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Catalysis Today 38 (1997) 157–162

CATALYSIS TODAY

Reduction of nitrogen oxides with hydrocarbons catalyzed by bifunctional catalysts

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Abstract

Usefulness of the concept of bi- or multifunctional catalysis in the catalyst design for the reduction of dilute nitrogen oxides by hydrocarbons in the presence of excess oxygen (so-called HC-SCR) is demonstrated. First, it is shown that the complex reaction of HC-SCR can be divided into (i) the oxidation of NO to NO_2 and (ii) the subsequent reactions between NO_2 and hydrocarbons. Further, two examples, where significant improvement of catalytic performance was obtained, based on the idea of bifunctional catalysis are presented: (a) NO–C_3H_6–O_2 catalyzed by mechanical mixtures of Mn_2O_3 and M–ZSM-5 (metal loaded ZSM-5), and (b) NO–CH_4–O_2 by Pd/H-ZSM-5 (Pd loaded H-ZSM-5).

Keywords: Nitrogen oxide; Reduction of NO_x; Bifunctionnal catalysis; Mn_2O_3; Sn-zeolite

1. Evolution of HC-SCR

There are two major catalytic technologies for the abatement of the emission of nitrogen oxides into the atmosphere. Both were developed in the seventies. The first comprises the selective reduction using ammonia as a reductant (NH_3–SCR). This is mainly applied to the emission of coal and oil-fired power plants. The other is the three-way catalysts (TWC) installed in gasoline-engined automobiles. Although both catalysts are very widely used in Japan, the concentration of nitrogen oxides in the atmosphere has not decreased recently, particularly in the urban areas. This is mainly due to the emission from motor vehicles, since (1) the number of gasoline-engined cars continues to increase and (2) the emission from diesel-engined cars is not sufficiently controlled, as the above two major technologies are not applicable to the emission of diesel engines [1]. The same problems exist in diesel as well as gas engines or turbines, namely co-generation systems.

This is the reason why we need a new catalytic technology which can be applied to dilute nitrogen oxides emitted together with excess oxygen from mobile or small stationary engines.

In 1986, Cu-ZSM-5 was reported to be much more active than the earlier known catalysts for the catalytic decomposition of NO [2]. This finding was remarkable, but the catalytic activity decreased sharply with a decrease in the NO concentration and the catalyst suffered from severe deactivation in the presence of oxygen or sulfur oxides. Yet, it was later demonstrated that Cu-ZSM-5 showed a significant activity when it was used for a real lean-burn engine and, moreover, the rate increased in the presence of oxygen. It was shown that the reaction taking place in this case was

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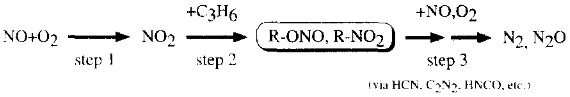
PII S0920-5861(97)00060-6

not the decomposition of NO but the reduction of NO by hydrocarbons contained in the emission gas [3]. Since then (1990–1992), many catalysts such as various kinds of solid acids and bases, including ZSM-5 loaded with metal ions – even with proton, were demonstrated to be active catalysts for this reaction [4]. We were highly optimistic during this period. This is sometimes called HC-SCR (selective catalytic reduction by hydrocarbons). Among them, transition metal loaded ZSM-5 catalysts were always the best. But it soon turned out that they were not resistant to water vapor. There were two serious negative effects of water vapor: (1) reversible retardation probably due to competitive adsorption; and (2) irreversible deactivation caused by dealumination and aggregation of metal ions followed by degradation of zeolite structure. So far, it seems that these two effects of water vapor are fatal and regrettably there is not much hope for zeolite catalysts for the moment.

As far as the mechanism of HC-SCR is concerned, it was assumed at first that the hydrocarbons are partially oxidized in the initial step and then the partially oxidized products react with NO. In 1992, Hamada and coworkers showed in the case of alumina and H-zeolite that NO is first oxidized to NO_2 and then NO_2 reacts with hydrocarbons [5]. Recently, this mechanism appears more popular including the cases described here. Hereafter, M-ZSM-5 denotes M-loaded ZSM-5 catalyst. Pd/H-ZSM-5 and Pd/Na-ZSM-5, respectively, represent Pd loaded on H-ZSM-5 and on Na-ZSM-5. Details of each catalyst may be found in the references cited.

2. Ce-ZSM-5

It was found that, among ZSM-5 loaded with various rare-earths, Ce and Pr were effective [6] and the activities of some Ce-ZSM-5 catalysts were comparable or higher than Cu-ZSM-5, even at space velocity of 100 000 h^{-1} [7] when propylene was used as a reductant. We had proposed a reaction mechanism in which the oxidation of NO to NO_2 is the important initial step [8]. The reactions between NO_2 and propylene to form organic nitro- and nitrite compounds are fast. The oxidative decomposition of the organic intermediates containing nitrogen and oxygen produce dinitrogen via several parallel and/or consecutive steps. The reaction scheme proposed is summarized in Scheme 1. Ce ion functions in steps 1 and 3. Some of the experimental results which support this scheme will be briefly given here.



Scheme 1. The main reaction paths of $NO–C_3H_6–O_2$ reactions catalyzed by Ce-ZSM-5. Ce-ZSM-5 functions in steps 1 and 3.

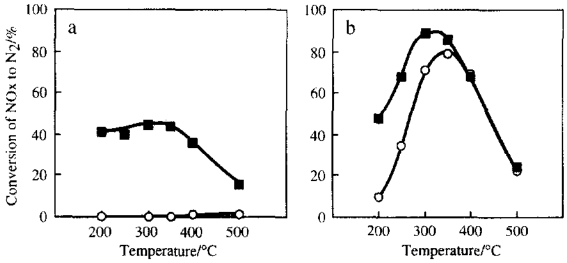


Fig. 1. Temperature dependences of conversion of NO (or NO_2) to N_2 for NO (or NO_2)–C_3H_6–O_2 reaction over (a) Na-ZSM-5 and (b) Ce(19%)-ZSM-5 [8]. (○) $NO–C_3H_6–O_2$ and (■) $NO_2–C_3H_6–O_2$. NO or NO_2, 1000 ppm; C_3H_6, 500 ppm; O_2, 2%; total flow rate, 150 cm^3 min^{-1}; catalyst weight, 0.50 g.

Fig. 1 compares the $NO–C_3H_6–O_2$ and $NO_2–C_3H_6–O_2$ reactions over Na- and Ce-ZSM-5 [7,8]. Although Na-ZSM-5 is not active for $NO–C_3H_6–O_2$ reaction, it can form N_2 if NO_2 is used in place of NO. Thus, Na-ZSM-5 cannot promote the oxidation of NO, but catalyzes the steps following the oxidation of NO. Even in the case of Ce-ZSM-5, $NO_2–C_3H_6–O_2$ proceeds faster than $NO–C_3H_6–O_2$ in the lower temperature region, where the oxidation of NO does not take place so fast over Ce-ZSM-5. The presence of O_2 is essential for HC-SCR. All these results are consistent with the reaction paths shown in Scheme 1.

A rapid formation of organic nitro- and nitrite compounds can be seen from the IR data [9,10]. As shown in Fig. 2 [10], the IR band assignable to the organic nitro-compounds (at ca. 1560 cm^{-1}) disappears upon contact with NO_2 and/or O_2 accompanied by the formation of N_2, N_2O, CO_2 and CO. The changes of nitrite and isocyanate were much smaller (at least in the absence of water; cf., Ref. [17]). It seems that there exist several intermediates different in reactivity. In some cases, the rate of N_2 formation is proportional to the concentration of the nitro-com-

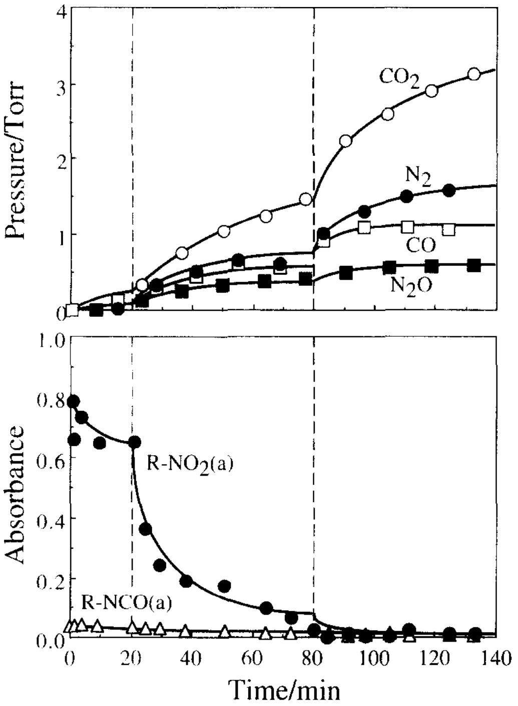


Fig. 2. Evolution of (●) N_2, (■) N_2O, (○) CO_2 and (□) CO in the gas phase (top) and the changes of the IR bands at (△) 2241 and (●) 1558 cm^{-1} (bottom) during the elevation of the temperature in NO_2 (10 torr) after the NO_2 (10 torr)–C_3H_6 (10 torr)–O_2 (45 torr) reaction was carried out over Ce-ZSM-5 at 373 and 423 K, and subsequent evacuation at 473 K [10].

pounds [10]. It may be recalled that NO_2, once formed, is readily reduced to NO in the presence of hydrocarbons [8]. This NO is again oxidized to NO_2 to react with hydrocarbons. With less active catalysts at lower temperatures, significant amounts of HCN, HCNO, C_2N_2 are formed [8].

3. Mn_2O_3+Ce-ZSM-5 – a bifunctional HC-SCR catalyst

As discussed in the foregoing, the NO–C_3H_6–O_2 reaction requires two major catalytic functions; oxidation of NO to NO_2 and oxidative decomposition of organic intermediates containing nitrogen and oxygen. Thus, one may be able to improve the catalytic performance by combining two catalyst components that, respectively, catalyze the two steps. We attempted to combine Ce-ZSM-5 which functions in both steps with metal oxides which are expected to catalyze the first step more efficiently than Ce-ZSM-5 [11].

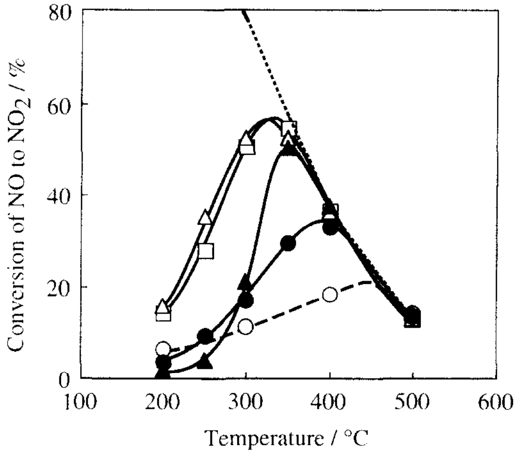


Fig. 3. Oxidation of NO to NO_2 over several metal oxides. (□) Mn_2O_3; (●) CeO_2; (▲) CuO; (△) Cr_2O_3; (○) Ce(15%)-ZSM-5. The dotted line indicates the % conversion at equilibrium, calculated and experimentally confirmed as in this figure. NO, 1000 ppm; O_2, 2%; total flow rate, 150 cm^3 min^{-1}; catalyst weight, 0.50 g.

Fig. 3 shows the oxidation of NO catalyzed by several metal oxides. Mn_2O_3 (4.6 m^{2}g^{-1}), Cr_2O_3 (44 m^{2}g^{-1}), CuO (1.6 m^{2}g^{-1}) and CeO_2 (102 m^{2}g^{-1}) are more active than Ce-ZSM-5. In Fig. 4 are presented the results of NO–C_3H_6–O_2 reaction over the mechanical mixtures of these oxides (0.25 g) and Ce-ZSM-5 (0.25 g). For comparison, the data observed for Ce-ZSM-5 (0.50 g) are also shown in Fig. 4. Significant improvement was achieved by mixing Ce–ZSM-5 with Mn_2O_3 and CeO_2. A similar enhancement was recently reported for Mn_2O_3 + Au/Al_2O_3 (Au is highly dispersed on Al_2O_3) [18].

If one plots the % conversion of NO to N_2 against the % conversion of C_3H_6 to CO_x, it becomes evident that the efficiency of utilization of C_3H_6 for NO reduction is much improved in the cases of Mn_2O_3 and CeO_2. The reason why Cr_2O_3 is not effective as an additive is mainly due to its extremely high activity for the oxidation of C_3H_6; C_3H_6 is exhausted before it reaches Ce-ZSM-5 on which C_3H_6 is expected to react with NO_2. This statement is deduced from the comparison of the C_3H_6–O_2, NO–C_3H_6–O_2 and NO_2–C_3H_6–O_2 reactions with Mn_2O_3 and Cr_2O_3 (metal oxides alone and those mixed with Ce-ZSM-5) [11]. This is schematically illustrated in Fig. 5.

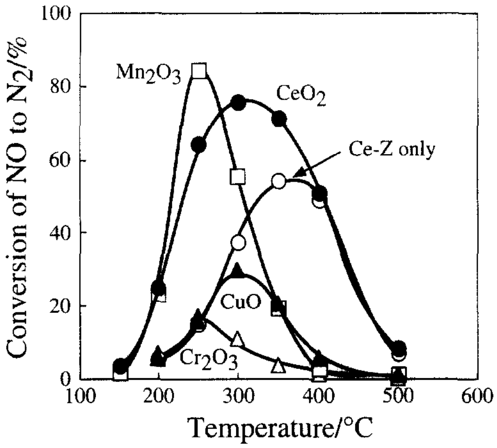


Fig. 4. Conversion of NO to N_2 in $NO+C_3H_6+O_2$ reaction catalyzed by mechanical mixtures of metal oxides (0.25 g) and Ce-ZSM-5 (0.25 g). Ce-Z only means Ce-ZSM-5 (0.50 g) without metal oxides.

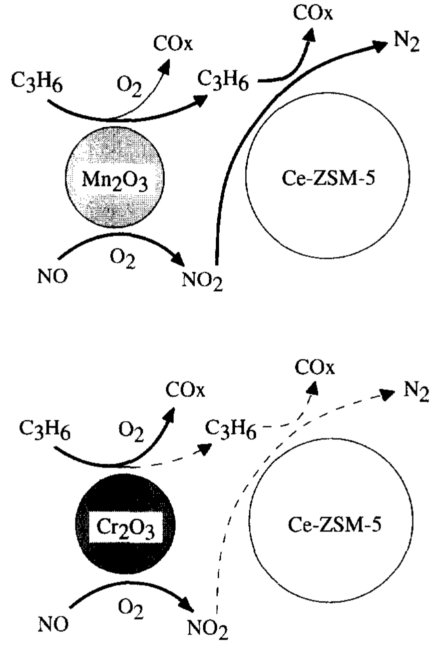


Fig. 5. Schematic illustration of $NO–C_3H_6–O_2$ reaction over Mn_2O_3 (or Cr_2O_3)+Ce-ZSM-5 mechanical mixture.

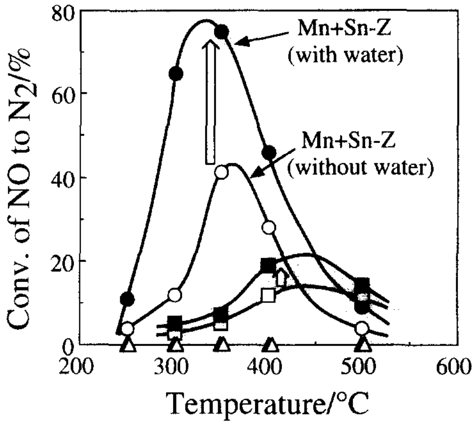


Fig. 6. The influence of the presence of water vapor on the conversion of NO to N_2 in $NO–C_3H_6–O_2$ reaction. (● and ○) Mn+Sn-Z; (■ and □) Sn-Z; (▲ and △) Mn. Filled symbols (●, ■, ▲) indicate the results obtained in the presence of water vapor, and open symbols (○, □, △) in its absence. NO, 1000 ppm; C_3H_6, 500 ppm; O_2, 2%; H_2O, 5.7%; total flow rate, 150 cm^3 min^{-1}. Mn+Sn-Z: Mn_2O_3 (0.25 g)+Sn-ZSM-5 (0.25 g); Mn: Mn_2O_3 (0.25 g); and Sn-Z: Sn-ZSM-5 (0.25 g).

4. Mn_2O_3Sn-ZSM-5 – an active bifunctional catalyst in the presence of water vapor

The concept of bifunctional catalysis may be applied to the development of water-resistant HC-SCR catalysts. The observation that the catalytic activity of Mn_2O_3 for the oxidation of NO does not change much in the presence of water vapor motivated us to try this idea. We combined Mn_2O_3 with zeolites containing various metal ions, and found, in the case of Mn_2O_3 + Sn-ZSM-5, a remarkable acceleration (!) of the activity in the presence of water vapor in the entire range of reaction temperatures. Fig. 6 shows the results [12]. The effects of water vapor are compared with other catalysts in Fig. 7. The contrast between the Mn_2O_3 + Sn-ZSM-5 catalyst and the other catalysts may be obvious. A high activity was also observed for Mn_2O_3 + Zn-ZSM-5, but the degree of acceleration was small.

When the partial pressure of water increased, the rates of N_2 and CO_x production increased until a saturation point was reached. The effect of water is more remarkably observed in the improvement of the selectivity (or the efficiency of C_3H_6 utilization for NO reduction). This is understandable, since the water suppresses sharply the $C_3H_6–O_2$ reaction over Mn_2O_3 but has only a small influence on the oxidation of NO. Therefore, according to a model shown in Fig. 5, the amount of C_3H_6 which reaches a zeolite particle increases in the presence of water without losing much of the NO_2 formation. This is one reason for the

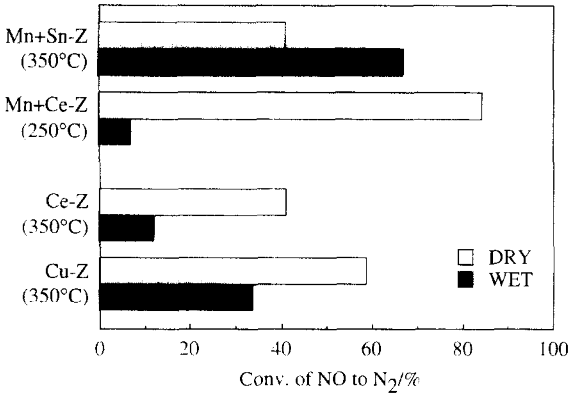
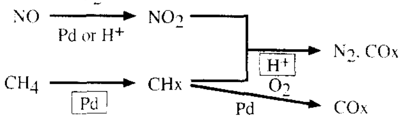


Fig. 7. Comparison of the effects of water vapor in NO–C_3H_6–O_2 reaction. Mn: Mn_2O_3. Sn, Ce and Cu-Z: Sn-, Ce- and Cu-ZSM-5.

observed acceleration. However, there should be other reasons for the acceleration by water, because, if this is the only reason, the acceleration should have been observed for other zeolite components as well. One of the other reasons is that the suppression of polymerization of C_3H_6 which would retard the NO_2–C_3H_6–O_2 reaction was more significant for Sn-ZSM-5. Here, it must be noted that the ion-exchange level and the state of metal were different among the zeolite components. For example, the content of Ce in Na-ZSM-5 was approx. 20% exchange level, while the Sn content was > 100% (SnO_2 is present). The extent of Sn exchange was estimated by the amount of Na released from ZSM-5 during ion-exchange procedure. However, the actual loading level of Sn was much larger. The elucidation of the mechanism of acceleration by water needs further examinations.

5. Pd/H-ZSM-5 for NO–CH_4–O_2 reaction – combination of Pd and proton

Noble metals (Ir, Pt, Pd and Rh) loaded in zeolites have been applied for HC-SCR since ca. 1990 [13]. CH_4 was believed to be a nonselective reductant. However, Pd/H-ZSM-5 is very efficient for the reduction of NO to N_2 in the NO–CH_4–O_2 reaction, while Pd/Na-ZSM-5 is completely inactive for the formation of N_2 [14]. What is more remarkable may be that the oxidation of CH_4 to CO_2, which takes place concurrently, proceeds at a very similar rate on both catalysts. Acidity measured by pyridine adsorption and the dispersion of PdO as measured by XRD and pyridine adsorption, as well as the presence of kinetic isotope effect observed when CD_4 is used instead of CH_4 [15], led to a reaction mechanism shown in Scheme 2. The primary role of protonic acidity is presumed to be in the reaction between NO_2 and CH_4. This scheme is supported by the fact that the rate of the NO_2–CH_4 reaction over Pd/Na-ZSM-5 is much slower than the rate over Pd/H-ZSM-5. The secondary role of proton may be to increase the Pd dispersion. Thus, in the NO–CH_4–O_2 reaction over Pd/H-ZSM-5, Pd activates CH_4 to form CH_x, and the reaction of CH_x with NO_2 is assisted by proton.



Scheme 2. Reaction paths of NO–CH_4–O_2 reaction over Pd/H-ZSM-5.

The bifunctional or cooperational effects have also been suggested by other research groups [16].

6. Summary

1. HC-SCR is a possible technology for $DeNO_x$ from oxygen-rich emission, but there are several difficulties to be overcome.
2. Since the catalytic performance for the $DeNO_x$ reactions depends on the delicate balance between several consecutive and/or parallel reactions, multi-functional catalysis is a promising concept for the design of the $DeNO_x$ catalysts, overcoming the aforementioned difficulties.
3. Two remarkable examples of bifunctional catalysts, Mn_2O_3 (or CeO_2) + M-ZSM-5 (M = Ce, Sn, etc.) and Pd/H-ZSM-5 (Pd and proton), show the usefulness of the multi-functional catalysts.

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