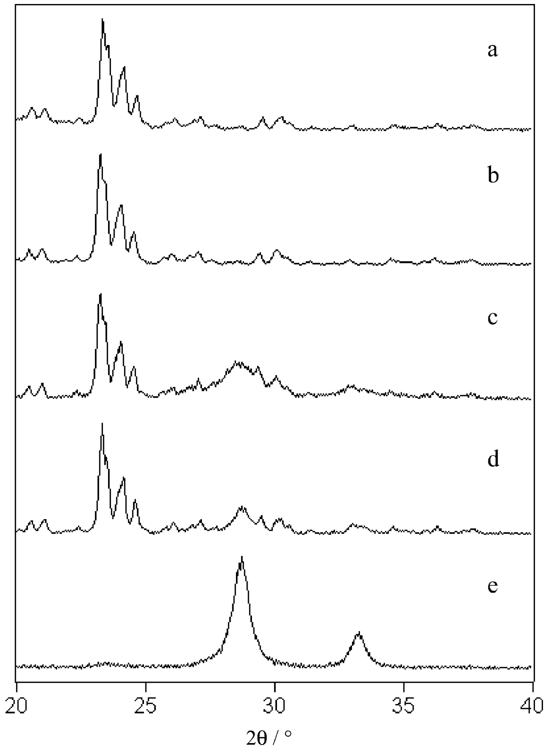

Fig. 1. XRD patterns of (a) H-ZSM-5, (b) Cu(60)-ZSM-5, (c) CeO_2 (20%)/Cu(60)-ZSM-5, (d) mechanical mixture of CeO_2:Cu(60)-ZSM-5 (1:5) and (e) bulk CeO_2. In (c) the broad CeO_2 reflexion at 28.7° relative to the physical mixture indicates smaller ceria particles in the coated material.

Fig. 3 shows the results of Si and Ce mapping by EDX and compares it to the image of the analyzed particle. The close match found by overlapping the images also suggests a complete coverage of the zeolite crystal by cerium atoms.

A backscattered electron image of the same sample is shown in Fig. 4. The difference in contrast on the surface of the catalyst particles indicates that the thickness of the ceria layer is not perfectly even around the crystals. However, most particles appear to be coated to a similar extent.

The BET results are listed in Table 1. The surface area per gram of catalyst is understandably lower for the ceria coated catalyst compared to Cu-ZSM-5 since it now contains only about 80% of the highly porous zeolite. The third column shows the surface area corrected per gram of Cu-ZSM-5. The slight increase in the bifunctional catalyst corresponds to the area contributed by the added nanocrystalline ceria. Hence, no drastic reduction in the surface area of the bifunctional catalysts relative to the parent copper-exchanged zeolite is observed suggesting limited blockage of the pore entrances and the presence of a permeable coating. This is not surprising, given the size of the ceria particles (>2 nm) and hence, the inability of them to enter the 0.5 nm zeolite pores.

3.2. Catalytic activity

The catalytic activity of Cu(127)-ZSM-5 under wet and dry HC-SCR conditions is shown in Fig. 5a. This activity is comparable to previous reports in the literature [8]. The maximum NO conversion is about 80% at 400 °C under dry conditions. The conversion drops to 60% in the presence of water. The propylene conversion is near 100% at these conditions, but a considerable amount of CO is produced at temperatures lower than 400 °C. Little N_2O is observed at 400 °C and NO_2 becomes a significant product above 350 °C.

The bifunctional material in Fig. 5b shows a significantly different behavior during the similar tests. Under dry conditions 24% CeO_2/Cu(127)-ZSM-5 converts a maximum of about of 30% NO at 350 °C. No significant amount of N_2O or CO is observed in the 150–550 °C range. In the presence of water the maximum NO conversion increases to 40–45% and the temperature of maximum NO conversion shifts to

Table 1
Surface area of coated catalysts compared to the native zeolite before and after copper exchange

Catalyst	BET surface area (m^2/g)	Corrected surface area (m^2/g of Cu-ZSM-5)
H-ZSM-5	413	N/A
Cu(127)-ZSM-5 (Si/Al = 25)	398	398
CeO_2(24%)/Cu-ZSM-5	350	434

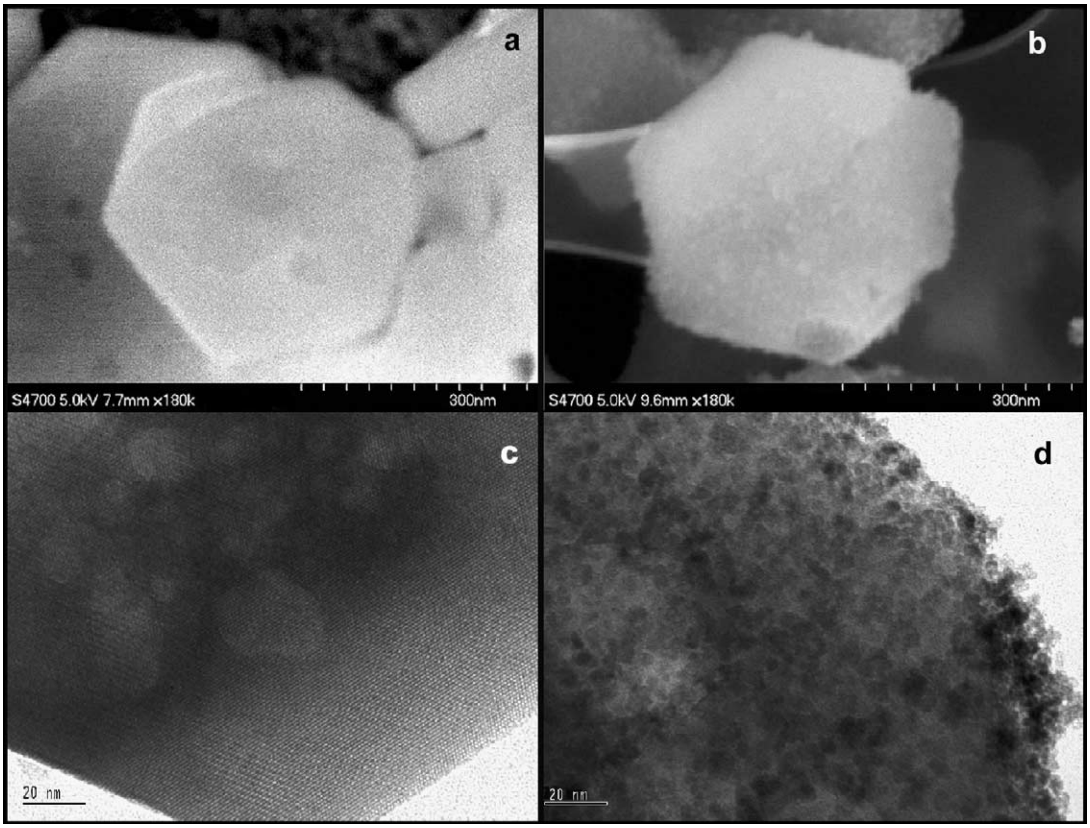

Fig. 2. Top: SEM images of (a) Cu(127)-ZSM-5 and (b) CeO_2(24%)/Cu(127)-ZSM-5. Bottom: TEM images of (c) Cu(127)-ZSM-5 and (d) CeO_2(24%)/Cu(127)-ZSM-5. The presence of a fine coating made by small particles (2–5 nm) is evident on top of the ceria-modified zeolite crystals.

250 °C. There is no formation of significant N_2O or CO at this point under wet conditions either. Above 300 °C, under both wet and dry conditions, a large amount of NO_2 is formed. For comparison reasons, a physical mixture of Cu-ZSM-5 and bulk CeO_2 was prepared in the same ratio as a bifunctional catalyst and tested. The maximum activity of this and comparable bifunctional samples are presented in Table 2. The activity of a series of analogous bifunctional catalysts with different zeolite structure is summarized in Table 3.

Fig. 6 shows the activity of the catalysts at different space velocities. For the Cu(127)-ZSM-5 sample, NO reduction is more efficient at lower space velocity. 100% conversion of NO to N_2 is reached at 5500 h^{-1} at 350 °C. The CeO_2-coated catalyst attains 100% conversion at only 250 °C at the same space velocity.

4. Discussion

4.1. Characterization

The addition of the oxide phase to the metal exchanged zeolites was intended to be limited to the outside of the zeolite surface. Based on the electron microscopy, BET

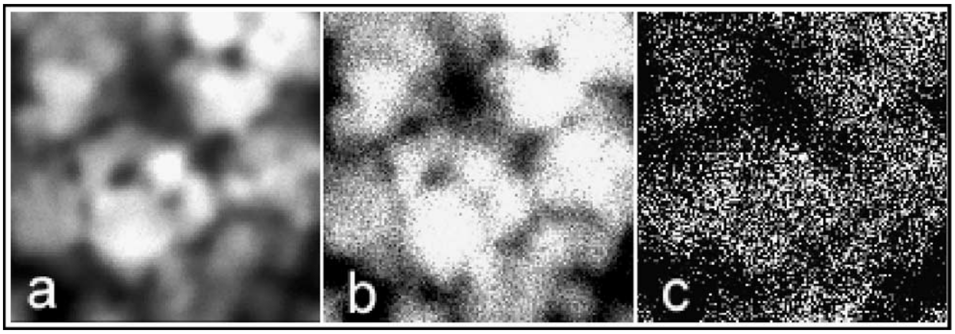

Fig. 3. (a) Image, (b) Si-K and (c) Ce-L mapping as determined by EDX. Despite the intrinsic weaker signal of the Ce-L line, the overlap of the three profiles suggests that the distribution of ceria reaches most zeolite surfaces.

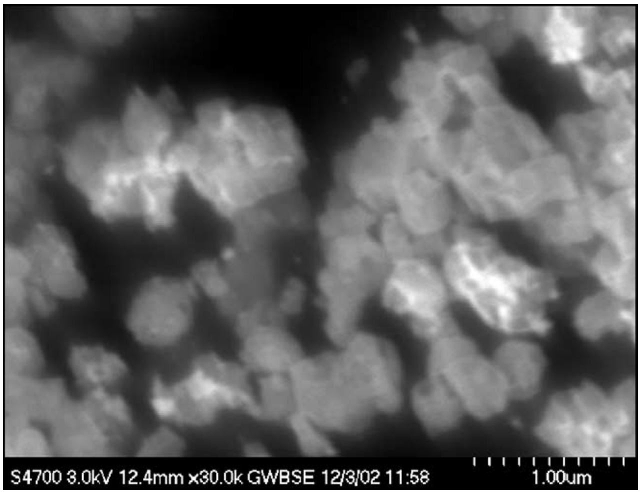

Fig. 4. Backscattered electron image of group of crystals of CeO_2 (24%)/Cu(127)-ZSM-5. Bright areas indicate the presence of high ceria concentration areas. Ceria seems uniformly distributed among the different zeolite crystals and most crystal surfaces appear to have an even coating.

measurements and XRD characterization of the CeO_2/Cu-ZSM-5 sample, the synthesis method indeed appears to lead to the formation of a CeO_2 coating on the external surface of the otherwise unmodified zeolite. The TEM image in Fig. 2d confirms this interpretation. Elemental mapping with EDX and backscattered images suggest that, even though the thickness of the coating is not uniform, the ceria particles cover practically the entire zeolite surface.

The incipient wetness impregnation of the zeolite with a nanoparticle dispersion of oxide provides a fine coating rather than a bulk physical mixture. The combination of the results obtained by the different microscopy techniques used eliminates the presence of large ceria agglomerates unattached to zeolite crystals, as expected in a simple mixture.

On the other hand, the surface area of the finished catalyst confirms that this is not a complete egg-shell layer, as most of the pore structure is still accessible. This suggests that most of the ceria does not block the zeolite pores and that gas diffusion through the nanocrystals is efficient.

The characterization techniques used do not suggest large-scale interaction between cerium and copper. Not much difference is expected between the X-ray diffraction patterns of pure cerium oxide and a copper-containing mixed phase, due to the similarity in size of Ce^{IV} and Cu^{I}. Therefore, the fact that no evidence of a copper–cerium mixed oxide is observed in the XRD spectrum is not conclusive. XAFS and DRIFTS studies presented in a separate manuscript could not detect such a phase, either [9].

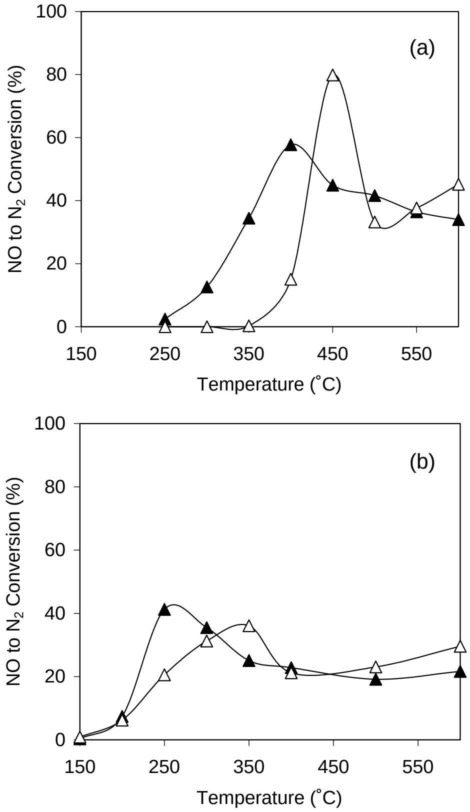

Fig. 5. Effect of water on NO to N_2 conversions of (a) Cu(127)-ZSM-5 and (b) CeO_2(24%)/Cu(127)-ZSM-5. Conditions: 1000 ppm NO, 1000 ppm C_3H_6, 2% O_2, balance He at GHSV = 40,000 h^{-1} (based on mass of catalyst). Open symbols (△): dry feed; closed symbols (▲): wet feed (10% H_2O).

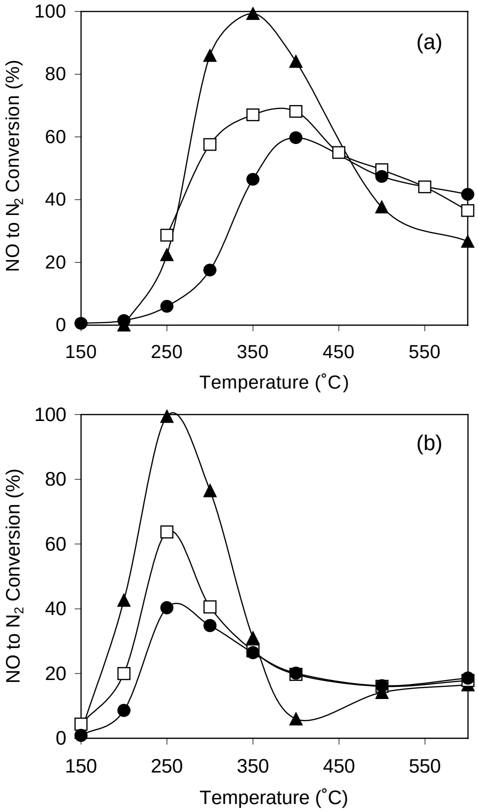

Fig. 6. Effect of space velocity on NO to N_2 conversions of (a) Cu(127)-ZSM-5 and (b) CeO_2(24%)/Cu(127)-ZSM-5. GHSV (based on mass of catalyst): (▲) 5500 h^{-1}; (☐) 17,000 h^{-1}; (●) 35,000 h^{-1}. Conditions: 1000 ppm NO, 1000 ppm C_3H_6, 2% O_2, 10% H_2O, balance He.

Table 2
Activity of different coated catalysts compared to the native zeolite

Sample	Maximum dry activity		Maximum wet activity	
	NO to N_2 conversion (%)	Temperature (°C)	NO to N_2 conversion (%)	Temperature (°C)
H-ZSM-5	<5	N/A	<5	N/A
CeO_2(24%)/H-ZSM-5	45	325	43	350
Cu(127)-ZSM-5 (Si/Al = 25)	80	450	58	400
CeO_2(24%)/Cu-ZSM-5	36	350	41	250
CeO_2:Cu-ZSM-5 (1:4 Mix)	–	–	46	350
Co-ZSM-5	30	550	25	500
CeO_2/Co-ZSM-5	32	450	47	400
Ag-ZSM-5	25	600	18	600
CeO_2/Ag-ZSM-5	35	500	27	400
ZrO_2(24%)/Cu-ZSM-5	–	–	49	400
MoO_3(20%)/Cu-ZSM-5	25	425	18	400

However, due to the drastic change in activity and TPR results observed in that work, the formation of Cu–Ce mixed oxide cannot be completely ruled out.

4.2. Catalytic activity

As expected from the literature ZSM-5 crystals exchanged with late-transition metals (Co, Cu, Ag) show appreciable HC-SCR activity [10]. As shown in Table 2, the addition of a ceria coating to these materials decreases the temperature of maximum NO conversion in all cases. The fact that under wet conditions CeO_2/H-ZSM-5 and Cu-ZSM-5 perform at about 100–150 °C higher temperatures than the coated CeO_2/Cu-ZSM-5 indicates a water-promoted synergistic effect between Cu and Ce. Moreover, the observed synergy appears to be significantly enhanced by the coating arrangement. A comparable physical mixture only reduces the maximum NO conversion temperature by 50 °C relative to Cu-ZSM-5.

Coating using ZrO_2 and MoO_3 as the metal oxide phase does not provide the same effect as CeO_2, indicating a chemical role for ceria. This is not surprising. It is believed that the oxygen storage capacity and oxidizing properties of ceria play a major role in the observed HC-SCR behavior. In NO decomposition, Zhang and Flytzani-Stephanopoulos have already shown that the addition of Ce^{III} ions to Cu-ZSM-5 can produce a 50 °C shift in the maximum activity to lower temperatures [11]. No cerium oxide was observed on the XRD patterns of the catalyst in that work but its presence on the surface was deduced from the identification of Ce^{IV} ions outside the zeolite pores. In that work it was concluded that Ce^{III} inside the channels were responsible for the activity enhancement at lower temperatures. Previously, however, other groups had not found the same results when the order of exchange between Cu and Ce was reversed [7]. The exchange order may affect the formation of undetectable cerium oxide particles. It is possible that the temperature shift observed in the case of co-exchange samples came from such a phase rather than from the intra-framework Ce^{III} co-cations. Reports on precipitating cerium hydroxide directly on indium-modified zeolites for methane- and propane-SCR also concluded that external cerium species were responsible for the observed enhancement of activity, while little activity was due to the cerium ions in the pores [12].

The pore size of the zeolite does not seem to play an important role in the bifunctional materials. Table 3 shows that all frameworks examined display a tendency

Table 3
Effect of the ceria coating on different zeolite frameworks

Sample	Maximum dry activity		Maximum wet activity	
	NO to N_2 conversion (%)	Temperature (°C)	NO to N_2 conversion (%)	Temperature (°C)
Cu(75)-MFI (Si/Al = 15)	80	450	48	400
CeO_2(2%)/Cu-MFI	57	400	44	350
Cu(75)-FER (Si/Al = 10)	80	425	52	350
CeO_2(2%)/Cu-FER	72	400	52	325
Cu(75)-BEA (Si/Al = 12.5)	56	500	35	450
CeO_2(2%)/Cu-BEA	50	500	27	425
Cu(75)–MOR (Si/Al = 10)	62	350	27	350
CeO_2(2%)/Cu-MOR	55	350	30	300
Cu(75)-FAU (Si/Al = 15)	20	550	10	500
CeO_2(2%)/Cu-FAU	17	450	15	400

towards lower temperature activity even with low ceria loadings.

The loading of cerium oxide on the coated samples has a substantial impact on the temperature shift and can be used to fine tune the catalyst. In particular, 24% CeO_2/Cu(60)-ZSM-5 displays the highest activity among the different bifunctional catalysts studied with a wet activity maximum found about 150 °C lower than that of the native Cu-ZSM-5. This temperature shift is not only larger than those reported with co-added ions, but it is also of great significance since it takes the activity of the catalyst down to the ideal lean-burn range of 200–300 °C.

Other parameters studied to optimize the catalyst show little or no effect on the assistance of the ceria coating to the material activity. Variations in copper exchange level between 50 and 200% do not produce dramatic changes in activity of the bifunctional catalysts. In Cu-ZSM-5-based samples, decreasing the Si/Al ratio of the zeolite between 280 and 30 typically increases the activity of the sample since the number of active copper sites is increased. For the most part, the addition of a ceria coating produces the same benefits to all samples regardless of the Si/Al ratio. In addition, the activity displayed by the ceria-coated catalysts is less susceptible to changes in Al content than that displayed by the Cu-ZSM-5 (Fig. 7). The fact that the bifunctional materials perform similarly over a wide range of Si/Al ratios is in agreement with the results obtained with different Cu^{2+} exchange levels and allows a higher tolerance in the preparation procedure of these novel bifunctional materials.

The loss of activity when Cu-ZSM-5 is exposed to a wet reactant feed, particularly under short-term conditions, suggests that water interferes with the HC-SCR reaction either through competitive adsorption with the reactants or by altering the metallic active sites, rather than damaging the zeolite structure. In the long-term, however, the hydrothermal dealumination of the zeolite becomes an issue with regard to catalyst deactivation. The CeO_2/Cu-ZSM-5 catalysts appear to be better catalysts for the HC-SCR reaction under wet conditions. While the activity is not as high as it is for the native Cu-ZSM-5, these coated materials display an activity enhancement when water is present in the reactant stream. This phenomenon is clearly different from the results reported for co-exchanged Ce, Cu materials and for physical mixtures of ceria and Cu-ZSM-5 reported in the literature. Further studies on the mechanism by which the coating enhances the activity of the catalyst in the presence of water are reported in a separate manuscript [9].

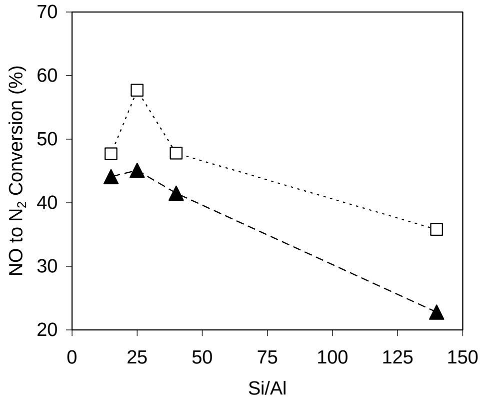

Fig. 7. Effect of Si/Al ratio on the maximum NO to N_2 conversion of (□) Cu-ZSM-5 and (▲) CeO_2(24%)/Cu-ZSM-5. Conditions: 1000 ppm NO, 1000 ppm C_3H_6, 2% O_2, 10% H_2O, balance He.

An increase in long-term stability is also observed in the coated materials relative to the native metal exchanged zeolite. The zeolite structure of samples of Cu-ZSM-5 steamed at 600 °C collapsed after 45 h according to XRD studies performed at BP Corporation. In contrast, it took 70 h under the same conditions for the zeolite structure of the CeO_2-coated catalyst to exhibit similar loss in crystallinity. This hydrothermal stabilization phenomenon has also been observed in Cu-ZSM-5 modified with different co-cations. In particular, Ce and La have been reported to maintain higher activity than the native catalyst after long steaming processes [4,7]. In both cases, it has been suggested that the role of the added rare-earth cation is to avoid dealumination via either the stabilization of the copper site or by reduction of the number of acid sites, respectively. However, cerium was not found to stabilize the zeolite in the latter work, suggesting that the stabilization depends on the synthesis procedure and, therefore, on the actual cerium phase present. Studies on the role of cerium oxide and the coating arrangement in this stabilization phenomenon of Cu-ZSM-5 are also included in the following paper.

As in the case of Cu-ZSM-5, the ceria-coated catalyst activity depends strongly on the space velocity. Interpolating the results, around GHSV $= 10{,}000\,h^{-1}$, both catalysts should reach 85% conversion of NO into N_2. CeO_2/Cu-ZSM-5, however, would meet that abatement level at 100 °C lower temperature than Cu-ZSM-5. This difference could be of significance in industry applications such as stack emissions where space velocities and temperatures are lower than in mobile applications.

5. Conclusions

A series of bifunctional materials comprising a metal-exchange zeolite coated by a metal oxide layer have been prepared and shown to be active catalysts for the selective catalytic reduction of NO using propylene as a reductant. The use of a nano-particle sol as metal oxide source provides a method for preventing the insertion of the oxide inside the zeolite pore. Characterization of the materials by various means shows that these particles adhere to the external zeolite surface and do not form separate oxide particles as in a physical mixture.

Ceria shows the best results as coating phase regardless of the tested base metal exchanged in the zeolite. The combination of phases lowers the maximum activity temperature of the HC-SCR reaction relative to the metal-zeolite only. In particular, CeO_2/Cu-ZSM-5 displayed the highest activity at the lowest temperature among the active catalyst screened. The performance of the catalyst is most affected by ceria content rather than Cu exchange level. Different degrees of performance enhancement by the ceria coating are displayed by different zeolite frameworks, but in all cases a tendency towards lower activity temperatures is observed. For the ZSM-5 framework a Si/Al ratio around 25 appears to be optimal.

The temperature benefits obtained by the coating technique largely exceed those observed in co-exchanged Ce, Cu zeolites or physical mixtures of the functional phases. In addition, the particular topology obtained by this technique provides a unique activity enhancement in the presence of water.

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References

[1] M. Iwamoto, H. Yahiro, Y. Torikai, T. Yoshioka, N. Mizuno, Chem. Lett. (1990) 1967.

[2] K.C.C. Kharas, H.J. Robota, A. Datye, in: J.N. Armor (Ed.), Environmental Catalysis, vol. 552, American Chemical Society, Washington, DC, 1994, Chapter 4, p. 39.

[3] J.Y. Yan, G.D. Lei, W.M.H. Sachtler, H.H. Kung, J. Catal. 161 (1996) 43.

[4] Y.P. Zhang, M. Flytzani-Stephanopoulos, J. Catal. 164 (1996) 131.

[5] C. Yokoyama, M. Misono, Catal. Lett. 29 (1994) 1.

[6] K. Krishna, G.B.F. Seijger, C.M. van den Bleek, H. van Bekkum, H.P.A. Calis, Chem. Commun. (2002) 948.

[7] P. Budi, E. CurryHyde, R.F. Howe, Catal. Lett. 41 (1996) 47.

[8] C. TorreAbreu, M.F. Ribeiro, C. Henriques, F.R. Ribeiro, G. Delahay, Catal. Lett. 43 (1997) 31.

[9] M.J. Castagnola, M.K. Neylon, C.L. Marshall, Catal. Today, 96 (2004) 61.

[10] Y. Traa, B. Burger, J. Weitkamp, Micropor. Mesopor. Mater. 30 (1999) 3.

[11] Y.P. Zhang, M. Flytzani-Stephanopoulos, in: J.N. Armor (Ed.), Environmental Catalysis, vol. 552, American Chemical Society, Washington, DC, 1994, Chapter 1, p. 7.

[12] H. Berndt, F.W. Schutze, M. Richter, T. Sowade, W. Grünert, Appl. Catal. B: Environ. 40 (2003) 51.