NO reduction by hydrocarbons in an oxidizing atmosphere over transition metal–zirconium mixed oxides

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Cu–Zr–O catalyst is active and selective in the NO reduction by propene in an oxidizing atmosphere. This is due to the inertness of ZrO_2 in hydrocarbon oxidation and its ability to disperse Cu. Other transition metal–zirconium mixed oxides were also tested for NO reduction by hydrocarbons in an oxidizing atmosphere. When propene is used as a reductant, Cu, Ni and Co supported on zirconia are active and selective catalysts. When propane is used as a reductant NO conversion decreases for all of the catalysts. The decrease is mild for Ni and Co but is very severe for Cu.

Keywords: Zirconium oxide; transition metal mixed oxides; NO reduction; hydrocarbon reduction of NO

1. Introduction

NO_x abatement is an urgent priority. Reduction of NO by hydrocarbon in an oxidizing atmosphere is an attractive way to achieve this goal. The most active catalysts reported to data are transition metal exchanged ZSM-5 catalysts [1–23]. However, these catalysts have poor hydrothermal stability due to the break down of the zeolitic framework [4–6]. Some of these catalysts also produce CO at low temperatures due to incomplete combustion of hydrocarbons [6]. In principle, if transition metal ions can be supported on an oxide such that they have properties similar to those of ZSM-5, active but more stable catalysts can be formed.

The most extensively studied of these zeolite catalysts is Cu-ZSM-5 [7–23]. Some of the unique properties of Cu-ZSM-5 that may contribute to its high catalytic activities are: (i) acidity [8,9], (ii) stabilization of Cu^+ cations by the frame-

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work, and (iii) highly dispersed and anchored Cu ions [10]. Many of the selective catalysts used in hydrocarbon reduction of NO are acidic, but the role of the acid sites is still unclear. Coke deposition on acid sites has been suggested by Ansell et al. [11] to contribute to the high activities on Cu-ZSM-5 catalyst and by d'Itri and Sachtler [12] as the cause of catalyst deactivation at low temperatures when propene is the reductant. Burch and Millington [31] regarded the role of carbon deposits in NO reduction to be insignificant.

Stabilized Cu^+ has been implicated as important in NO decomposition [10,13], but its role in the reduction reaction is not known. NO forms different adducts with Cu^{2+} and Cu^+, as indicated by IR spectroscopy [14,15], and these adducts may react differently with the adsorbed hydrocarbon. Thus the relative ratio of the two cations at steady state could affect the activity and selectivity of the reduction reaction. The role of a stabilized Cu^+ ion in the reduction reaction is being pursued in another study.

This paper reports the results of a study that was based on the assumption that highly dispersed transition metal ions in an inert matrix would result in active and selective catalysts in NO reduction by hydrocarbons. The assumption was based on the mechanism that NO reacts with an adsorbed hydrocarbon intermediate in the selective reduction of NO [16,17]. In principle, an adsorbed hydrocarbon can react with adsorbed oxygen, lattice oxygen or adsorbed NO. The relative rates of reaction of the adsorbed hydrocarbon with these three oxygen species determine the selectivity in NO reduction. (The reaction is highly selective if the hydrocarbon preferentially react with NO.) Thus the presence of reactive lattice oxygen would be detrimental to NO conversion by hydrocarbons. The Cu ions in ZSM-5 are well dispersed, and even though extra-lattice oxygen may be present in ion-exchanged ZSM-5 [18] and small clusters of CuO may be present in impregnated Cu-ZSM-5 catalysts [19], the number of reactive oxygen per accessible Cu in these preparations is small when compared with bulk CuO. For Cu-ZSM-5 the small concentration of extra-lattice oxygen may be responsible for lowering the selectivity of the catalyst at high Cu exchange levels. As the Cu exchange level increases beyond 100%, extra-lattice oxygen atoms are present to balance the charge of the catalyst. Iwamoto et al. [20] reported that the optimal exchange level of Cu for the reduction reaction is between 100 and 120%, although many of his studies were on overly exchanged Cu-ZSM-5 catalysts [21,23]. Bartholomew et al. [22] noted that their Cu-ZSM-5 with a 90% exchange level was superior to Iwamoto's preparation (exchange level between 140 and 150%) [21]. Reaction of hydrocarbon with lattice oxygen is commonly known in oxidation catalysis [32]. Such a reaction would lower the selectivity for the hydrocarbon intermediate to react with NO, and it may be the reason that generally oxides are less selective than the ZSM-5 exchanged catalysts. Cu/Al_2O_3 is one of the best oxide catalysts for the selective reduction of NO with hydrocarbons [24]. However, its performance declines beyond 0.3 wt% Cu loading. This decline may be due to the growth of CuO clusters. Severino et al. [25] reported that after a 5 wt% Cu/Al_2O_3 was subjected to redox cycles, CuO crystallites large enough to be detected by XRD were formed. Along this line of reasoning, it appears that it should be possible to synthesize catalysts of transition metal ions on an oxide support that are effective for the selective reduction of NO by hydrocarbons provided that the support stabilizes a high dispersion of the transition metal ions and is quite inert for oxidizing hydrocarbons.

This paper reports the results of the investigation of NO reduction by hydrocarbon on transition metal cations supported on an inert oxide matrix, ZrO_2, which is quite inactive in the oxidation of hydrocarbons [26]. One of the catalysts, Cu–Zr–O, has also been reported by Walker and coworkers [28] to be active and selective in the reduction of NO by hydrocarbons.

2. Experimental

Catalyst preparation: Mixed oxides of transition metal and Zr were prepared from their nitrate salts using urea as the precipitating agent as in the methods of Amenomiya [27]. Co-precipitation was important as Amenomiya et al. [27] found that on such preparations CuO only appears at quite high Cu loadings. After precipitation, the samples were boiled vigorously. The precipitate was suction filtered, washed and dried in a 373 K oven. The dried powder was ground and was then either heated in an oven at 623 K for 3 h or in flowing air to 623 K with a temperature ramp of 1 K per minute. The temperature was maintained at 623 K for 3 h. The latter heating method generally resulted in larger surface area catalysts. In the case of the Cu–Zr–O catalyst, Na_2CO_3 was also tested as a possible precipitating agent. The metal contents of the catalysts were determined by ICP using a Thermo Jerrell-Ash Instrument.

The ion exchanged Cu-ZSM-5 catalyst, with a Cu loading of 3.2% and a Si/Al ratio of approximately 70, was provided by GM corporation and was the same as the one used by Cho [30].

Catalytic reactions: The feed stream contained C_3H_6 or C_3H_8, NO and O_2 in He. The C_3 and NO concentrations varied from 890 to 1100 ppm and O_2 varied from 0.95 to 1.04% from one experiment to another but remained constant during an experiment. The concentration of each gas was calibrated before each experiment and C_3H_6/NO was kept at unity. For reaction studies, 0.2–1.9 g of catalyst was heated in He to the reaction temperature, and then NO, C_3 and O_2 were admitted. The exit gases from the reactor were analyzed with gas chromatography. N_2, O_2 and CO were analyzed with a 1.5 ft Carbosphere column linked in series with a 1.5 ft molecular sieve 5A column at room temperature. CO_2, and hydrocarbons were analyzed with a 6 ft Porapak Q column at 403 K. N_2O was analyzed by the same Porapak Q column at 303 K.

Control experiments were performed to ensure that the N_2 produced was not due to nitrogen species that may remain after calcination. This was accomplished by noting that N_2 production was observed only when the feed gas contained NO,

O_2 and C_3H_6, but not when it contained only O_2 and C_3H_6, or only O_2 and NO. Transient production of N_2 was observed, but very rarely, with freshly calcined samples when C_3H_6 and O_2 (without NO) were used, indicating that some nitrogen species were left behind from the preparation. However, this N_2 production was not sustained. The reaction data reported were collected after it was ascertained that no nitrogen impurities remained.

The reaction results are described in terms of NO conversion and NO selectivity, which are defined as:

$$\%\mathrm{NO\ conversion} = 2N_2 \times 100/\mathrm{NO}_{\mathrm{in}}\,, \tag{1}$$

$$\%\mathrm{NO\ selectivity} = 2N_2 \times 100/(2O_2\ \mathrm{consumed} + \mathrm{NO\ consumed})\,. \tag{2}$$

%NO selectivity is a measure of the efficiency of NO versus O_2 to react with the hydrocarbon reductant.

XPS analysis was performed in a VG Scientific spectrometer system using Al radiation (1486 eV). The relative concentrations of the metal were calculated using sensitivity factors of 4.0 (Cu $2p_{3/2}$), 1.1 (Zr $3d_{5/2}$), 0.2 (C 1s) and 1.09 (Na 1s). The above values were supplied by the manufacturer of this particular instrument. Relative sensitivity factors of 5.7 (Nd 3d) and 2.6 (Zr 3d), taken from ref. [29], were used to calculate Nd/Zr ratio. The post reaction samples used in the analysis were catalysts after reaction of NO with propene in excess oxygen. They were cooled in He rapidly after reaction and were stored in air.

3. Results and discussion

Table 1 lists the physical characteristics of the transition metal–zirconium mixed oxides. Generally, these oxides are very dense. Sustained reduction of NO by

Table 1
Physical characteristics of the transition metal–zirconium mixed oxides

Catalysts [a]	wt. of TM salts [b]	Color	Density [c]	BET area (m^2/g)
6.1 wt% Cu–Zr–O	1.86 g $Cu(NO_3)_2 \cdot 2.5H_2O$	green	2.2	92.2
8.9 wt% Cu–Zr–O	2.11 g $Cu(NO_3)_2 \cdot 2.5H_2O$	green	2.3	154.2
7.6 wt% Ni–Zr–O	4.64 g $Ni(NO_3)_2 \cdot 6H_2O$	tan	2.0	97.8
7.8 wt% Mn–Zr–O	5.20 g [d] $Mn(NO_3)_2 \cdot nH_2O$	black	1.0	10.5
2.0 wt% Co–Zr–O	4.59 g $CO(NO_3)_2 \cdot 6H_2O$	grey	2.4	142.0
3.9 wt% Fe–Zr–O	1.49 g $FeC_2O_4 \cdot 2H_2O$	rusty red	1.9	48.2
ZrO_2	–	white	1.7	75.9
Cu-ZSM-5	–	pale blue	0.5	–

[a] Determined by ICP.
[b] Weight of salt added to 125 ml of zirconyl nitrate solution (0.37 M).
[c] g/cm^3.
[d] Mn assay = 19.1% and is supplied by Aldrich Chemical Co.

hydrocarbons in the presence of O_2 is observed for all of the oxides for the duration of the experiment, which is generally about 6 h. In the case of Cu–Zr–O tests as long as 30 h have been conducted and sustained reaction is observed. The catalysts can be reused repeatedly without pretreatment. Fig. 1 shows NO conversion as the result of NO reaction with propene in 1% O_2 over a ZrO_2 catalyst at 683 K and a freshly calcined 8.9% Cu–Zr–O catalyst at 523 K as a function of time. The Cu–Zr–O catalyst is more active than the support alone. For all transition metal–Zr–O catalysts the products of hydrocarbon oxidation are CO_2 and H_2O. On ZrO_2, a mixture of 47% CO_2 and 53% CO is observed. The product from NO reduction is N_2 when hydrocarbons are used as reductants. Water suppresses the NO conversion activity. The effect of water depends strongly on temperature. At 529 K the activity is decreased by 50% in the presence of 2.4% H_2O. Additional studies of the effect of water are underway.

Fig. 2 shows the changes in propane conversion and NO conversion as a function of temperature over the 8.9 wt% Cu–Zr–O catalyst. The rise in N_2 conversion follows that of propene conversion and reaches a broad maximum where propene conversion is close to completion. This profile is similar to that of Cu-ZSM-5 [30]. When propane is the reductant, a similar volcano shaped curve is observed for NO conversion. However, at the maximum NO conversion a substantional amount of propane still remains.

Table 2 shows that the activity of Cu–Zr–O catalysts can be modified by the preparation method and by the Cu loading. Preparations using Na_2CO_3 instead of urea as the precipitating agent resulted in a catalyst of lower surface area. The maximum NO conversion is much lower than that prepared by using urea as the

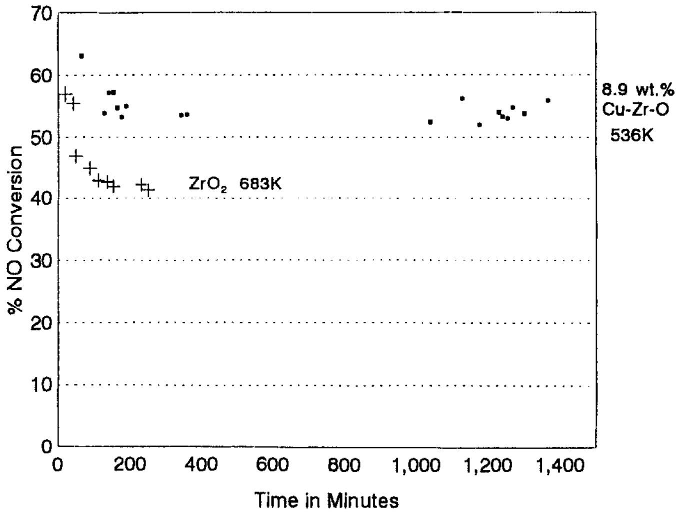

Fig. 1. NO conversion with time on stream. NO = C_3H_6 = 1000 ppm, O_2 = 1%. SV = 17250 h^{-1} for Cu–Zr–O and 6800 h^{-1} for ZrO_2.

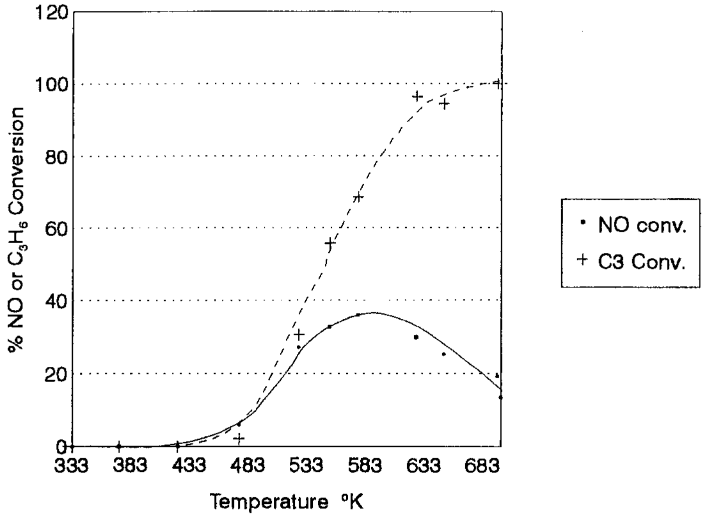

Fig. 2. NO and C_3H_6 conversion as a function of temperature over a 8.9 wt% Cu–Zr–O catalyst. $NO = C_3H_6 = 1000$ ppm, $O_2 = 1\%$, $SV = 128000\ h^{-1}$.

precipitating agent. Increasing the Cu loading to 18 wt% has an adverse effect on both the NO conversion and selectivity. The addition of a small amount of Nd to Cu–Zr–O catalyst has a positive effect.

Table 3 shows the XPS and ICP analysis of several Cu–Zr–O catalysts. Using the Cu–O distance of the (001) plane of CuO, it is estimated that a Cu loading of 13.6 wt% on a 100 m^2/g ZrO_2 support would be equivalent to a monolayer coverage. Using this information and the fact that significant surface enrichment of Cu occurred for the 18.7 wt% Cu–Zr–O catalyst that had a low surface area of 15.5 m^2/g, one can conclude that the surface Cu on this sample is poorly dispersed. For low loading Cu–Zr–O samples (6.0 wt%) the Cu/Zr ratio on the surface indicates no surface enrichment of Cu before and after the reaction of NO with pro-

Table 2
Effect of preparation and composition of Cu–Zr–O on catalytic performance

Catalysts	BET area (m^2/g)	W/F (g min/cm^3)	%NO conv. [a]	%C_3 conv. [b]	%NO sel. [a]	T[a] (K)
8.1 wt% Na_2CO_3 prep.	13.8	0.01	20.1	39.0	5.7	583
8.9 wt% urea prep.	154.2	0.008	54.6	76.2	8.0	533
18.7 wt% urea prep.	15.5	0.016	19.8	54.3	4.3	509
6.3 wt% + 0.7% Nd urea prep.	139.0	0.015	73.1	94.0	8.6	538

[a] Value at maximum NO conversion with an average feed composition of 1000 ppm NO, 1000 ppm C_3H_6 and 1% O_2.

[b] C_3H_6 conversion is also at maximum NO conversion.

Table 3
XPS (ICP) analysis of Cu–Zr–O catalysts

Catalysts	Cu/Zr	Na/Zr	Nd/Zr	C/(Cu+Zr)
8.1 wt% Na_2CO_3 prep. [a]	0.08 [c] (0.13) [d]	0.23 [c] (–) [d]	–	0.46
6.0 wt% urea prep. [a]	0.06 [c] (0.09) [d]	–	–	0.58
6.0 wt% urea prep. [b]	0.07 [c] (0.09) [d]	–	–	0.87
6.0 wt% urea prep. [a] (promoted by 0.7% Nd)	0.06 [c] (0.10) [d]	–	0.52 [c] (0.01) [d]	0.51
18.7 wt% urea prep. [b]	1.05 [c] (0.40) [d]	–	–	0.66

[a] Catalyst before reaction.
[b] Catalyst after reaction.
[c] XPS results.
[d] ICP analysis.

pene, and since its surface area is 92 m^2/g, the surface Cu on this sample should be well dispersed.

The Cu–Zr–O catalyst prepared using Na_2CO_3 as a precipitating agent has a substantional amount of Na left on the surface. For the Nd–Cu–Zr–O sample (urea preparation) the large Nd/Zr ratio suggests, even with the uncertainty in estimating the Nd sensitivity factor [29], that Nd is probably enriched on the surface of the Cu–Zr–Nd–O catalyst. The surface concentrations of Na and Nd are significant compared with that of Cu and this may account for the difference in the catalytic behavior of these catalysts with respect to Cu–Zr–O catalysts prepared using urea as the precipitating agent.

Fig. 3 shows the XPS spectra of Cu, Zr and C for the 6.0 wt% Cu–Zr–O catalyst before and after reaction. The Cu ions in the fresh 6.0 wt% sample are fully oxidized as indicated in fig. 3b by the 933.6 peak and the presence of the two prominent satellite peaks at 943 and 962 eV. The Cu 2p peaks in the post reaction sample are clearly shifted to a lower energy and the satellite peaks are now less intense. This indicates the presence of Cu in the lower oxidation state on this sample, even though it has undergone reaction in a net oxidizing atmosphere and it has been exposed to the ambient atmosphere at room temperature prior to XPS analysis. For the 18 wt% Cu sample no such changes are observed. The observed surface Cu enrichment for this sample indicates the existence of clusters of CuO on the surface of the ZrO_2 support. The oxidized Cu within the clusters may mask the changes due to surface Cu reduction. Alternatively, the surface oxidation state of the higher loading catalyst may differ from that of the dispersed Cu sample as its reduced Cu may be reoxidized more rapidly by gas phase O_2 and NO. For the 6 wt% Cu–Zr–O catalyst it is observed that the C (1s) and O (1s) peaks are different before and after reaction. The C/(Cu + Zr) ratios indicate carbon deposition after reaction. No N (1s) peaks are observed for the fresh and post reaction samples.

Other transition metal–zirconium mixed oxides were also studied. Table 4 compares the activities and selectivities of NO reduction by propene over various transition metal zirconium mixed oxides and Cu-ZSM-5. Cu, Ni and Co catalysts

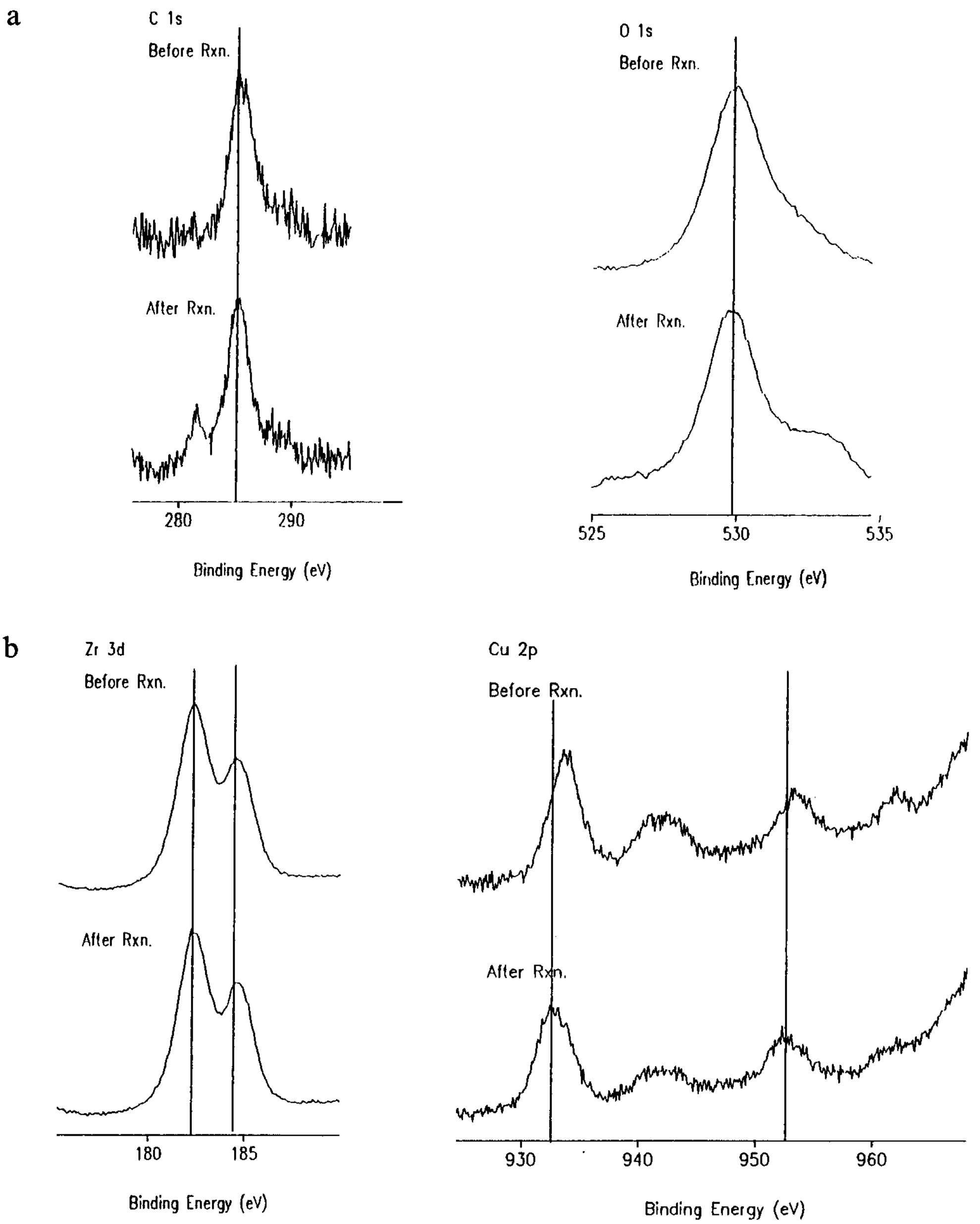

Fig. 3. XPS spectra of 6.0 wt% Cu–Zr–O catalyst before and after reaction. (a) C(1s) and O(1s), (b) Zr (3d) and Cu (2p).

compare well with the ZSM-5 catalyst when propene is used as a reductant. Two catalysts with a ninefold difference in surface areas are reported for the Ni–Zr–O (the low surface area catalyst was not ground before calcination). The change in surface areas shifts the temperature of maximum NO conversion by 83 K but does

Table 4
Reduction of NO by C_3H_6 over transition metal and Zr mixed oxides. Feed: $NO/C_3H_6/O_2 = 0.1\%/0.1\%/1.0\%$

Catalyst[a]	BET[b]	W/F[c] (SV)	%NO conv.	%C_3H_6 conv.	%NO sel.[d]	T_{max}[e] (K)
6.0% Cu–Zr–O	92.2	0.014 (9430)	58.8	92.9	7.4	561
8.9% Cu–Zr–O	154.2	0.008 (17250)	54.6	76.2	8.0	533
7.6% Ni–Zr–O	97.8	0.009 (13330)	61.9	84.1	8.3	601
6.7% Ni–Zr–O	10.4	0.014 (9000)	59.5	80.9	8.2	684
7.8% Mn–Zr–O	10.5	0.015 (3960)	20.7	79.3	2.8	555
2.0% Co–Zr–O	142	0.024 (5900)	55.7	59.2	11.7	564
3.9% Fe–Zr–O	48.2	0.023 (4930)	42.2	87.0	5.9	615
ZrO_2	75.9	0.015 (6800)	38.5	25.8	22.8	683
Cu-ZSM-5[f]		0.003 (12000)	72.0	100.0	8.3	642

[a] The numbers are weight% of transition metal oxide.
[b] Surface area, m^2/g.
[c] W/F in g cat/cm^3 min. Values in parentheses are space velocity, h^{-1}.
[d] % hydrocarbon oxidized by NO (rest by O_2).
[e] Temperature of maximum activity.
[f] Feed composition: 0.1% NO, 0.1% C_3H_6, 2.5% O_2.

not affect the maximum %NO conversion significantly. Table 5 is a comparison of the different oxides when propane is used as a reductant. In general, propene is a much more effective reductant than propane. The effectiveness of propene versus propane varies greatly among the transition metals. Cu exhibits the strongest preference for propene.

4. Conclusions

Cu–Zr–O is the most active oxidic catalyst reported to-date for propene reduction of NO at low temperature. Nd promoted Cu–Zr–O catalyst, with a 73% NO conversion and 8.9% NO selectivity at a feed composition of 1000 ppm NO, 1000 ppm C_3H_6 and 1% O_2, compares favorably with Cu-ZSM-5. Furthermore the complete oxidation of propene to CO_2 at all temperatures studied is more desirable than the Cu-ZSM-5 catalyst where CO formation occurs at low temperatures. Although water suppression of NO conversion decreases its attractiveness as a practical catalyst, the fact remains that high NO conversion and selectivity is

Table 5
Reduction of NO by C_3H_8 over transition metal and Zr mixed oxides. Feed: $NO/C_3H_8/O_2 = 0.1\%/0.1\%/1.0\%$

Catalyst[a]	BET[b]	W/F[c] (SV)	%NO conv.	%C_3H_6 conv.	%NO sel.[d]	T_{max}[e] (K)
6.0% Cu–Zr–O	92.2	0.015 (8800)	14.9	54.0	2.6	607
7.6% Ni–Zr–O	97.8	0.012 (10300)	32.7	40.3	7.3	637
6.7% Ni–Zr–O	10.4	0.015 (8400)	27.9	48.7	5.9	693
7.8% Mn–Zr–O	10.5	0.015 (3960)	10.5	34.3	5.9	582
2.0% Co–Zr–O	142	0.024 (5900)	56.5[f]	62.2	8.0	605
3.9% Fe–Zr–O	48.2	0.022 (5100)	26.9	62.7	4.4	682
Cu-ZSM-5[g]	–	0.003 (10465)	67.95	93.68	8.3	593

[a] The numbers are weight% of transition metal oxide.
[b] Surface area, m^2/g.
[c] W/F in g cat/cm^3 min. Values in parentheses are space velocity, h^{-1}.
[d] % hydrocarbon oxidized by NO (rest by O_2).
[e] Temperature of maximum activity.
[f] Deactivation of the catalyst was observed for this catalyst due to carbon built up. Conversion was that at the end of the experiment when the catalyst was still deactivating at a very slow rate.
[g] Feed composition: 0.1% NO, 0.1% C_3H_8, 2.5% O_2.

achieved in a catalyst without the ZSM-5 framework. A possible explanation for the high reactivity and selectivity of low loading Cu–Zr–O catalysts is that the CuO cluster size is limited. We suggest that reactive lattice oxygen in bulk CuO reduces the selectivity of the catalyst for NO reduction by hydrocarbons in an oxidizing atmosphere. Limiting the cluster size of CuO dispersed in inert matrices would reduce the non-selective reaction of the hydrocarbon with lattice oxygen. While we have not shown conclusively that low loading Cu–Zr–O catalysts have highly dispersed Cu, the low surface Cu/Zr ratios and high surface areas suggest that high Cu dispersion is possible on these catalysts. These low loading Cu–Zr–O catalysts are more active and selective than a low surface area 18.7 wt% loading Cu–Zr–O where high surface dispersion has been precluded. The need for an inactive oxide matrix is consistent with the fact that the observed NO selectivity is the highest on ZrO_2 compared to the transition metal–zirconium mixed oxides as the former is much less active towards hydrocarbon oxidation.

The performance of the catalyst is also dependent on the nature of the hydrocarbon. In general, there is a decrease in the efficiency when propane is a reductant, but this decrease is highly dependent on the transition metal. This phenomenon is interesting and is still under investigation.

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References

[1] T.J. Truex, R.A. Searles and D.C. Sun, Platinum Metals Rev. 36 (1992) 2.
[2] Y. Li and J.N. Armor, Appl. Catal. B (1992) L31.
[3] W. Held, A. Konig, T. Richter and L. Ruppe, SAE Paper No. 900496 (1990).
[4] K.C.C. Kharas, H.J. Robota and D.J. Liu, Appl. Catal. B 2 (1993) 225.
[5] R.A. Grinsted, H.-W. Jen, C.N. Montreuil, M.J. Rokosz and M. Shelef, 13th North American Meeting of the Catalysis Society, 2–6 May 1993.
[6] D.R. Monroe, C.L. Dimaggio, F.A. Matekunas and D.D. Beck, General Motors Research Publication 7799 (1992).
[7] M. Iwamoto, N. Mizuno and H. Yahiro, in: *Proc. 10th Int. Congr. on Catalysis*, Budapest 1992, eds. L. Guczi, F. Solymosi and P. Tétényi (Akademiai Kiado, Budapest, 1993) p. 1285.
[8] H. Hamada, Y. Kintaichi, M. Sasaki, T. Ito and M. Tabata, Appl. Catal. 70 (1991) L15.
[9] Y. Kintaichi, H. Hamada, M. Tabata, M. Sasaki and T. Ito, Catal. Lett. 6 (1990) 239.
[10] M. Iwamoto, in: *Future Opportunities in Catalytic and Separation Technology*, ed. M. Misono (Elsevier, Amsterdam, 1990).
[11] G.P. Ansell, A.F. Diwell, S.E. Golunski, J.W. Hayes, R.R. Rajaram, T.J. Truex and A.P. Walker, Appl. Catal. B 2 (1993) 81.
[12] J. d'Itri and W.M.H. Sachtler, Appl. Catal. B 2 (1993) L7.
[13] Y. Li and W.K. Hall, J. Catal. 129 (1991) 202.
[14] J. Valyon and W.K. Hall, J. Phys. Chem. 97 (1993) 1204.
[15] M. Iwamoto, H. Yahiro, N. Mizuno, W.-X. Zhang, Y. Mine, H. Furukawa and S. Kagawa, J. Phys. Chem. 96 (1992) 9360.
[16] M. Sasaki, H. Hamada, Y. Kintachi and T. Ito, Catal. Lett. 15 (1992) 297.
[17] C.N. Montreuil and M. Shelef, Appl. Catal. B 1 (1992) L1.
[18] J. Valyon and W.K. Hall, J. Phys. Chem. 97 (1993) 7054.
[19] J.L. d'Itri and W.M.H. Sachtler, Catal. Lett. 15 (1992) 289.
[20] N. Sato, Y. Yu-u, H. Yahiro, N. Mizuno and M. Iwamoto, Appl. Catal. 70 (1991) L1.
[21] M. Iwamoto, H. Yahiro, Y. Yu-u, S. Shundo and N. Mizuno, Shokubai 32 (1990) 430.
[22] C.H. Bartholomew, R. Gopalakrishnan, P.R. Stafford, J.E. Davidson and W.C. Hecker, *Symp. on Catalytic Systems for a Better Environment*, AICHE Annual Meeting, Miami Beach, paper 240a.
[23] M. Iwamoto and H. Hamada, Catal. Today 10 (1991) 57.
[24] T. Torikai, H. Yahiro, N. Mizuno and M. Iwamoto, Catal. Lett. 9 (1991) 91.
[25] F. Severino, J. Brito, O. Carias and J. Laine, J. Catal. 102 (1986) 172.
[26] J.E. Germain and R. Laugier, Bull. Soc. Chim. France (1972) 54.
[27] Y. Amenomiya, I.I. Ali Emesh, K. Oliver and G. Pleizier, *Proc. 9th Int. Congr. on Catalysis*, Calgary 1988, eds. M.J. Phillips and M. Ternan (Chem. Inst. of Canada, Ottawa, 1988) p. 634.
[28] G.P. Ansell, A.F. Diwell, S.E. Golunski, J.W. Hayes, R.R. Rajaram, T.J. Truex and A.P. Walker, 205th ACS National Meeting, Denver CO, 29 March–1 April 1993.

[29] J.F. Moulder, W.F. Stickle, P.E. Sobol and K.D. Bomber, in: *Handbook of X-Ray Photoelectron Spectroscopy*, ed. J. Chaslain (Perkin-Elmer Corp., Minnesota, 1992).
[30] B.Y. Cho, J. Catal. 142 (1993) 418.
[31] R. Burch and P.J. Millington, Appl. Catal. B 2 (1993) 101.
[32] A. Bielanski and J. Haber, in: *Oxygen and Catalysis* (Dekker, New York, 1991).