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Metal oxide catalysts for lean NO_x reduction

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Abstract

A summary of the current understanding of the lean NO_x reduction reaction on various metal oxides, particularly Cu–ZrO_2, is presented. Whenever appropriate, a comparison with the behavior of the corresponding ZSM-5-based catalysts is made. It is concluded that there are many mechanistic similarities between metal oxide-based and zeolite-based catalysts. Thus, the catalytic properties are determined more by the nature of the active centers than by the nature of the support. Potential advantages offered by metal oxides should make them attractive candidates for practical applications.

Keywords: NO_x; Exhaust gas treatment catalysts; Reduction; Copper–metal oxide catalyst; Hydrocarbon–NO reaction

1. Introduction

Lean NO_x reduction with hydrocarbons, (i.e., reduction of NO_x in the presence of a large excess of O_2), is an attractive means to convert the NO formed in industrial boilers and automotive engines to N_2 and O_2. For a catalyst to be industrially practical for either of these applications, the hydrocarbon must react selectively over the catalyst with NO rather than with adsorbed oxygen or lattice oxygen despite the large excess of O_2 present in the feed. In addition, the catalyst must retain its activity in the presence of SO_2 and H_2O. An effective automobile catalyst has the additional requirement of having to maintain its activity over a wide range of temperatures, space velocities, O_2 concentrations and hydrocarbon/NO ratios [1]. To date, no industrially practical catalyst for lean NO_x reduction with hydrocarbons has been reported, although several catalysts such as Cu-ZSM-5 [2], Co-ZSM-5 [2], Ga-ZSM-5 [3], Cu-ZrO_2 [4], Al_2O_3 [5] and H-ZSM-5 [6] have been found to be quite active for this reaction.

The majority of the catalysts which have been reported to date can be divided into two classes: zeolites and metal oxides. This article focuses on lean NO_x reduction over metal oxides. Metal oxides have several properties which may make them more suitable for industrial use than zeolites. First of all, unlike zeolites, metal oxides exist in thermodynamically stable forms. This is important as an automotive catalyst experiences high temperatures during certain portions of the drive cycle. Secondly, the composition of metal oxides can be varied to a greater extent than the composition of zeolites, thus providing more flexibility for optimization. Finally, the narrow pores in a zeolite may result in diffusion limitation which could be avoided in a metal oxide.

This article emphasizes materials not covered by a recent review by Hamada et al. [7], which should be referred to for additional information

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regarding lean NO_x reduction over metal oxides. It is divided into three main sections. The first section will examine the role of the metal ion and the support by comparing the lean NO_x reduction behavior of metal-ZSM-5 and metal–Al_2O_3 catalysts. The next section, and primary focus of this review, will cover Cu mixed metal oxides, specifically Cu–ZrO_2 and Cu–Ga_2O_3. The final section will examine the lean NO_x reduction behavior of single metal oxides: Al_2O_3, Ga_2O_3, ZrO_2 and La_2O_3.

One characteristic of catalytic lean NO_x reduction is that as the temperature is increasing, the NO conversion to N_2 increases, reaches a maximum and finally decreases [2,8]. The temperature at which the maximum occurs is typically referred to as the temperature of maximum NO conversion, T_{max}. The T_{max} commonly corresponds to the temperature at which the hydrocarbon is almost completely consumed [9], although this is not always the case [4]. A measure of the ability of the hydrocarbon to be oxidized by NO rather than by adsorbed oxygen or lattice oxygen is the competitiveness factor (%). It is defined as $NO_{rxted} \times 100\% / (n \times HC_{rxted})$, where NO_{rxted} is the NO reacted to form N_2, and n is the number of O atoms needed to combust the reacted hydrocarbon, HC_{rxted}, completely to CO_2 and H_2O. For example, $n = 9$ for propene. The term competitiveness factor is used rather than selectivity in order to avoid confusion with the selective reduction of NO to N_2.

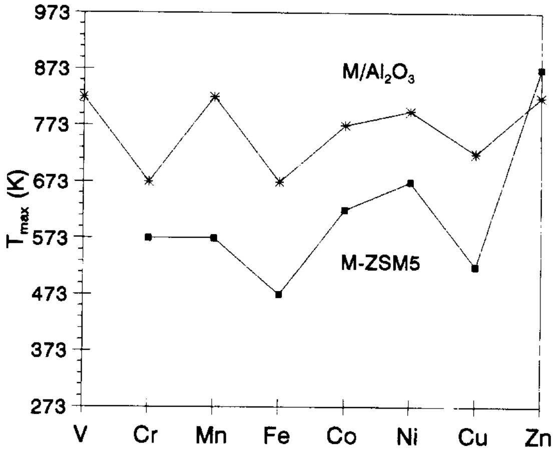

Fig. 1. T_{max} for M/Al_2O_3 and M-ZSM-5 catalysts [10]. M-ZSM-5 (% exchange): Cr (22), Mn (127), Fe (94), Co (90), Ni (99), Cu (102), Zn (96). 0.2 wt.-% M/Al_2O_3. 1000 ppm NO, 250 ppm C_2H_4, 2% O_2, 0.5g, 150 ml/min.

2. Comparison of metal-zeolites and metal-oxides

Cu-ZSM-5 [2], Co-ZSM-5 [2] and Fe-MOR [10] have been found to be quite active for lean NO_x reduction even though their corresponding metal oxides are quite inactive [7]. The ability of the zeolite to maintain a high dispersion of metal ions has been suggested as an explanation for the high activity [11]. However, if the sole role of the zeolite is to maintain a high dispersion of metal ions, then it should be possible for metal ions on a non-zeolite support to also exhibit a high activity for lean NO_x reduction, provided that they are also well dispersed. Furthermore, if the support has little influence on the reactivity of the metal ions, then the supported metal catalysts should exhibit behavior similar to their zeolite counterparts.

Indeed, there are examples of oxide supported metal catalysts which exhibit traits similar to those exhibited by the corresponding metal-zeolites. In lean NO_x reduction over Pt-ZSM-5 [12] with ethene and Pt/Al_2O_3 [7] with propene, the T_{max} for each catalyst is very low, typically below 523 K. In addition, both catalysts form a substantial amount of N_2O, and are unaffected by the presence of as much as 8% H_2O when an alkene is used as the feed. The behavior of Ga-ZSM-5 [3] and Ga/Al_2O_3 [13] are also similar; both show an extremely high competitiveness factor and activity for NO reduction even in the presence of 10% O_2.

It would be interesting to compare the lean NO_x activity of metal-zeolites and metal-oxide catalysts. However, such a comparison would be meaningful only if the metal-oxide catalysts were of similar weight loadings, the metal-zeolite catalysts were of similar levels of exchange, and the catalysts were tested under the same reaction conditions. Fig. 1 and Fig. 2 show such results for

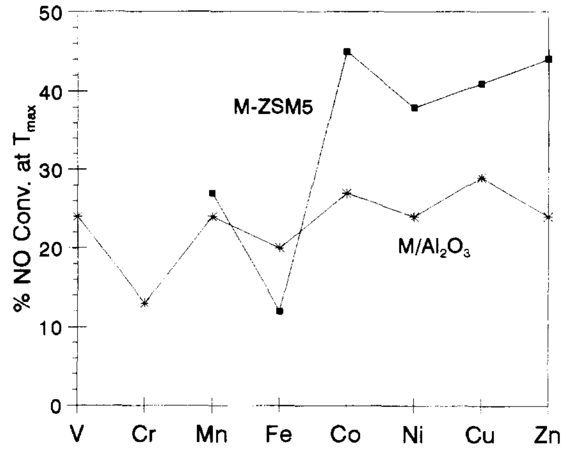

Fig. 2. %NO Conversion at T_{max} for M/Al_2O_3 and M-ZSM-5 catalysts [10]. Conditions are the same as in Fig. 1.

ZSM-5 and Al_2O_3-supported samples taken from Sato et al. [10].

Fig. 1 shows the variation in the T_{max} for the first row transition metal ions exchanged into ZSM-5 or supported on Al_2O_3 for ethene reduction of NO_x. The loading of the transition metal ions on Al_2O_3 was 0.2 wt.-%, and the exchange level of the metal ions in ZSM-5 ranged from 90–102%, which corresponds to about 3 wt.-% metal loading, with the exception of Mn-ZSM-5-127 and Cr-ZSM-5-22, (the number after the zeolite indicates the extent of exchange) [10]. Since, in general, the T_{max} is lower when the metal loading is higher [14,15], the T_{max} for Cr-ZSM-5-22 is expected to be significantly higher than the T_{max} for Cr-ZSM-5-100, while the T_{max} for Mn-ZSM-5-127 is expected to be lower than the T_{max} for Mn-ZSM-5-100. The figure shows a good qualitative relationship between the two series, especially if one considers how the T_{max} of Cr-ZSM-5 and Mn-ZSM-5 would change if the exchange levels were closer to 100%.

Fig. 2 displays a plot of the NO conversions at T_{max} for the same catalysts. As it is difficult to predict how the NO conversion at T_{max} would be affected by increasing the Cr exchange level to 100%, the point for Cr-ZSM-5 was not plotted. While the NO conversions over Al_2O_3 only varied from 13–29%, the NO conversions over the zeolite ranged from 12–45%. Interestingly, this figure also shows similarities in the pattern for the ZSM-5 and Al_2O_3-supported catalysts. Because of the low metal loading in the Al_2O_3-supported samples, the metal ions are likely highly dispersed. The similarities in the behavior patterns in these figures show that the catalytic properties are determined more by the electronic and chemical properties of the metal ions than by the nature of the support. The higher NO conversion to N_2 at T_{max} for the zeolite-supported samples is in part due to the much lower temperatures at which they were obtained. The much higher activity of the zeolite-supported samples than that of the Al_2O_3-supported ones could be attributed to the much higher loading on the zeolite. A simple calculation, assuming an average reaction temperature of 623 K, an apparent activation energy of 20 kcal/mol, and other kinetic parameters being identical, would show that a catalyst would require a higher reaction temperature of about 100 K to achieve the same activity as a catalyst with a density of active sites fifteen times higher. The ZSM-5 samples contained about fifteen times more transition metal ions than the Al_2O_3 supported ones. Thus, these data suggest that highly dispersed metal ions on ZSM-5 and Al_2O_3 possess similar activities.

It is informative to examine the effect of loading of transition metal ions using the data of Sato et al. [10] who used ethene as a reductant over 0.2 wt.-% metal/Al_2O_3 and the data of Miyadera [16] who used propene as the reductant over 2 wt.-% metal/Al_2O_3. Table 1 shows the T_{max} and the % NO conversion at T_{max}, respectively, for V, Cr, Co

Table 1
Comparison of 0.2 wt.-% [10][a] and 2.0 wt.-% [16][b] M/Al_2O_3

Metal	Wt.-%	T_{max}(K)	% NO conv. at T_{max}
V	0.2	823	23
Cr	0.2	673	14
Co	0.2	773	26
Cu	0.2	723	28
V	2.0	723	11
Cr	2.0	573	10
Co	2.0	673	76
Cu	2.0	623	36

[a] 1000 ppm NO, 250 ppm C_2H_4, 2% O_2, 0.5 g, 150 ml/min.
[b] 500 ppm NO, 500 ppm C_3H_6, 10% O_2, 10% CO_2, 10 g, 2000 ml/min.

and Cu/Al_2O_3 catalysts. The T_{max} for 2 wt-% Cr/Al_2O_3 was estimated to be 573 K based on the published data showing a small difference between the NO conversion at this temperature and at 623 K. The trend for T_{max} for the two sets of samples agrees fairly well, but less of an agreement exists for the NO conversion at T_{max}.

There are also examples in which no simple correlation exists between the lean NO_x reduction behavior of a metal-zeolite and its oxide-supported counterpart. One example is Ce-ZSM-5, which is quite active for lean NO_x reduction, even though Ce/Al_2O_3 is relatively inactive [17]. The difficulty of developing a simple correlation is due to the strong dependence of lean NO_x reduction behavior on the support, metal loading and preparation procedure. Variations in these factors lead to catalysts of different dispersions of the active component and possibly different extents of participation of the support in the reaction. This is illustrated by the following examples:

(1) Although Pt/Al_2O_3 is effective at lean NO_x reduction with propane, Pt/SiO_2 is inactive [7].

(2) Supporting 0.2 wt.-% Ag on Al_2O_3 suppressed the lean NO_x activity of Al_2O_3 [18], but the presence of 2 wt.-% Ag enhanced its activity [16].

(3) Co/Al_2O_3 prepared from cobalt acetate and calcined to 773 K was active for lean NO_x reduction, while Co/Al_2O_3 prepared in a similar manner from cobalt nitrate was inactive [19].

(4) The activity of Co/Al_2O_3 prepared from cobalt acetate and calcined at 773 K was significantly lower than the same sample calcined at either 873 K or 1073 K [19].

3. Cu mixed metal oxides

3.1. General considerations

The above comparison of ZSM-5 and Al_2O_3-supported samples shows that highly dispersed metal ions exhibit similar catalytic behavior without a strong dependence on the nature of the support. This implies that a more active catalyst can be obtained if it can be prepared with a higher transition metal content while maintaining the high dispersion. The common method of preparation by impregnation can produce samples of high metal contents and high dispersion, but only on supports that interact strongly with the metal ions. Coprecipitation is another method which has been successfully applied to a number of systems, including ZrO_2- and Ga_2O_3-based catalysts.

Coprecipitated Cu-, Ni-, Fe-, Co-, and Mn-ZrO_2 have been reported to be effective catalysts for lean NO_x reduction [4]. High NO_x conversions can be obtained at lower temperatures than on ZrO_2 (Table 2). These catalysts were prepared by coprecipitating metal nitrate and zirconyl nitrate solutions with urea using the method of Amenomiya et al. [20]. In contrast, Hamada reported that no metal/ZrO_2 catalyst prepared by impregnation exhibited better lean NO_x activity than ZrO_2 [7]. This dependence of the lean NO_x reduction activity on the preparation method has been observed also for Cu–SiO_2. A Cu/SiO_2 catalyst prepared by impregnation was inactive [10] whereas a 1 wt.-% Cu–SiO_2 prepared by gelation from $Si(OC_2H_5)_4$ and $Cu(C_5H_7O_2)_2$ was able to convert 58% of NO to N_2 at 573 K using 0.33 g of catalyst, and a feed of 1% O_2, 0.1% NO, 0.1% CO and 0.1% C_3H_6 flowing at 100 ml/min [21].

3.2. Cu–ZrO_2

Since the initial reports that Cu–ZrO_2 was an effective lean NO_x reduction catalyst [4,22], data have become available concerning the effect of Cu content on NO_x conversions, the reduction properties of the solid, and the NO_2 reduction mechanism. This oxide is interesting because it is the first Cu catalyst reported which showed a lean NO_x reduction activity comparable to that of Cu-ZSM-5 [4]. Just as interesting, is a patent that a mixture of Cu-ZrO_2 and Cu-ZSM-5 yields higher NO conversions to N_2 at 755 K than Cu-ZSM-5 alone [23].

Table 2
Lean NO_x reduction over M-ZrO_2 catalysts with C_3H_6 and C_3H_8[a]

Metal	Wt.-%	BET (m^2/g)	Reductant	W/F (g·min/ml)	SV (h^{-1})	T_{max} (K)	%NO Conv. to N_2^b	$\%HC^b_{Conv.}$	$\%NO^{b,c}_{Compet.}$
	ZrO_2	109	C_3H_6	0.010	13000	773 <[d]	33[d]	30[d]	12[d]
Cu	2.1	164	C_3H_6	0.010	13000	601	68	91	8.6
	6.0	92	C_3H_6	0.014	9700	561	58	92	7.7
	7.6	138	C_3H_6	0.0098	14000	538	64	90	8.3
	8.9	158	C_3H_6	0.010	13000	536	58	81	7.9
	11	152	C_3H_6	0.011	13000	518	54	82	7.9
	15	161	C_3H_6	0.0094	14000	511	52	91	6.8
	24	118	C_3H_6	0.0098	14000	511	46	90	5.9
	33	136	C_3H_6	0.010	13000	504	43	91	5.5
Ni	7.6	98	C_3H_6	0.009	13000	601	62	84	8.3
Mn	7.8	10	C_3H_6	0.015	4000	555	21	79	2.8
Co	2.0	142	C_3H_6	0.024	5900	564	56	59	11
Fe	3.9	48	C_3H_6	0.023	4900	615	42	87	5.9
Cu	6.0	92	C_3H_8	0.015	9700	607	15	54	2.6
Ni	7.6	98	C_3H_8	0.012	10000	637	33	40	8.3
Mn	7.8	10	C_3H_8	0.015	4000	582	11	34	3.2
Co	2.0	142	C_3H_8	0.024	5900	605	57	62	9.2
Fe	3.9	48	C_3H_8	0.022	5100	682	27	63	4.4

[a] Feed: 0.1% NO, 1.0% O_2, 0.1% C_3H_6 or 0.1% C_3H_8, balance He.

[b] At T_{max}.

[c] NO Compet. = $(NO_{rxted} \times 100\%)/(n \times HC_{rxted})$.

[d] Not at T_{max}. $T_{max} > 773$ K.

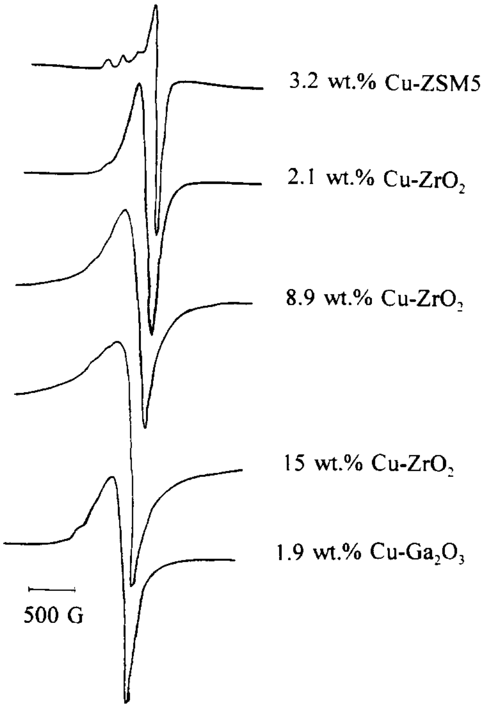

Fig. 3. X-band EPR spectra taken in air. Cu-ZSM-5 and Cu-ZrO_2 catalysts at 77 K; Cu–Ga_2O_3 at room temperature.

Effect of Cu loading

The catalytic properties of Cu–ZrO_2 with copper contents ranging from 2.1 to 33 wt.-% are shown in Table 2. As the Cu loading of the catalysts increased, the activity increased as indicated by the decrease in T_{max}. However, beyond about 10 wt.-% Cu, both the NO conversion at T_{max} and the competitiveness factor decreased; that is, the catalyst became increasingly active for C_3H_6 combustion by oxygen. The 33 wt.-% catalyst was found to have a lower competitiveness factor than the 2.1 wt.-% catalyst even at differential conversions. Under these conditions, the competitiveness factor of 2.1 wt.-% Cu–ZrO_2 ranged from 4.5% at 601 K to 14% at 504 K and was about four times higher than the 33 wt.-% Cu–ZrO_2, which was 1.5% to 3.9% over the same temperature range. The decreasing T_{max} with increasing Cu loading agrees with the results of Hosose et al. [14] on Cu/SiO_2–Al_2O_3 and Jen et al. [15] on Cu-ZSM-5.

Dispersion of Cu

Coupling of the nuclear magnetic dipole moment of Cu^{2+} causes broadening of the Cu EPR signal. Thus, the width of Cu^{2+} EPR signals can be used as an indication of the dispersion of the Cu species. Fig. 3 shows the EPR spectra taken in air at 77 K of 2.1, 8.9, and 15 wt.-% Cu–ZrO_2 as well as 3.2 wt.-% Cu-ZSM-5. As the Cu content of Cu–ZrO_2 increased, the EPR spectra became broader and deviated significantly from the baseline, indicating increasing dipole-dipole interactions between cupric ions [24]. These interactions are so strong in the CuO that its EPR signal becomes so broad that it cannot be distinguished from the baseline. Thus, the spectra showed that the Cu ion dispersion increased in the order 15 wt.-% Cu–ZrO_2 < 8.9 wt.-% Cu–ZrO_2 < 2.1 wt.-% Cu–ZrO_2 < 3.2 wt.-% Cu-ZSM-2. The EPR spectra of 3.2 wt.-% Cu-ZSM-5 was in agreement with the spectra reported by Kucherov et al. [24] and showed partially resolved hyperfine splitting. This is consistent with the high dispersion of Cu ions in this sample. The EPR signals provided information about the Cu^{2+} dispersion in the bulk. In order to use them to interpret catalytic results, it is necessary to extrapolate the conclusions to the surface. The validity of such an extrapolation is based on the XPS results of a 6 wt.-% Cu–ZrO_2 sample which showed no surface segregation of Cu: the Cu/Zr ratio estimated by XPS was close to that of the bulk [4].

Temperature programmed reduction (TPR) by CO and H_2

CO TPR was performed over ZrO_2, 2.1 wt.-% Cu–ZrO_2, 7.4 wt.-% Cu–ZrO_2 and 33 wt.-% Cu–ZrO_2. The results are summarized in Fig. 4 and Table 3. In these experiments, both the consumption of CO and the evolution of CO_2 were measured. In general, these two quantities agreed well with each other, as shown for the 33 wt.-% Cu–ZrO_2 sample (Fig. 4a). However, for the samples of lower Cu loading, the CO consumption at temperatures below the first prominent peak was not accompanied by the corresponding evolution of CO_2 (Fig. 4b). This was due to retention of small amounts of CO_2 by exposed ZrO_2. This was illustrated by the experiment in which ZrO_2 was mechanically mixed with a sample of 33 wt.-% Cu–ZrO_2. The CO TPR of this mixture showed a shift of the CO_2 profile to a higher temperature (Fig. 4c). Likewise, in the TPR of ZrO_2, CO consumption occurred, albeit at a low rate, beginning at about 373 K while noticeable CO_2 desorption only began at about 666 K.

Fig. 4d compares the CO_2 production profile of different samples. It is apparent that the temperature at which significant CO_2 evolution occurred shifted to lower temperatures with increasing Cu content. The shift was much larger than that which could be accounted for due to different amounts of exposed ZrO_2, as the experiment in Fig. 4c showed. Thus, bulk reduction of the oxide by CO became increasingly facile when the Cu loading increased. Since the CO molecule is too large to diffuse into the bulk of an oxide, reduction of the bulk requires diffusion of lattice oxygen to the surface region. Thus, such diffusion is more facile for the higher Cu content samples.

For 7.4 wt.-% and 33 wt.-% Cu–ZrO_2, the area of the reduction peaks corresponded to the complete reduction of all the Cu ions from Cu^{2+} to Cu^0. However, only 80% of the Cu^{2+} were reduced to Cu^0 in 2.1 wt.-% Cu–ZrO_2. This may be an indication of the presence of isolated Cu^{2+} ions in this catalyst.

Since the prominent CO consumption and CO_2 production peaks occurred at the same temperature, the desorption of CO_2 from Cu–ZrO_2 is not the rate limiting step in the oxidation of CO, except for the small amount adsorbed on ZrO_2. It is probable that the rate limiting step involves the breakage of the catalyst-oxygen bond as has been observed over several metal oxides [25]. If this is the case, the fact that the temperature for CO oxidation decreases with the increasing Cu loading in Cu–ZrO_2 would indicate that the lattice oxygen in the poorly dispersed Cu–ZrO_2 can be extracted more easily than the lattice oxygen in highly dispersed Cu–ZrO_2. If one of the pathways to oxidize the hydrocarbon in lean NO_x reduction involves extraction of lattice oxygen, it would fol-

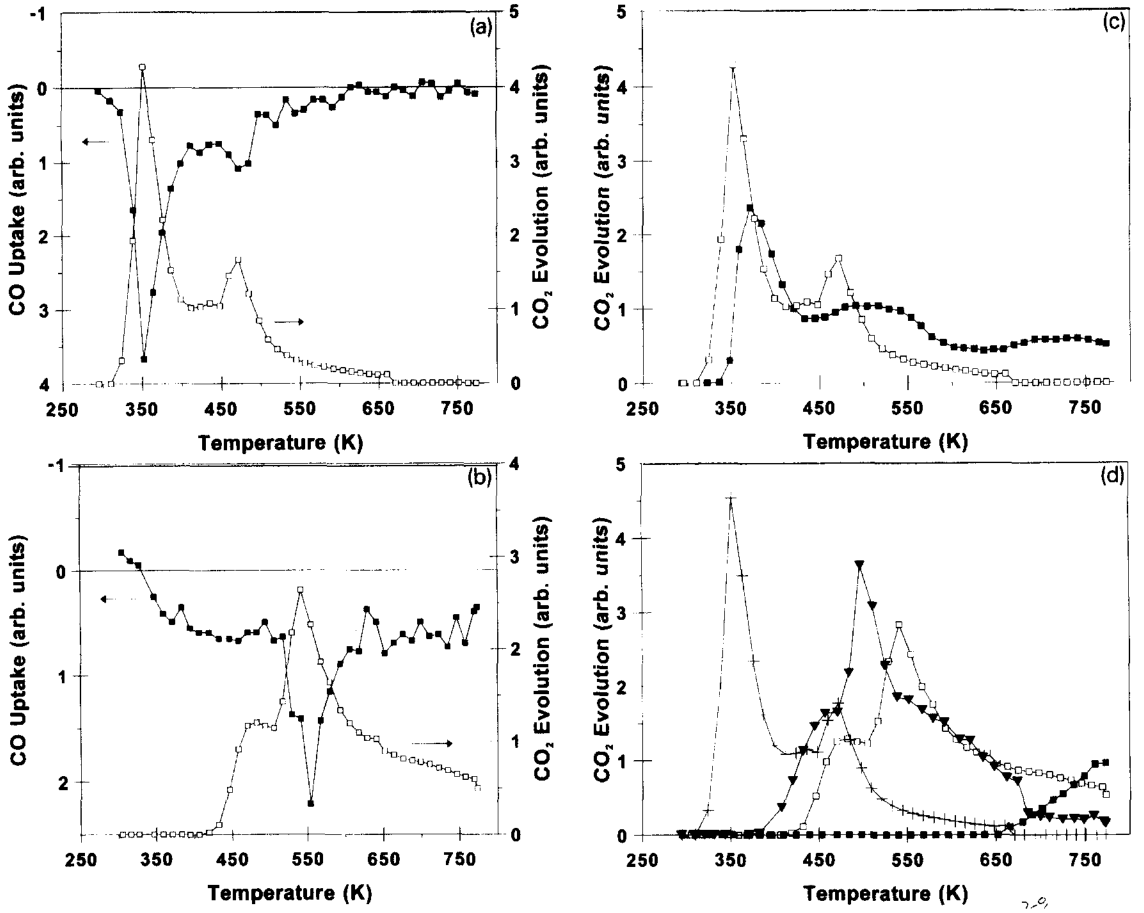

Fig. 4. CO–TPR profiles of ZrO_2 and Cu–ZrO_2. Experimental conditions: 60 ml/min of 10% CO in He; ramp: 2.5 K/min. (a) 0.15 g of 33 wt.-% Cu–ZrO_2. (■) CO uptake, (□) CO_2 evolution. (b) 1.0 g of 2.4 wt.-% Cu–ZrO_2. (■) CO uptake, (□) CO_2 evolution. (c) CO_2 evolution over (□) 0.15 g of 33 wt.-% Cu–ZrO_2. (■) Physical mixture of 0.15 g of 33 wt.-% Cu–ZrO_2 + 0.87 g of ZrO_2. (d) CO_2 evolution over (■) 2.0 g of ZrO_2, (+) 0.15 g of 33 wt.-% Cu–ZrO_2, (▼) 0.70 g of 7.4 wt.-% Cu–ZrO_2, (□) 1.0 g of 2.4 wt.-% Cu–ZrO_2.

low that the contribution of such a pathway is less on low loading Cu–ZrO_2, which would result in a higher competitiveness factor in lean NO_x reduction than a high loading sample. This is in agreement with the data (Table 2).

It is interesting to compare the CO TPR and H_2 TPR results. The H_2 TPR data of 7.4 wt.-% and

Table 3
Temperature Programmed Reduction of Cu–ZrO_2 by CO[a]

Catalysts (wt.)	Onset T of CO_2 desorption (K)	CO_2 peak T (K) (ht. arb. units)	% Cu reduced[b,c]
ZrO_2 (2.0 g)	666	–	–
2.4 wt.-% Cu (1.0 g)	448	480,553	78
7.4 wt.-% Cu (0.70 g)	387	460,506 shoulder 569	108
33 wt.-% Cu (0.15 g)	324	351,473	94
33 wt.-% Cu (0.15 g) + ZrO_2 (0.87 g)	336	371,517	96

[a] Feed: 10% CO in He at 60 ml/min. Ramp: 2.5 K/min to 773 K.

[b] Assuming all reduction Cu^{2+} to Cu^0.

[c] CO reaction with ZrO_2 subtracted from calculation.

Table 4
Activation energies for NO and C_3H_6 consumption

Catalyst	E_a NO (kcal/mol)	E_a C_3H_6 (kcal/mol)	Ref.
2.1 wt.-% Cu–ZrO_2	10±3	17±3	[26]
33 wt.-% Cu–ZrO_2	14±3	20±3	[26]
2.5 wt.-% Cu-ZSM-5	11±3	10±2	[27]
2 wt.-% Cu/Al_2O_3	15±3	13±2	[27]
5 wt.-% Cu-ZSM-5	25±1	11.2±0.7	[28]

33 wt.-% Cu–ZrO_2 showed that the amounts of H_2 consumed over these catalysts corresponded to complete reduction of all the Cu ions from Cu^{2+} to Cu^0. The 7.4 wt.-% catalyst exhibited one reduction peak at 408 K. In contrast, 33 wt.-% Cu–ZrO_2 exhibited a main reduction peak at 453 K with a shoulder at 423 K. The low temperature reduction peak was assigned to the reduction of dispersed Cu^{2+} ions or small CuO clusters while the high temperature reduction peak was assigned to large CuO clusters [20]. The lower reduction peak temperature for the 7.4 wt.-% than the 33 wt.-% sample is opposite to that showed for CO TPR. The reason for this is not clear. It is possible that in H_2 TPR, activation of H_2 is the rate limiting step which is different from that in CO TPR. Measuring the evolution of water would be informative. Another possibility is that H_2 molecules are small and can diffuse into the bulk of the oxide quite readily. Thus, reduction of the bulk oxide by H_2 does not require diffusion of lattice oxygen to the surface, unlike reduction by CO.

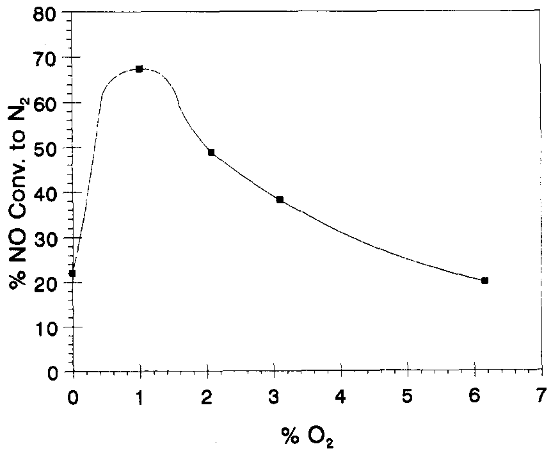

Fig. 5. Effect of O_2 concentration on NO conversion over 2.1 wt.-% Cu–ZrO_2. 1000 ppm NO, 1000 ppm C_3H_6. 1 g, 100 ml/min.

3.3. Kinetics

The apparent activation energies for 2.1 wt.-% and 33 wt.-% Cu–ZrO_2 were determined under differential conditions [26]. The NO conversions to N_2 were kept below 10%, and C_3H_6 conversions were kept below 30%. Despite the large difference in lean NO_x reduction behavior of 2.1 wt.-% and 33 wt.-% Cu–ZrO_2, the apparent activation energies of NO conversion to N_2 and C_3H_6 conversion to CO_x for the two catalysts were similar. The activation energy for NO consumption equalled 10±3 kcal/mol for 2.1 wt.-% Cu–ZrO_2 and 14±3 kcal/mol for 33 wt.-% Cu–ZrO_2. The activation energies for C_3H_6 consumption were slightly higher, being 17±3 kcal/mol for 2.1 wt.-% Cu–ZrO_2 and 20±3 kcal/mol for 33 wt.-% Cu–ZrO_2. Table 4 compares these results with results reported in the literature for Cu-ZSM-5 and Cu/Al_2O_3. The apparent activation energies for the Cu–ZrO_2 catalysts were close to the values determined by Jen and Gandhi [27] for both 2.5 wt.-% Cu-ZSM-5 and 2 wt.-% Cu/Al_2O_3. However, they were different from those for the 5 wt.-% Cu-ZSM-5 reported by Bennett et al. [28]. As suggested by Jen and Gandhi [27], the difference may be due to the manner in which the apparent activation energies were determined. Bennett et al. used a simple power rate equation to determine the rate constants and then the activation energies, whereas those for the other catalysts were determined directly from the rates.

The dependence of the lean NO_x reduction activity of 2.1 wt.-% Cu–ZrO_2 on the oxygen concentration is shown in Fig. 5. The addition of up to 1% O_2 was found to increase the rate of NO conversion to N_2, but further additions of O_2 decreased the rate. This trend is similar to that observed over Cu-ZSM-5 [11]. Surprisingly, the variation in O_2 concentration had no effect on the C_3H_6 conversion. This is in contrast to the behavior of ZrO_2 and Ga_2O_3 [26], where an increase in

Table 5
Comparison of EtOH and C_3H_6 as lean NO_x reductants over 11 wt.-% Cu–ZrO_2[a]

Reductant	T (K)	% O_2	% H_2O	% NO conv. to N_2	% $NO^{b}_{Compet.}$
C_3H_6	498	1	0	54	7.6
EtOH	498	1	0	76	8.6
C_3H_6	523	1	0	58	7.3
EtOH	523	1	0	61	7.1
C_3H_6	523	4	0	35	4.0
EtOH	523	4	0	41	4.1
C_3H_6	523	4	2	15	2.6
EtOH	523	4	2	29	3.7

[a] 1000 ppm NO, 1000 ppm C_3H_6 or 1500 ppm EtOH. 1 g, 100 ml/min.
[b] $NO_{Compet.} = (NO_{rxted} \times 100\%) / (n \times HC_{rxted})$.

the propene conversions over both catalysts, an increase in the NO conversions over Ga_2O_3, and no change in the NO conversions over ZrO_2.

The NO conversion was suppressed by H_2O. The degree of suppression increased with decreasing temperatures. At 529 K, the addition of 2.4% H_2O to the feed flowing over 8.9 wt.-% Cu–ZrO_2 decreased the NO conversions by half. The NO conversions recovered to their original level after the H_2O was removed, indicating that the suppression was due to reversible blocking of the active sites. Similar observations have been made on several other catalysts [12,29,30].

Similar to Cu-ZSM-5 [31], propene is a more active reductant than propane on Cu–ZrO_2 (Table 2), and requires a lower temperature to achieve a certain NO_x conversion. This is probably because propene adsorbs strongly as a π-allyl species, whereas propane is only weakly adsorbed [32].

Various alcohols have also been examined as reductants for the lean NO_x reaction, including methanol, ethanol, 2-propanol, and 2-butanol. Table 5 compares the effectiveness of EtOH and C_3H_6 over 11 wt.-% Cu–ZrO_2 at 498 K and 523 K. For comparison purposes, the concentration of the reductants per carbon atom was kept constant. As shown in the table, in the absence of H_2O, the T_{max} for EtOH occurred at 498 K while the T_{max} for propene occurred at 523 K. At 498 K and 1% O_2, the NO conversion with EtOH was higher than with propene, but the difference disappeared at 523 K. The addition of H_2O suppressed the NO conversion with propene more than with EtOH. In fact, in the presence of H_2O, all of the alcohols investigated with the exception of MeOH were more effective than propene over a La-promoted Cu–ZrO_2 (Fig. 6). La promotion increased the competitiveness factors. These results agree with the expectation that polar molecules, such as alcohol, compete for surface sites with water more effectively than nonpolar molecules, such as propene.

When compared at the same carbon concentration, NO conversion at 498 K for different alcohol reductants followed the order of 2-propanol > 2-butanol > ethanol > propene > methanol. Thus, secondary alcohols are more active than primary alcohols. These results agree with those reported over Ag/Al_2O_3 in the presence of water, which was 2-propanol > acetone > ethanol > 1-propanol > methanol [16]. In contrast, when Montreuil and Shelef compared various oxygenated hydrocarbon reductants with propene over Cu-

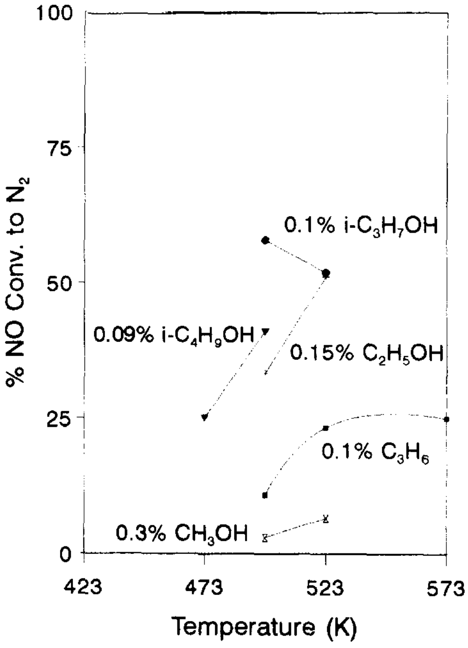

Fig. 6. NO conversion over 1.4 wt.-% La–6.3 wt.-% Cu–ZrO_2 using different reductants. 1000 ppm NO, 1000 ppm CO, 2% H_2O, 4% O_2. 2 g, 100 ml/min.

Table 6
Effects of space velocity on lean NO_x reduction with 2-propanol over 33 wt.-% $Cu–ZrO_2^a$

T (K)	SV (h^{-1}) (W/F^b)	% O_2	% $NO_{Conv.}$	% HC to C_3H_6O	% HC to CO_2	% NO compet.[c]
528	800 000 (0.00017)	2	7.3	43.1	23.5	3.0
523	13 000 (0.010)	4	5.7	0	100	5.6

[a] 1000 ppm NO, 1000 ppm 2-propanol, 100 ml/min.
[b] g-min/ml.
[c] $NO_{compet.} = (NO_{rxted} \times 100\%)/(n \times HC_{rxted})$.

ZSM-5 at 755 K, the highest NO conversion to N_2 was obtained with propene [33]. However, these results could be due to the fact that this temperature corresponded to the T_{max} for propene. If the T_{max} for the various oxygenated hydrocarbons are lower, as was observed over $Cu–ZrO_2$ and Ag/Al_2O_3, then the oxygenated compounds could be more active than propene in a lower temperature range.

The data shown in Fig. 6 were obtained with a space velocity of 6000 h^{-1} where sustained activity was obtained for at least 8 h. However, it was found that at 523 K and a higher space velocity of 250 000 h^{-1}, both the NO and ethanol conversions decreased with time on stream. Under the same conditions, the conversions associated with propene showed no deactivation. The rate of deactivation for the ethanol-containing feed decreased with time on stream. The deactivation was due to a build up of carbonaceous deposits, and the catalytic activity could be restored by heating in O_2 at 623 K. Similar experiments were conducted with the other alcohols, and all deactivated in a similar fashion at high space velocities.

Intermediate oxidation products of the reductant could be detected in experiments with high space velocities. This is shown in Table 6 for the reduction with 2-propanol over a 33 wt.-% $Cu–ZrO_2$ catalyst. Acetone and CO_2 were detected at the high space velocity, but only CO_2 was observed at the low space velocity. The competitiveness factor was higher for the low space velocity experiment even though the O_2 concentration was higher in this case. Comparable results were observed when EtOH was the reductant. In this case, the oxidized intermediate was acetaldehyde. These results suggest that a partially oxidized species is more effective than the parent alcohol for lean NO_x reduction.

3.4. Active site and mechanism

As $Cu–ZrO_2$ exhibited significantly higher lean NO_x activity than ZrO_2, it appears that Cu plays a significant role in the reaction. From the reaction studies which compared the lean NO_x reduction behavior of $Cu–ZrO_2$ of various Cu contents and the corresponding EPR, XPS and TPR results, it appears that dispersed $Cu–ZrO_2$ catalysts have a higher competitiveness factor than less dispersed catalysts. This can be explained if one assumes that the lattice O atom in the surface of CuO plays a significant role in hydrocarbon oxidation. If this is the case, then catalysts in which the Cu ions exist as CuO crystallites would be more active in the combustion of hydrocarbons than catalysts in which the Cu ions are well dispersed, and consequently have lower competitiveness factors. It should be emphasized that the observation does not necessarily imply that isolated Cu ions are the active sites. It is possible (and plausible) that dimers or very small clusters of Cu ions are the active sites, the concentration of which increases with decreasing Cu loading in the catalysts studied.

The effect of Cu ion dispersion on the lean NO_x reduction mechanism has also been studied over Cu/Al_2O_3 and Cu/ZSM-5. Torikai et al. [18] have found that the highest NO conversion over Cu/Al_2O_3 occurred when the Cu content was only 0.3 wt.-%. The decrease in conversion for the higher loading samples was probably due to the formation of CuO particles. Serverino et al. [34] have detected the presence of CuO particles by

XRD in a 5 wt.-% Cu/Al_2O_3 catalyst which had undergone redox cycles. In addition to these results, Sato et al. [2] have found that the conversion of NO in reduction by ethene over Cu-ZSM-5 at 523 K decreased when the exchange level of Cu was increased above 100%.

It is interesting to note that Kharas [35] reported that the overall effectiveness of Cu-ZSM-5 to remove NO by reduction over the temperature range of 373 K to 873 K was the greatest when the exchange level of Cu was 207%. Although the definition of overall effectiveness includes a combination of activity and competitiveness factor at different temperatures, and it is not obvious how to relate these results to those of other investigators, this observation suggests that the most interesting catalysts for practical applications may not have the highest competitiveness factor.

Chajar et al. [36] studied three Cu-ZSM-5 samples of different Cu loadings that were prepared by different methods. The dispersion of Cu of these catalysts was determined by CO adsorption on vacuum-reduced samples. It was found that the lowest loading sample had the highest dispersion as well as the highest rate of N_2 produced per Cu atom. Although the assumption that CO adsorption is an accurate measure of dispersion needs to be validated, the observation shows that samples in which the Cu ions can be more easily reduced to Cu^{+1} (which adsorbs CO) are more active for NO_x reduction.

Grünert et al. [37] also studied Cu-ZSM-5 catalysts prepared by several methods. Through the use of XPS and EXAFS, they were able to correlate increased Cu dispersion with increased reactivity. They suggested a scheme in which isolated Cu ions are needed for hydrocarbon activation and small CuO clusters are needed for high lean NO_x activity.

Thus far, the discussion centers on the model that CuO particles or large clusters of $(Cu–O)_x$ are ineffective for NO_x reduction because of their high activity for hydrocarbon combustion. The role of Cu ions in the reduction reaction needs to be explored. A number of possibilities have been proposed. Among them are activation of hydrocarbon, oxidation of NO to NO_2, and formation of N-containing reaction intermediates that results in N_2 production.

There have been suggestions in the literature that the formation of NO_2 from NO and O_2 is necessary for lean NO_x reduction [8,19,31,38–40]. In order to establish the role of NO_2, the reduction of NO and NO_2 was studied over 7.4 wt.-% Cu–ZrO_2 using propene and propane as reductants and over 3.2 wt.-% Cu-ZSM-5 using propane as the reductant [41]. In agreement with the literature results for Cu-ZSM-5 with various reductants [8,40,42,43], the amount of NO_x converted to N_2 over either catalyst under lean conditions was nearly the same for a feed containing a mixture of NO and NO_2 as for a feed containing solely NO. These results, along with the observations that the rate of N_2 production over Cu–ZrO_2 in the presence of propene was faster than the rate of NO oxidation in the absence of the hydrocarbon, and that the rates of N_2 formation decreased with an increase in O_2 concentration led to the conclusion that formation of gaseous NO_2 does not precede N_2 formation. This conclusion is in agreement with that of Chajar et al. [42] for Cu-ZSM-5.

However, the observations do not exclude the possible importance of the formation of adsorbed NO_2. In fact, it was observed in these experiments that the NO_2 in the feed was rapidly reduced to NO. Thus, it was proposed that in the lean NO_x reduction reaction, the reaction of NO with O_2 (adsorbed O) to form adsorbed NO_2 is an important step for the activation of saturated hydrocarbons, which is oxidized to a surface intermediate, and the adsorbed NO_2 is reduced to NO [41]. It is likely that the Cu ions are the active sites for these reactions.

Under steady state reaction conditions, adsorbed CN and NCO species were detected on Cu–ZrO_2 [44]. Pulse reaction of NO or NO_2 over the catalysts containing these species resulted in the formation of N_2, the amount of which was much more than the amount of NO or NO_2 consumed. Thus, N_2 was formed by the reaction of the surface CN and/or NCO species with NO or

NO_2. Similar to the flow experiments, the NO_2 in the pulse was converted to NO over the catalyst.

3.5. *Comparison of Cu–ZrO_2 and Cu–Ga_2O_3*

Cu–Ga_2O_3 has also been found to be an effective lean NO_x reduction catalyst. Compared with 2.1 wt.-% Cu–ZrO_2, a 1.9 wt.-% Cu–Ga_2O_3 catalyst had a higher competitiveness factor and a higher NO conversion at any of the oxygen concentrations investigated. The competitiveness factors (%) for Cu–ZrO_2 at 601 K were 8, 5, and 2 at 1%, 3%, and 6% O_2, respectively, while those for Cu–Ga_2O_3 at 621 K were 10, 6, and 3 at 1%, 4%, and 7% O_2 in a feed of 0.1% NO and 0.1% C_3H_6. The EPR spectrum of 1.9 wt.-% Cu–Ga_2O_3 was almost identical to the spectrum of 2.1 wt.-% Cu–ZrO_2 (Fig. 3). This indicated that a similar level of Cu dispersion existed in both catalysts.

The different catalytic behavior of Cu–Ga_2O_3 and Cu–ZrO_2 is thought to result from the different contributions of the Ga_2O_3 matrix versus ZrO_2. To determine the extent of involvement of the matrix, a feed containing 0.1% C_3H_6, 0.1% NO and 1% O_2 was flowed over ZrO_2 and 2.1 wt.-% Cu–ZrO_2 at 598 K, and over Ga_2O_3 and 1.9 wt.-% Cu–Ga_2O_3 at 643 K. These temperatures are very close to the $T_{\max}$ of the two Cu containing catalysts. The NO conversions over 1 g of catalyst in a reactant flow of 100 ml/min were 21% over Ga_2O_3, 77% over Cu–Ga_2O_3, 66% over Cu–ZrO_2, and negligible over ZrO_2. Thus, a significant portion of the observed conversions over Cu–Ga_2O_3 could be attributed to lean NO_x reduction over Ga_2O_3, whereas none of the conversion over Cu–ZrO_2 was due to reaction on ZrO_2.

4. Other metal oxides

Few single component oxides have been reported to be effective lean NO_8 catalysts. Among the few that are effective, none is an oxide of a readily reducible transition metal. Presumably, reducible metal oxides are too active for combustion of the hydrocarbon.

Table 7
Comparison of ZrO_2, Al_2O_3, and Ga_2O_3[a,b]

Catalyst	% O_2	T (K)	% NO conv. to N_2	% $C_3H_{6\,\mathrm{Conv.}}$	% $NO^{c}_{\mathrm{Compet.}}$
ZrO_2	6	679	16	33	5.0
		709	20	48	4.4
		741	25	64	4.1
		781	27	84	3.4
Al_2O_3	6	673	9.0	14	7.4
		723	30	38	9.0
		773	68	97	7.9
		823	47	100	5.2
Ga_2O_3	7	709	91	92	11
Ga_2O_3	1	622	15	11	17
		648	21	17	14
		709	55	63	10
ZrO_2	1	637	8.0	2.9	31
		719	22	17	14

[a] 0.1% NO, 0.1% C_3H_6 and 1, 6 or 7% O_2. 1 g, 100 ml/min.
[b] Surface areas: ZrO_2, 168 m^2/g; Al_2O_3, 119 m^2/g; Ga_2O_3, 38 m^2/g.
[c] $NO_{\mathrm{Compet.}} = (NO_{\mathrm{rxted}} \times 100\%)/(9 \times C_3H_{6\mathrm{rxted}})$.

4.1. *ZrO_2, Ga_2O_3 and Al_2O_3:*

Table 7 compares the activities of ZrO_2, Ga_2O_3 and Al_2O_3. In the presence of 6–7% O_2, Ga_2O_3 was the most active and competitive catalyst and ZrO_2 was the least. This order was reversed when the O_2 concentration was decreased to 1%. Al_2O_3, Ga_2O_3 and ZrO_2 exhibited a different O_2 dependency than Cu-ZSM-5 and Cu–ZrO_2, over which NO conversions were decreased by more than 2% O_2. Increasing the O_2 concentration from 0–7% over Al_2O_3 [45] and Ga_2O_3 [26] resulted in an increase in the rate of both N_2 formation and hydrocarbon combustion. Increasing the O_2 concentration from 1–6% over ZrO_2 enhanced the rate of C_3H_6 combustion but had little effect on the rate of N_2 formation.

The different O_2 dependence observed for the single metal oxides compared with Cu-ZSM-5 and Cu–ZrO_2 may be explained by NO_2 formation. Fig. 7 compares the reduction of NO versus NO_2 over ZrO_2. Unlike Cu-ZSM-5 or Cu–ZrO_2, reduction of NO_2 to N_2 over ZrO_2 was faster than the reduction of NO to N_2 at temperatures lower than

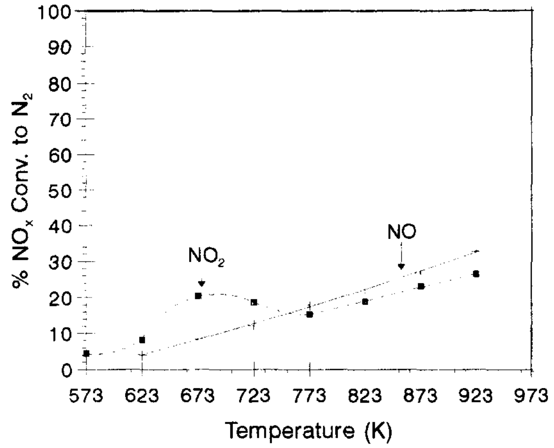

Fig. 7. Percentage NO_x conversion vs. temperature over ZrO_2 using a feed containing either 1000 ppm NO or 650 ppm NO_2 and 350 ppm NO. 1000 ppm C_3H_6, 2% O_2. 1 g, 100 ml/min.

about 773 K. This has also been observed for Ga_2O_3 [26] and Al_2O_3 [39]. At higher temperatures where NO_2 is no longer thermodynamically stable, the rate of reduction of either NO_2 or NO over ZrO_2 (Fig. 7) or Al_2O_3 [39] was the same. The higher N_2 production rate is a result of the fact that these oxides are not very active in the oxidation of NO to NO_2 [39,41]. Thus, the presence of NO_2 in the feed leads to a higher surface coverage of adsorbed NO_2, which is important for the activation of the hydrocarbon. Another possibility is that NO_2 efficiently removes carbonaceous deposits that block the active sites on these oxides. This latter possibility was observed in the reaction of ZrO_2 with EtOH. If the feed contained only NO, rapid deactivation due to carbonaceous deposits was observed at 523 K. However, if the feed contained NO_2, no deactivation was observed at this temperature for 6 h, the duration of the test.

4.2. La_2O_3 and Li/MgO

Li/MgO [46] and La_2O_3 [47] have been reported to be active catalysts for lean NO_x reduction with CH_4 above 773 K (joining the group of Ni-, Co-, Mn- [48], and Ga-zeolites [49,50] that have all been reported to be active for this reaction). The NO_x reduction activity of La_2O_3 was found to be comparable to Co-ZSM-5 when the activity was expressed on a surface area basis in the presence or absence of oxygen. Li/MgO, however, was much less active, especially in the presence of O_2 which suppressed its activity significantly. In addition to being more active, La_2O_3 was more selective, producing virtually 100% N_2 at all temperatures, whereas Li/MgO produced as much as 40% N_2O. This difference may result from the rapid rate of N_2O decomposition to N_2 and O_2 over La_2O_3, which was five times greater than the rate of NO reduction by CH_4.

Kinetic studies also revealed a difference between the two catalysts [46,47]. The activation energies for La_2O_3 were 24.4 kcal/mol in the absence of O_2 and 26.0 kcal/mol in the presence of 1% O_2. For 4% Li/MgO, they were noticeably higher, being 30.5 kcal/mol in the absence of O_2 and 35.0 kcal/mol in the presence of 1% O_2. The reaction orders for La_2O_3 were 0.26 in CH_4, 0.98 in NO, and 0.5 in O_2, and those for 4% Li/MgO were 0.70 in CH_4, 0.35 in NO, and -0.54 in O_2.

NO decomposition to N_2 and O_2 was believed to be an unimportant pathway over either catalyst. It was not found to occur over Li/MgO, and could account for no more than 20% of the N_2 produced in the presence of CH_4 over La_2O_3. As both La_2O_3 and Li/MgO are catalysts for oxidative coupling of methane, it has been suggested that their activity for lean NO_x reduction with CH_4 is due to their ability to form CH_3 radicals. This is supported by the fact that both the oxidative coupling ability of the catalysts and their lean NO_x reduction ability increase with temperature.

5. Conclusions

A number of metal oxides are effective lean NO_x reduction catalysts. Incorporation of reducible transition metal ions into the metal oxides, such that the transition metal ions are highly dispersed, greatly increased the activity of the catalysts such that lean NO_x reduction occurs readily at temperatures below 573 K. A comparison of the catalytic behavior of first row transition metal ions in ZSM-5 and in Al_2O_3 shows that the catalytic properties are dictated more by the chemical nature of the metal ions and less by the nature of the support. Thus, mixed metal oxide catalysts of ZrO_2 containing Cu, Co, Fe, and Ni, which are as active as the corresponding ZSM-5-based catalysts, can be prepared by coprecipitation which produces mixed metal oxides of a rather high concentration of well dispersed transition metal ions. Other active mixed metal oxides can be prepared by a similar method.

The reaction mechanism on Cu–ZrO_2 has been investigated. The results show some similarities with a Cu-ZSM-5 catalyst. Surface CN and NCO species have been detected under reaction conditions on Cu–ZrO_2, and there is evidence suggesting that these species react to form N_2. Similarly, Hayes et al. [51] observed an organic nitrile species on Cu-ZSM-5 which reacted to form N_2. In addition, the role of NO and NO_2 in the reaction is very similar in both systems.

Unlike zeolites which have metastable structures, mixed metal oxides can be potentially much more stable hydrothermally, which is one important criterion for commercial application. In addition, the larger pores of metal oxides than zeolites, and the flexibility to prepare mixed metal oxides with a wide range of compositions are potential advantages of metal oxides as practical catalysts. Hopefully, the results summarized in this article serve to illustrate the promises offered by metal oxides, and the current understanding of these systems in the lean NO_x reduction reaction.

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References

[1] T.J. Truex, R.A. Searles and D.C. Sun, Platinum Metals Rev., 36 (1992) 2.
[2] S. Sato, Y. Yu-u, H. Yahiro, N. Mizuno and M. Iwamoto, Appl. Catal., 70 (1991) L1.
[3] K. Yogo, S. Tanaka, M. Ihara, T. Hishiki and E. Kikuchi, Chem. Lett., (1992) 1025.
[4] K. Bethke, D. Alt and M.C. Kung, Catal. Lett., 25 (1994) 37.
[5] Y. Kintaichi, H. Hamada, M. Tabata, M. Sasaki and T. Ito, Catal. Lett., 6 (1990) 239.
[6] H. Hamada, Y. Kintaichi, M. Sasaki, T. Ito and M. Tabata, Appl. Catal., 64 (1990) L1.
[7] H. Hamada, Catal. Today, 22 (1994) 21.
[8] J.O. Petunchi and W.K. Hall, Appl. Catal. B: Environmental, 2 (1993) L17.
[9] R. Gopalakrishnan, P.R. Stafford, J.E. Davidson, W.C. Hecker and C.H. Bartholomew, Appl. Catal. B: Environmental, 2 (1993) 165.
[10] S. Sato, H. Hirabayashi, H. Yahiro, N. Mizuno and M. Iwamoto, in Catal. Lett., 12 (1992) 193; M. Iwamoto, N. Mizuno and H. Yahiro, in L. Guczi, F. Solymosi and P. Tétényi (Editors), Proc. 10th Int. Congress on Catal., Akadémiai Kiadó, Budapest, Part B, 1993, p. 1285.
[11] M. Iwamoto and H. Hamada, Catal. Today, 10 (1991) 57.
[12] H. Hirabayashi, H. Yahiro, N. Mizuno and M. Iwamoto, Chem. Lett., (1992) 2235.
[13] T. Miyadera and K. Yoshida, Chem. Lett., (1993) 1483.
[14] H. Hosose, H. Yahiro, N. Mizuno and M. Iwamoto, Chem. Lett., (1991) 1859.
[15] H.W. Jen, R.W. McCabe, R.J. Gorte and D.J. Parrillo, Symposium on NO_x Reduction, 207th National Meeting, ACS, San Diego, CA., 13–18 March, 1994.
[16] T. Miyadera, Appl. Catal. B: Environmental, 2 (1993) 199.
[17] M. Misono and K. Kondo, Chem. Lett., (1991) 1001.
[18] Y. Torikai, H. Yahiro, N. Mizuno and M. Iwamoto, Chem. Lett., 9 (1991) 91.
[19] H. Hamada, Y. Kintaichi, M. Sasaki, T. Ito and M. Tabata, Appl. Catal., 75 (1991) L1.
[20] Y. Amenomiya, I.T. Ali Emesh, K.W. Oliver and G. Pleizier, in M.J. Phillips and M. Ternan (Editors), Proc. 9th Int. Congress on Catal., Calgary, 1988, Chem. Inst. of Canada, Ottawa, 1988, p. 634.
[21] B. Yang, M.C. Kung and H.H. Kung, unpublished results 1993.
[22] G.P. Ansell, A.F. Diwell, S.E. Golunshi, J.W. Hayes, R.R. Rajaram, T.J. Truex and A.P. Walker, 205th ACS National Meeting, Denver, CO, 29 March–1 April 1993.
[23] C. Montreuil, H.S. Gandhi and M.S. Chattha, U.S. Patent 5 155 077 (1992).
[24] A.V. Kucherov, A.A. Slinkin, D.A. Kondrat'ev, T.N. Bondarenko, A.M. Rubinshtein and Kh. M. Minachev, Kinet. Katal., 26 (1985) 409.
[25] G.K. Boreskov, Kinet. Katal., 8 (1967) 1020.
[26] M. Kung, K. Bethke, D. Alt, B. Yang and H. Kung, in U. Ozkan, S. Agrawal and G. Marcelin (Eds.), ACS Symposium Series No. 587, American Chemical Society, Washington, DC, 1995, p. 96.
[27] H.W. Jen and H.S. Gandhi, in J.N. Armor (Editor), Environmental Catalysis, ACS Symp. Series 552, 1994, p. 53.

[28] C.J. Bennett, P.S. Bennett, S.E. Golunski, J.W. Hayes and A.P. Walker, Appl. Catal. A: General, 86 (1992) L1.

[29] R. Burch and S. Scire, Appl. Catal. B: Environmental, 3 (1994) 295.

[30] H. Hamada, Y. Kintaichi, T. Yoshinari, M. Tabata, M. Sasaki and T. Ito, Catal. Today, 17 (1993) 111.

[31] J.O. Petunchi, G. Sill and W.K. Hall, Appl. Catal. B: Environmental, 2 (1993) 303.

[32] H.W. Jen and K. Otto, Catal. Lett., 26 (1994) 217.

[33] C.N. Montreuil and M. Shelef, Appl. Catal. B: Environmental, 1 (1992) L1.

[34] F. Severino, J. Brito, O. Carías and J. Laine, J. Catal., 102 (1986) 172.

[35] K.C.C. Kharas, Appl. Catal. B: Environmental, 2 (1993) 207.

[36] Z. Chajar, M. Primet, H. Praliaud, M. Chevrier, C. Gauthier and F. Mathis, Appl. Catal. B: Environmental, 4 (1994) 199.

[37] W. Grünert, N.W. Hayes, R.W. Joyner, E.S. Shpiro, M.R.H. Siddiqui and G.N. Baeva, J. Phys. Chem., 98 (1994) 10832.

[38] J. Valyon and W.K. Hall, J. Phys. Chem., 97 (1993) 1204.

[39] M. Sasaki, H. Hamada, Y. Kintaichi and T. Ito, Catal. Lett., 15 (1992) 297.

[40] M. Shelef, C.N. Montreuil and H.W. Jen, Catal. Lett., 26 (1994) 277.

[41] K.A. Bethke, C. Li, M.C. Kung, B. Yang and H.H. Kung, Catal. Lett., 31 (1995) 287.

[42] Z. Chajar, M. Primet, H. Praliaud, M. Chevrier, C. Gauthier and F. Mathis, Catal. Lett., 28 (1994) 33.

[43] F. Witzel, G.A. Sill and W.K. Hall, J. Catal., 149 (1994) 229.

[44] C. Li, K.A. Bethke, H.H. Kung and M.C. Kung, J. Chem. Soc., Chem. Commun., (1995) 813.

[45] H. Hamada, Y. Kintaichi, M. Sasaki, T. Ito and M. Tabata, Appl. Catal., 70 (1991) L15.

[46] X. Zhang, A.B. Walters and M.A. Vannice, J. Catal., 146 (1994) 568.

[47] X. Zhang, A.B. Walters and M.A. Vannice, Appl. Catal. B: Environmental, 4 (1994) 237.

[48] Y. Li and J.N. Armor, Appl. Catal. B: Environmental, 2 (1993) 239.

[49] Y. Li and J.N. Armor, J. Catal., 145 (1994) 1.

[50] K. Yogo, M. Ihara, I. Terasaki and E. Kikuchi, Chem. Lett., (1993) 229.

[51] N.W. Hayes, W. Grünert, G.J. Hutchings, R.W. Joyner and E.S. Shpiro, J. Chem. Soc., Chem. Commun., (1994) 531.