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# Catalytic lean $NO_x$ reduction over mixed metal oxides, and its common features with selective oxidation of alkanes

H.H. Kung *, M.C. Kung

*Ipatieff Laboratory, Center for Catalysis and Surface Science, Northwestern University, Evanston, Illinois 60208, USA*

## Abstract

In catalytic reactions involving molecular oxygen, activation of oxygen by dissociative adsorption can be an important step. When the rate of this step is slow compared to other steps in the reaction, the activation of other oxygen sources and the formation of products that require smaller number of oxygen atoms become more competitive. This can be accomplished by highly dispersing the redox centers in the catalyst, which are commonly transition metal ions. This hypothesis can be used to explain the results of the catalytic lean $NO_x$ reduction by hydrocarbon over mixed metal oxides, as well as catalytic selective oxidation of butane and selective epoxidation of alkenes. However, when the activation of molecular oxygen is a crucial step in determining the overall activity of the catalyst, possibly as in the $NH_3$-SCR reaction over $V/TiO_2$, a balance between the ability of the catalyst to activate molecular oxygen and the selectivity to $N_2$ when NO is reduced will determine the form of a desirable catalyst.

*Keywords:* $NO_x$ reduction; NO reduction; Butane oxidation; Pentane oxidation; Selective oxidation; Mixed metal oxides

## 1. Introduction

Transition metal oxides are commonly found as an important component in heterogeneous catalysts where selective activation of hydrocarbon by oxygen is a critical step of the catalytic cycle. Partial oxidation of hydrocarbons to ketones, aldehydes, or other products is a typical example where controlling the reaction between the adsorbed hydrocarbon and the surface oxygen species is critical for high yields of the desired products. It has been suggested that in such reactions, one of the properties of the catalyst that affects the selective formation of partial oxidation product is the number of lattice oxygen atoms (or ions) available to react with an adsorbed hydrocarbon molecule: the fewer the number, the lower the tendency for combustion reactions [1,2]. This implies that catalysts in which the active redox centers are dispersed in an inert matrix and isolated from each other would be more selective for partial oxidation than such centers in clusters because, in the dispersed form, a fewer number of oxygen atoms (ions) are available for oxidation. This concept has been applied to explain different catalytic properties of supported vanadia catalysts for butane oxidation [3] and other catalytic systems [4].

In recent years, because of the interest to increase the fuel efficiency of gasoline-fueled, internal combustion engines but at the same

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* Corresponding author.

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time reduce the $NO_x$ emission, automobile companies have been studying the operation of lean-burn engines, which run with an air-to-fuel ratio higher than the stoichiometric ratio. Such engines provide up to 15% increase in fuel economy over the stoichiometric engines. However, their use is impossible at present because the exhaust does not meet the environmental standards. In particular, there are no efficient catalysts available to reduce the $NO_x$ concentration in the exhaust. A typical composition of the exhaust gas from such engines contains about 0.05% $NO_x$ (primarily NO), 5% $O_2$, 10% $H_2O$, and 0.05 to 0.1% hydrocarbon. Therefore, in principle, there is sufficient hydrocarbon reductants present to completely reduce $NO_x$ to $N_2$, provided that the hydrocarbon is not consumed first due to combustion by $O_2$, which is present in a concentration that is two orders of magnitude higher than $NO_x$. That is, a necessary property of a desirable catalyst for effective $NO_x$ reduction under lean condition is the selective promotion of the reaction between NO and hydrocarbon, and not the reaction between $O_2$ and hydrocarbon. More specifically, the catalyst needs to preferentially activate NO instead of $O_2$. Since dissociative adsorption of $O_2$ requires at least two adjacent metal ions in the redox center, whereas adsorption of NO needs only a single metal ion, it seems that the presence of highly dispersed transition metal ions may be a desirable feature for an effective $NO_x$ reduction catalyst. As mentioned earlier, this is also a desirable feature for a selective oxidation catalyst. The purpose of this paper is to examine this hypothesis using relevant experimental results.

## 2. Lean $NO_x$ reduction of metal oxides

As stated earlier, $O_2$ is present at a concentration up to 100 times higher than NO in the exhaust of a lean-burn, gasoline engine. A similar ratio is found in exhaust from power plants, but an even higher ratio is found in exhaust from diesel engines (Table 1). In order to lower the NO concentration from 500 ppm to 50 ppm in an exhaust containing 500 ppm hydrocarbon and 5% $O_2$, the catalyst must be able to selectively catalyze the reaction of hydrocarbon with up to 1000 molecules of NO for one molecule of $O_2$ (i.e. a high competitiveness factor, which is the ratio of the actual number of NO molecules converted to $N_2$ by hydrocarbon to the theoretical maximum number, assuming that the hydrocarbon is oxidized to $CO_2$ and $H_2O$). This has to be accomplished in the presence of high concentrations of water and $CO_2$, and small amounts of $SO_2$. Thus, it is very interesting that Cu-exchanged ZSM-5 is an effective lean $NO_x$ reduction catalyst [5–7]. Although the potential

Table 1
Properties of exhaust gases from various sources

| Source | | Temp., °C | $[NO_x]$, % | $[O_2]$, % | Other |
|---|---|---|---|---|---|
| Stationary | power plants | 200–450 | 0.04–0.1 | 4–10 | $SO_x$ (0.001–0.3%)<br>$H_2O$ (10–15%)<br>$CO_x$ (5–7%) |
| Mobile | diesel engine | 200–400 | 0.002–0.07 | 4–10 | $CO_x$<br>$H_2O$<br>hydrocarbons<br>particulate<br>$SO_x$ |
| | gasoline engine (lean burn) | 400–700 | 0.002–0.15 | 4–6 | $CO_x$<br>$H_2O$<br>hydrocarbons<br>$SO_x$ |

for commercial application of this catalyst is limited by its lack of long term hydrothermal stability, the understanding generated by the study of this catalyst has been useful for the development of other catalytic systems.

Since the initial report, many other studies have been conducted on Cu-ZSM-5. One very interesting observation reported is the linear relationship between the NO conversion to $N_2$ and the exchange level of $Cu^{2+}$ in ZSM-5 up to about 100% exchange [7]. Beyond that, there is no further increase in NO conversion activity. This is shown schematically in Fig. 1. Since most of the $Cu^{2+}$ is ion-exchanged as isolated ions [8], this observation suggests that isolated $Cu^{2+}$ ions are the desirable species for active sites. In contrast, the NO conversion in NO decomposition (without the use of hydrocarbon reductant) is low at $Cu^{2+}$ exchange levels below 100%, and increases rapidly when the exchange level reaches about 100% (Fig. 1) [9]. This is consistent with the fact that in NO decomposition, the formation of molecular $O_2$ product requires recombination of two oxygen atoms and a change in the formal oxidation state of four in the solid. This is better accomplished by a transition metal oxide cluster than an individual transition metal ion.

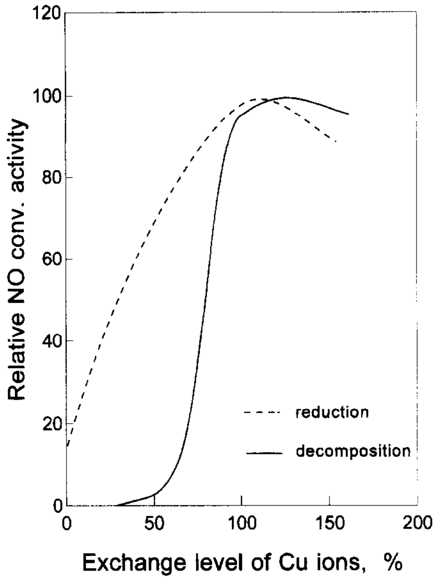

Fig. 1. Schematic dependence of NO conversion activity on the Cu-exchange level in Cu-ZSM-5 for NO decomposition and NO reduction with ethylene.

If dispersed $Cu^{2+}$ ions are desirable, one might expect that active catalysts could be obtained by dispersing $Cu^{2+}$ ions in other matrices

Table 2
Illustrative examples of NO reduction activities of oxides containing dispersed Cu ions

| Sample | Cu, wt.% | SV, $h^{-1}$ | Temp., K [a] | NO, conv. % | NO, compet. % | Feed composit., % | | |
|---|---|---|---|---|---|---|---|---|
| | | | | | | NO | $O_2$ | $C_3H_6$ |
| $Cu-ZrO_2$ | 2.1 | 13,000 | 601 | 68 | 8.6 | 0.1 | 2.5 | 0.1 |
| | 8.9 | 13,000 | 536 | 58 | 7.9 | 0.1 | 2.5 | 0.1 |
| | 15 | 14,000 | 511 | 52 | 6.8 | 0.1 | 2.5 | 0.1 |
| | 33 | 13,000 | 504 | 43 | 5.5 | 0.1 | 2.5 | 0.1 |
| $Cu-SiO_2$ | 1 | 15,000 | 573 | 58 | 8 [b] | 0.1 | 1 | 0.1 [c] |
| $Cu-Ga_2O_3$ | 1.9 | 6,000 | 632 | 77 | 9 | 0.1 | 1 | 0.1 |
| | 13.6 | 6,000 | 552 | 79 | 10 | 0.1 | 1 | 0.1 |
| $Cu-Al_2O_3$ [d] | 2 | 6,400 | 623 | 36 | – | 0.05 | 10 | 0.05 |
| Cu-ZSM5 | 3.2 | 10,400 | 642 | 72 | 8.3 | 0.1 | 2.5 | 0.1 |
| $Cu-Ga-Al_2O_3$ | 0.02 [e] | 24,000 | 713 | 84 | 11 | 0.1 | 4 | 0.1 |
| | | 24,000 | 773 | 68 | 8.6 | 0.1 | 4 [f] | 0.1 |

[a] Temperature of maximum NO conversion.
[b] Based on $C_3H_6$ only, neglecting the presence of CO in the feed.
[c] Also contained 0.1% CO.
[d] Data from Ref. [30].
[e] Contained 2 wt.% Ga.
[f] Also contained 2% $H_2O$.

that are inactive for hydrocarbon combustion. Indeed, this has been accomplished with Cu–$ZrO_2$ [10], Cu–$SiO_2$ [11], and Cu–$Ga_2O_3$ [11,12]. As shown by the examples in Table 2, when the Cu–metal oxides are prepared by controlled hydrolysis such that the copper oxide is present in a dispersed state in the matrix oxide, the resulting solid is a good catalyst to reduce NO in the presence of a large excess of oxygen. In some cases, the conversion of NO is comparable to that observed with Cu-ZSM-5. Furthermore, they show comparable competitiveness factors as Cu-ZSM-5 (Table 2). A catalyst of good NO conversion activity can also be prepared by depositing these oxides onto $Al_2O_3$, as illustrated by the Cu–Ga/$Al_2O_3$ sample. For comparison, Cu/$ZrO_2$ [13], Cu/$SiO_2$ [14] or Cu/$Al_2O_3$ [15] prepared by impregnation of copper salt onto the support and calcination are ineffective for lean $NO_x$ reduction. Presumably, these samples contain CuO crystallites which are too active for hydrocarbon combustion.

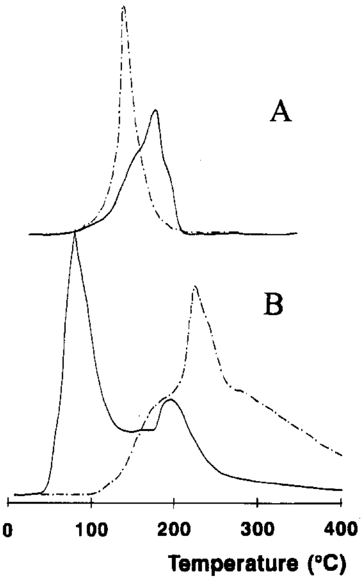

Fig. 2. Temperature programmed reduction profiles for 7.4 wt.% Cu–$ZrO_2$ (------) and 33 wt.% Cu–$ZrO_2$ (————) by (A) 5% $H_2$ in Ar, and (B) 10% CO in He. Heating rate = 2.5 K/min.

The effect of loading of Cu in Cu–$ZrO_2$ has been examined in detail [10]. Some selected examples are shown in Table 2. As expected, when the Cu content in Cu–$ZrO_2$ increases, the activity of the catalyst increases, as indicated by the lower temperature required for reaction. There is no decline in the competitiveness factor up to about 10 wt.% Cu. Beyond 10 wt.%, the hydrocarbon oxidation activity continues to increase, but the ability of the catalyst to convert NO declines (declining competitiveness factor). This is interpreted according to the hypothesis stated earlier that at these high loadings, there is significant clustering of Cu species, which activate oxygen efficiently and cause significant combustion of hydrocarbon.

The redox behavior of the Cu species in these mixed oxides depends on their dispersion, as illustrated by the temperature programmed reduction (TPR) profiles of these samples for reduction by $H_2$ and by CO (Fig. 2). The profiles for $H_2$-TPR show one reduction peak for the 7.4 wt.% Cu sample, and three peaks for the 32 wt.% Cu sample, where one of the three peaks is at the same position as the single peak for the former sample. Thus, there might be one common Cu species in both samples. The CO-TPR profiles are more complicated. They show multiple peaks. Again, there appears to be one reduction peak common to both samples. These TPR results show that, depending on the Cu content, the Cu–$ZrO_2$ sample contains different Cu species of different redox properties. The difference between the TPR profiles for CO and $H_2$ is due to the different rate-limiting steps in the reduction process.

The idea that highly dispersed redox centers are preferred for effective lean $NO_x$ reduction applies to other transition metal ions in addition to Cu. It has been shown that samples containing highly dispersed Fe, Co, or Ni ions in $ZrO_2$ are also active [10]. These results suggest the possibility that other oxide catalysts might be also effective for lean $NO_x$ reduction. The use of oxides as a matrix instead of zeolites has a number of potential advantages. In general, it is much easier to change the chemical composition and properties of an oxide than a zeolite. Most oxides have larger pores than zeolite. Thus,

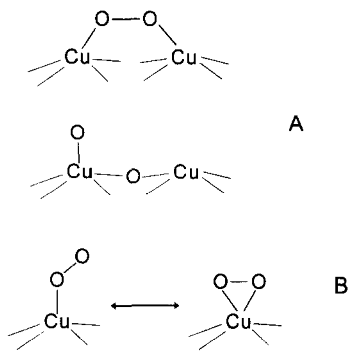

Fig. 3. Schematic drawing showing different modes of adsorption of $O_2$ on dispersed Cu species (B) and on Cu ion clusters (A).

there should be less diffusional limitation on the reaction rates. Oxides can be hydrothermally more stable than zeolite. There are commercially available oxides that are stable to over 1000°C, such as stabilized alumina. Therefore, to pursue the development of oxide materials for lean $NO_x$ conversion should be most likely a fruitful direction.

The fact that highly dispersed Cu species can effect NO reduction to $N_2$ under lean conditions, while large clusters do not, implies that the dispersed species can activate NO much more readily than $O_2$. This could be accomplished if one or more of the following apply:

(a) NO is adsorbed more strongly than $O_2$, and this difference is much more pronounced on highly dispersed Cu species than on large clusters. A possible mechanism that could lead to this result is depicted in Fig. 3. $O_2$ is adsorbed molecularly on dispersed Cu species, because dissociative adsorption would require a formal oxidation state change of four, which is difficult to accomplish with a single metal ion. Such molecular adsorption would be weak. Dissociative adsorption of oxygen is much more feasible on clusters of Cu species because a smaller change in the formal oxidation state is needed for each ion. It follows that the rate of combustion of adsorbed hydrocarbon on a highly dispersed Cu species is slower. Highly dispersed Cu ions in an inert, irreducible matrix would be less reducible and, correspondingly, there will be less labile lattice oxygen that oxidize and consume the hydrocarbon reductant.

(b) The reaction intermediates for hydrocarbon oxidation are different on dispersed versus clustered Cu species. Those on dispersed Cu species react with NO more readily than those on clusters of Cu species to form N-containing surface intermediates, which subsequently react with another NO molecule to form $N_2$.

(c) The different ability of Cu species of different extent of clustering results in Cu ions of different redox behavior, and thus different distributions of oxidation states of Cu at steady state. Since the strength of adsorption of NO depends on the oxidation state of Cu, the ability of the Cu species to activate NO will depend on the extent of clustering.

Which of these possibilities is more likely than the others is not known at present, because there is insufficient information about the reaction mechanism or the rate limiting step.

## 3. Selective oxidation of hydrocarbons by oxygen

The idea presented above, that highly dispersed redox centers supply a smaller number of oxygen atoms for oxidation of adsorbed reaction intermediates and cannot activate molecular oxygen as easily as larger clusters, should be relevant to hydrocarbon oxidation reactions. For these reactions, reaction stoichiometry dictates that the extent of oxidation of a hydrocarbon molecule is directly related to the number of oxygen atoms consumed. This is illustrated with a few reactions selected from the oxidation of butane:

$$C_4H_{10} + O_2 \rightarrow C_4H_6 + 2H_2O \qquad (1)$$

$$C_4H_{10} + 7/2O_2 \rightarrow C_4H_2O_3 + 4H_2O \qquad (2)$$

$$C_4H_{10} + 13/2O_2 \rightarrow 4CO_2 + 5H_2O \qquad (3)$$

The formation of dehydrogenation product butadiene consumes one $O_2$ molecule (Eq. 1), while the formation of partial oxidation product maleic anhydride consumes 7/2 $O_2$ molecules (Eq. 2), and the combustion reaction consumes 13/2 $O_2$ molecules (Eq. 3). Therefore, it should be possible that, by limiting the number of oxygen atoms available to an active site during the residence of a hydrocarbon molecule on the surface, less combustion and more partial oxidation products can be obtained.

There are different methods to dispersed the redox centers, such as by the formation of a compound in which the redox centers are not connected to each other [16], by dispersing them in a high surface area gel (as illustrated by examples in the last section), or by supporting them on an inert support. In the latter case, the redox centers would be dispersed at low loadings.

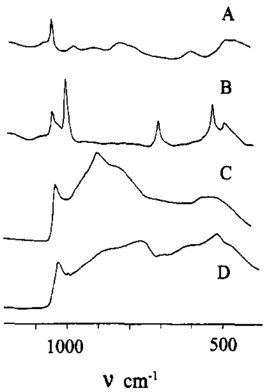

Fig. 4. Raman spectra of (A) 1 and (B) 10 wt.% $V_2O_5/SiO_2$, and (C) 8.2 and (D) 23.4 wt.% $V_2O_5/Al_2O_3$ collected using dehydrated samples.

The product distributions in the oxidation of butane have been measured over $SiO_2$- and $Al_2O_3$-supported vanadia samples of different vanadia loadings [3,17]. Table 3 shows some illustrative results. It has been determined by Raman spectroscopy that the vanadia species on the two $SiO_2$-supported samples are different (Fig. 4). The species in the 1 wt.% $V_2O_5/SiO_2$ sample show only a band at about 1040 cm$^{-1}$, which has been assigned to the V=O vibration of a $(SiO)_3V{=}O$ species [18,19]. This assignment is supported by the $^{51}V$ NMR spectrum which shows that the spectrum from such a sample is very similar to those from compounds of the type $(RSiO)_3V{=}O$ [20]. Thus, the vanadia species in this sample exist as isolated $VO_4$ units. On the other hand, the 10 wt.% $V_2O_5/SiO_2$ sample shows at least two types of vanadia species: the dispersed $(SiO)_3V{=}O$ units and $V_2O_5$ crystallites, the latter being characterized by Raman peaks at 997, 703, and 526 cm$^{-1}$. When these two sample are used to catalyze butane oxidation, a much higher selectivity for butenes is observed with the 1 wt.% sample. The same trend is observed for pentane oxidation. Thus, the isolated $(SiO)_3V{=}O$ units are much more selective for oxidative dehydrogenation than $V_2O_5$ crystallites, consistent with the hypothesis that these units have fewer numbers of oxygen atoms available for oxidation of adsorbed hydrocarbon. It is interesting to note that a substantial selectivity to maleic anhydride

Table 3

Comparison of $V/SiO_2$ and $V/Al_2O_3$ in oxidation of butane and pentane. Reaction conditions: $V/SiO_2$: 425°C for $C_4$ and $C_5$, $V/\gamma\text{-}Al_2O_3$: 400°C for $C_4$, 300°C for $C_5$. Hydrocarbon/$O_2$/He = 4/8/88

| Support | $V_2O_5$, wt.% | Alkane | Conv., % | Selectivity, % | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | | | CO | $CO_2$ | alkenes | diene | MA [a] | PA [a] |
| $SiO_2$ | 1 | $C_4$ | 7 | 17 | 17 | 40 | 4 | 0 | – |
| | | $C_5$ | 12 | 20 | 23 | 52 | 0 | 0 | 0 |
| | 10 | $C_4$ | 11 | 64 | 35 | 0 | 0 | 0 | – |
| | | $C_5$ | 11 | 39 | 31 | 3 | 0 | 26 | 0 |
| $Al_2O_3$ | 8.2 | $C_4$ | 7 | 20 | 37 | 38 | 5 | 0 | – |
| | | $C_5$ | 9 | 32 | 46 | 0 | 0 | 27 | 2 |
| | 23.4 | $C_4$ | 8 | 39 | 34 | 12 | 0 | 13 | – |
| | | $C_5$ | 19 | 29 | 28 | 0 | 6 | 41 | 0 |

[a] MA = maleic anhydride, PA = phthalic anhydride.

is observed in the oxidation of pentane over the 10 wt.% $V_2O_5/SiO_2$ sample but none from butane. The number of oxygen atoms required for the formation of maleic anhydride from pentane is 10, and for combustion is 16 (Eqs. 4 and 5):

$$C_5H_{12} + 5O_2 \rightarrow C_4H_2O_3 + CO_2 + 5H_2O \quad (4)$$

$$C_5H_{12} + 8O_2 \rightarrow 5CO_2 + 6H_2O \quad (5)$$

Apparently, some $V_2O_5$ crystallites are capable of supplying more than 7/2 $O_2$ (Eq. 2), but not as many as 8 $O_2$ (Eq. 5) to the adsorbed hydrocarbon, resulting in the production of maleic anhydride from pentane.

The trend of higher selectivity for partial oxidation products with lower loading of vanadia is observed on $\gamma$-$Al_2O_3$-supported catalysts also. As shown in Table 3, the 8.2 wt.% $V_2O_5/Al_2O_3$ is more selective for butene formation from butane than the 23.4 wt.% sample. However, the situation for pentane oxidation is less clear cut. A substantially higher selectivity for maleic anhydride is observed for the 23.4 wt.% sample than the 8.2 wt.% sample, while less phthalic anhydride is detected from the latter sample.

The Raman spectra of the two $VO_x/Al_2O_3$ samples show that the vanadia species are different from those on $SiO_2$. In addition to the isolated $VO_4$ units characterized by the Raman peak at about 1030 $cm^{-1}$, most of the vanadia species exist as $VO_x$ oligomers or chains characterized by overlapping peaks in the 750–1000 $cm^{-1}$ region. This overlapping peaks differ for the two $Al_2O_3$ samples, suggesting that the size and distribution of the oligomers are different.

Finally, it is interesting to note that the catalytic properties of the isolated vanadyl units depend on the support. This has been shown for the oxidation of methanol (Table 4) [21]. Depending on the support, the catalytic activity, measured as the turnover rate per vanadium ion, differed by three orders of magnitude. At present, the reason for this large difference is not understood.

## 4. Epoxidation of olefins

Dispersed transition metal ions in silica gel have been shown also to be more selective for epoxidation of olefins. One example is the Ti–$SiO_2$ gel [23]. Highly dispersed $Ti^{4+}$ ions in the matrix of $SiO_2$ gel can be prepared by controlled hydrolysis of a mixture of Ti and Si alkoxides. Low temperature dehydration of the gel results in a solid in which the Ti ions are well dispersed, as evidenced by the high intensity of the Ti–O–Si vibration at 950 $cm^{-1}$. Calcining this gel to high temperature causes segregation of Ti from the gel to form $TiO_2$, which can be detected by XRD, and the concomitant decrease in the intensity of the Ti–O–

Table 4
Methanol oxidation over 1 wt.% $V_2O_5$/support. Reaction conditions: 230°C, $CH_3OH/O_2/He = 6/11/83$; < 10% conversion

| Support [a] | $\nu_{V=O}$, $cm^{-1}$ | Cat. act. TOR, $s^{-1}$ | $T_{max}$ in TPR of support, K | Surf. area of support, $m^2$ | Sel. HCHO [b], % |
|---|---|---|---|---|---|
| $SiO_2$ | 1038 | 0.002 | 790 | 300 | 79 |
| $Al_2O_3$ | 1026 | 0.026 | 743 | 180 | tr [c] |
| $Nb_2O_5$ | 1031 | 0.7 | – | 60 | – |
| $TiO_2$ | 1030 | 1.8 | 715 | 55 | 98 |
| $ZrO_2$ | 1026 | 2.3 | 723 | 39 | – |
| Bulk $V_2O_5$ | 996 | 0.02 | 790 | – | 89 |

Data from Ref. [21,22].

[a] All commercial supports.

[b] Other products are mostly CO and $CO_2$, minor dimethylether.

[c] > 95% of product is dimethyl ether. The TOR is calculated for oxidation to methylal and HCHO.

Si vibrational band in the IR [24]. When these Ti–$SiO_2$ gels, calcined to different temperatures, are used for the epoxidation of cyclohexene with cumene hydroperoxide, the samples with the higher concentration of dispersed Ti is more selective for epoxide formation, and they are all more selective than $TiO_2$ (see Table 5). A possible explanation for this phenomenon is that isolated Ti ions can form Ti peroxy species readily, whereas Ti ion pairs present on $TiO_2$ surfaces have a higher tendency to adsorb the peroxide dissociatively to form Ti–OH.

The much better selectivity for epoxidation is observed not only for Ti–$SiO_2$ gel, but also for samples of low loadings of $TiO_2$ on $SiO_2$. When the $TiO_2$ loading is low, it is likely that the $TiO_x$ species exist as isolated units, similar to the case of supported vanadia. Thus, such samples behave like Ti–O–Si gel, as is shown by the example in Table 5. Also shown in the table are data for the epoxidation of 1-octene, which show that similarly, $TiO_x/SiO_2$ is much more selective than $TiO_2$ [25].

## 5. $NH_3$-SCR reaction

Dispersed redox centers are not necessarily preferred for all reactions involving molecular oxygen. Selective catalytic reduction of NO with $NH_3$ on $VO_x/TiO_2$ is one in which isolated $VO_x$ units on a $TiO_2$ support are less active than clusters of $VO_x$ units. It has been found that the turnover rate, on the basis of per vanadium ion, increases with vanadia loading [26–28]. Raman spectroscopic characterization of the catalysts shows the presence of isolated $VO_x$ units with a V=O vibration at about 1030 $cm^{-1}$, and polymeric $VO_x$ species that show Raman bands at 920–955 $cm^{-1}$ due to dioxo V=O stretch, at 960 $cm^{-1}$ due to V=O stretch in the polymeric chain, and 830–850 $cm^{-1}$ due to V–O–V vibration [29]. The activity for NO conversion is greatly enhanced with the appearance of the polymeric species [26]. It is estimated that the polymeric species are ten times more active than the monomeric species [27]. Interestingly, however, the selectivity for the production of $N_2O$ increases significantly at the expense of $N_2$ for catalysts of high vanadia loadings, and is more prominent at high oxygen concentration [27]. This loss in $N_2$ selectivity correlates with the increase in polymeric $VO_x$ species, consistent with the fact that on $V_2O_5$, $N_2O$ is the primary product observed.

The difference between the requirement for a desirable active site for $NH_3$-SCR and hydrocarbon SCR is not yet understood. It could be

Table 5
Epoxidation of alkenes over Ti–Si–oxides

| Sample | $TiO_2$, wt.% | $D_{SiOTi}$ [a] | Pore vol. [b], cc/g | Reaction time, h | Cyclohexene epoxidation [d] | | |
|---|---|---|---|---|---|---|---|
| | | | | | $X_{HC}$% | $S_{OOH}$% | $S_{HC}$% |
| aerogel | 5 | 9.5 | 0.99(8) | 4 | 89 | 92 | 100 |
| aerogel | 10 | 6 | 1.7(10) | 1.5 | 84 | 92 | 100 |
| aerogel | 10 | 1.7 | 3.6(24) | 2 | 13 | 83 | 96 |
| TS-1 zeolite | 3 | 17 | 0.5(5) | 17 | 6 | 85 | 90 |
| $Ti/SiO_2$ | 1 | – | – | 1.5 | 80 | 89 | 100 |
| $TiO_2$ amorph | – | – | – | 20 | 37 | 63 | 69 |
| xerogel | 10 | 7.1 | 0.03(0.3) | 18 | 10 | 2 | 88 |
| $Ti/SiO_2$ | – | – | – | – | 86 [c] | – | 90 [c] |
| $TiO_2$ Degussa | – | – | – | – | 40 [c] | – | 0 [c] |

Data from Ref. [23,24]. Cyclohexene epoxidation with cumene hydroperoxide at 333 K.

[a] Dispersion of Ti; equals (IR peak area of Si–O–Ti/IR peak of Si–O–Si) × ($X_{Si}/X_{Ti}$).

[b] Values in bracket are 4(pore volume)/$S_{BET}$, in nm.

[c] For 1-octene epoxidation by TBHP, Ref. [25].

[d] $X_{HC}$ is conversion of hydrocarbon, $S_{OOH}$ is selectivity based on hydroperoxide, and $S_{HC}$ is selectivity based on hydrocarbon.

related to the large difference in the adsorption strength of the reductants. $NH_3$ is adsorbed on vanadia species rapidly and rather strongly, both at the Brønsted and Lewis acid sites. Thus, reduction of the vanadia species by $NH_3$ can be rapid, leading to facile reduction of NO. Then the rate of the overall reaction could be enhanced if reoxidation of the reduced vanadium ion is facilitated when the $VO_x$ units form oligomers. The increased formation of $N_2O$, when polymeric $VO_x$ clusters are present, is consistent with the fact that these polymeric species are (kinetically) stronger oxidizing agents. On the other hand, for hydrocarbon SCR, the adsorption of hydrocarbon on the active sites is generally weaker. Thus, competition between the activation of NO and $O_2$ become much more important.

## 6. Conclusion

From examples in the literature, a postulate is formulated that the rate of activation of oxygen relative to the rates of other catalytic steps can be strongly influenced by the dispersion of the redox centers, which in turn has a significant impact on the selectivity among the reaction pathways. In the reaction of lean $NO_x$ reduction by hydrocarbons, highly dispersed transition metal redox centers are much less active for combustion of hydrocarbon by molecular oxygen, presumably due to the lower rates of dissociative adsorption of oxygen on these isolated redox centers than on clusters of them. As a consequence, such catalysts become effective for lean $NO_x$ reduction. Likewise, the selectivity for partial oxidation products in the reaction of hydrocarbon with oxygen is higher on catalysts containing dispersed than clusters of metal ions. This is because the lower rate of activation of molecular oxygen by dispersed metal ions lowers the number of oxygen atoms available to react with the adsorbed hydrocarbon species, thereby decreasing the tendency for complete oxidation which requires a large number of oxygen atoms.

Since highly dispersed redox centers need to be supported by a matrix, the nature of the matrix can have a strong effect on the catalytic properties of the system. In addition to the possibility that the matrix is active and participates in the reaction, it could also change the local bonding of the transition metal ion redox center because of different metal–oxygen bond lengths, bond angles, and coordination numbers. These could affect the catalytic activity.

Finally, although the dispersed redox centers catalyze reactions that require fewer number of oxygen atoms more selectively, for reactions in which activation of molecular oxygen is a slow step, these sites may show activities substantially inferior to sites of clusters of redox centers. In that case, a balance between the need for high activity and high selectivity will determine the desirability of a catalyst for the application.

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