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NO_x/hydrocarbon reactions over gallium loaded zeolites: A review

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Abstract

Among the large number of catalysts that are known to catalyze the reduction of NO_x by various hydrocarbons are a series of gallium impregnated or exchanged zeolites. These are remarkable in part because most of the other catalysts can be described as acidic or containing an active transition metal ion. There is something unique and unusual about these gallium based catalysts and their performance will be reviewed in this article.

Keywords: Zeolites; Gallium exchange; Gallium impregnation; NO_x; Hydrocarbons; Methane; Brönsted acidity

1. Introduction

The incorporation of gallium into a variety of catalysts has generated a number of remarkable reactions without parallel in activity. While most of the attention on gallium based catalysts has been placed upon the aromatization of propane [1–6], several recent examples of gallium based catalysts have been used for an entirely different reaction, the reduction of NO_x by various hydrocarbons. The manuscript will summarize the recent work in the literature, attempt to analyze the results, and offer some perspectives about these materials as catalysts for this important environmental problem.

Concern about our environment and the ever stringent environmental regulations have stimulated extensive research in removal of NO_x from stationary and mobile sources. The commercially practised technology is the selective catalytic reduction (SCR) of NO_x with ammonia. This technology is efficient in removing NO_x in an O_2 rich environment but has several shortcomings, such as ammonia slip (the breakthrough of the unreacted ammonia), equipment corrosion and the transportation of ammonia through residential areas [7].

Over the past few years, extensive work has proceeded to search for alternative reducing agents for NO_x, such as hydrocarbons. Several groups reported interesting results on NO_x reduction in the presence of excess O_2 with non-methane hydrocarbons, e.g. propane, propene, and ethylene. Recent reviews [8,9] discuss the use of hydrocarbons as reductants for NO_x with Cu-ZSM-5 being among the most active; unfortunately, the latter suffers irreversible decomposition [10–12] upon prolonged exposure to high levels of moisture [typical of engine exhaust

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conditions]. The current, popular approach with hydrocarbons envisions the

$$2\,NO + C_xH_y + (4x + y - 4)/4O_2 \rightarrow N_2 + xCO_2 + y/2H_2O \qquad (1)$$

use of the unburned hydrocarbons in the exhaust, supplemented by post injection of the fuel to reduce the NO_x [Eq. (1)]. This will depend on the concentration and type of hydrocarbon available. Propane, propene, ethylene and more recently isobutane were found to selectively reduce NO_x in an O_2 rich atmosphere over a variety of catalysts [13–16]. For NO reduction with propane, the most frequently studied catalyst is Cu-ZSM-5 [17]. Additional work has also focused on the use of methane as a reductant (equation 2) [18–21]. The best catalyst to date, Co-ZSM-5, is estimated to be about a factor of four too low in activity in wet streams [20]. While Co-ZSM-5 seems to offer the hydrothermal stability, it still suffers from a reduction in activity due to the large levels of water vapor in real exhaust streams, which block and inhibit effective NO_x reduction.

$$2NO + CH_4 + O_2 \rightarrow N_2 + CO_2 + 2H_2O \qquad (2)$$

Ga-zeolites were first reported active for NO reduction with propane having comparable activities to Cu-ZSM-5 [22]. Ga/H-ZSM-5 is also reported to be more active than Cu-ZSM-5 for NO reduction by ethylene [23]. More recently, Ga-zeolites were reported, independently by Kikuchi et al. [24] and by Li and Armor [25,26], to be active for NO reduction with methane.

2. NO_x reduction by higher hydrocarbons with gallium loaded zeolites

Kikuchi et al. reported that Ga-ZSM-5 was highly active and selective for the reduction of NO by ethane [23,24]. With ethane, the molar ratio of NO/ethane was 1.5. With propane high conversion of NO was also reported [22]. With propane the NO/propane stoichiometry [23] was 3. Interestingly, the conversion of propane on Ga-ZSM-5 was lower than on Cu-ZSM-5, although the conversion of NO on Ga-ZSM-5 was higher than on Cu-ZSM-5. With 1000 ppm NO, 10% O_2, 0.5 g catalyst at a feed rate of 100 cm^3/min, there was a strong dependence of NO conversion upon the level of propane. NO was completely consumed with < 500 ppm propane. Ga-ZSM-5 was more reactive for NO reduction than H-ZSM-5 above 500°C. The reactivity order with a variety of zeolites was Ga-ZSM-5 $\sim$ Ga-FER > Ga-MOR $\gg$ GaY, which is quite temperature dependent. Ga-FER was the most selective catalyst [23].

With an olefin such as ethylene, the limiting molar ratio of NO/ethylene was 2. NO conversion was limited by the ethylene concentration. CO_2 was a secondary product from the reaction of CO with O_2. Yogo et al. report [27] that with ethylene Ga-ZSM-5 showed high activity and selectivity over a wide range of temperatures [300–600°C] even in the presence of excess O_2 When compared to Cu-ZSM-5, Ga-ZSM-5 displayed high activity even at high space velocities, once again due to the lower levels of hydrocarbon required with Ga-ZSM-5.

In 1993 a US patent [28] was issued to Idemitsu Kosan Company, Ltd. to Hayasaka and Kimura on gallium containing and zeolite promoted exhaust catalysts. Treatment of the NO_x was achieved by addition of LPG gas to a model diesel exhaust feed [at 400°C] with the composition: 1000 ppm NO_x, 1000 ppm O_2, 8% SO_2, 140 ppm CO, 400 ppm CO_2, and 230 ppm total hydrocarbons [with the total hydrocarbon/NO_x ratio of 2.1]. Comparative examples of the gallium loaded zeolites versus aluminosilicates and Y zeolite, indicated a clear improvement in NO_x removal using the gallium loaded zeolites even with extended runs after heating the catalysts for 5 h at 500 or 800°C. Substantial reduction in the NO_x level of $\sim$ 43% was seen with a GHSV of $\sim$ 30000. Addition of promoters such as iron, nickel, or cobalt salts further enhanced the efficiency of NO_x removal. Apparently, only a few runs were made with 0.2%

water, which is far below the typical level of water in a real engine exhaust.

Not much work has been reported on the effect of high levels of water vapor upon the performance of these gallium loaded catalysts with higher hydrocarbons. However, from the studies below [section 3.0] with CH_4, it is clear that even for higher hydrocarbons high levels of water vapor will impact seriously the performance of these gallium catalysts.

3. NO_x reduction by methane with gallium loaded catalysts

Since natural gas, which contains > 90% methane, is widely used as a fuel source for many combustion processes and electric utilities and is readily available in most parts of the world, its use as a reductant for NO_x would be desirable for industrial applications. Co, Mn and Ni exchanged zeolites such as ZSM-5, ferrierite and mordenite are effective catalysts for the NO reduction with CH_4 [18–20,29]. Cu-ZSM-5 is a poor catalyst because on Cu-ZSM-5, CH_4 preferably reacts with O_2 rather than with NO. Further, the presence of O_2 is essential for the reaction and NO conversion is proportional to the CH_4 level in the feed. The active centers of these transition metal based zeolites are believed to be the isolated metal ions which are activated by the zeolite lattice [20].

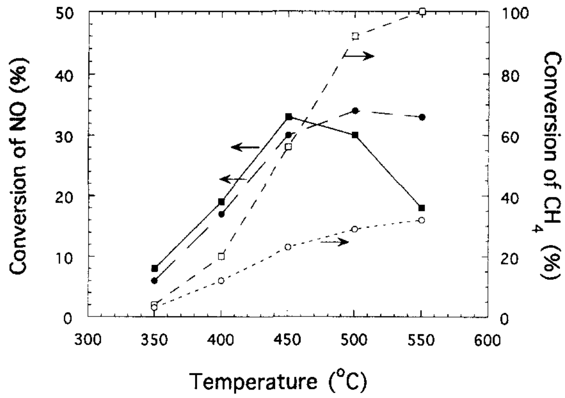

Fig. 1. Conversions of NO (solid symbols) and CH_4 (open symbols) as a function of reaction temperature over Ga-H-ZSM-5 (circles) and Co-ZSM-5 (squares). The reactions were run with a feed consisting of 1610 ppm NO, 1000 ppm CH_4 and 2.5% O_2 at a GHSV of 30000.

Li and Armor reported the use of gallium exchanged [designated Ga-ZSM-5] vs. Ga impregnated [designated Ga/ZSM-5] ZSM-5 for the reduction of NO by methane [26]. Extensive reaction studies, kinetics, and characterization [IR, TPD with NH_3, isopropylamine, and NO, and pore volume measurements] were also reported. The conversions of NO and CH_4 on Ga-H-ZSM-5 and Co-ZSM-5 are compared in Fig. 1 as a function of temperature. Ga-H-ZSM-5 has similar NO conversions compared to Co-ZSM-5 at temperatures between 350 to 450°C, and the conversion increases with temperature. Above 450°C, the NO conversion on Ga-H-ZSM-5 levels-off, while that on Co-ZSM-5 drops sharply. The difference in NO conversion on these two catalysts is most pronounced at 550°C, 33% on Ga-H-ZSM-5 and 18% on Co-ZSM-5. The difference in CH_4 conversion between these two catalysts is more dramatic. The CH_4 conversion on Co-ZSM-5 increases dramatically with temperature and reaches ~ 100% at $T > 500$°C. On Ga-H-ZSM-5, CH_4 conversions are lower and weakly dependent on temperature; the CH_4 conversion is only 32% at 550°C. Therefore the selectivity of CH_4 toward reacting with NO is much higher on Ga-H-ZSM-5 (100% at 450°C, which means CH_4 reacts with only NO without needless combustion) than on Co-ZSM-5 (46% at 450°C), and this difference increases with temperature (82 and 22% at 550°C for Ga-H-ZSM-5 and Co-ZSM-5, respectively). The NO reduction rate is first order in NO partial pressure with varied, fractional orders in CH_4 partial pressure. The presence of O_2 is essential for the NO reduction. Clearly some hydrocarbon activation is necessary, but it is difficult to envision how C–H activation occurs on a non transition metal center [26]. Several mechanisms for gallium zeolites catalysts have been proposed [26,30] for these reactions and they are summarized below.

Reactions of NO/O_2/hydrocarbon with Co-ZSM-5 and Cu-ZSM-5 are now believed to proceed following the formation of a M-NO_2 species which then reacts with the hydrocarbon [31]. With Ga-ZSM-5, a gallium NO_2 complex is less likely. Perhaps the gallium center reacts more readily with CH_4 and hydrocarbon activation by the gallium center is more likely than by a cobalt center. Certainly there is no reason for Co-ZSM-5, Cu-ZSM-5, and Ga-ZSM-5 to all have the same mechanism.

For transition metal loaded zeolites, such as the Co-ZSM-5 catalysts, the preparation route is very important with careful ion exchange being necessary [simple impregnation is not as effective]. To further investigate how the preparation method and support influence the NO reduction activity and to identify the active sites, a series of impregnated gallium samples, Ga/H-ZSM-5, Ga/Na-ZSM-5 and Ga/Al_2O_3 were tested for this reaction. The NO conversions on Ga/H-ZSM-5 are slightly lower than those on Ga-H-ZSM-5. Gallium impregnated on Na-ZSM-5, Ga/Na-ZSM-5, does not show appreciable activity for the NO reduction. H-ZSM-5 has low activity for this reaction. [Others have reported higher reactivity for H-ZSM-5 under different operating conditions. We have repeated our work under realistic process conditions of low NO (<500 ppm) and methane in wet atmospheres at high space velocities and do not observe very high activity for H-ZSM-5 [21]. With hydrocarbons other than CH_4 in a dry system, H-ZSM-5 may appear to be a good catalyst under these less demanding conditions. In a recent article, Kikuchi and Yogo [30] now report that in 10% levels of water vapor both Ga-ZSM-5 and H-ZSM-5 undergo dramatic loss in activity.] NO conversions on Ga/Al_2O_3 are much lower than those of either Ga-H-ZSM-5 or Ga/H-ZSM-5 but similar to those of H-ZSM-5. Ga-H-mordenite has similar NO reduction activity to Ga/H-ZSM-5. However, Ga-H-Y has a very low activity. Thus the support has a very strong influence on the NO reduction activity of the gallium loaded catalysts. The type of zeolite is important; Ga-H-ZSM-5 and Ga-H-mordenite are active for the NO reduction but Ga-H-Y is not. It seems that there is an intimate, cooperative interaction between H-zeolite and gallium, where the zeolite exerts its influence (via either its shape selectivity, acidity or the crystal field) on the gallium. This type of interaction likely occurs on those sites where Ga^{3+} and H^+ are within proximity in zeolite pores. As one referee pointed out it is well known that redispersion of the metal phase and inter-reaction between metal and zeolite acid centers occur upon activation in flowing hydrogen at 800 K [32]. It has also been observed [33] that ion exchange of multivalent cations for high silica zeolites may cause some of the metal cations to remain on the external surface as salts. Further in non-activated, ion exchanged Ga-ZSM-5, there is a balance between gallium species, showing different degrees of dispersion and/or interaction with zeolite acid centers [1]. Precipitation of Ga species during the ion exchange process may occur and be due to the hydrated gallium cation being too large to enter the internal pores of the ZSM-5 zeolite, as suggested in the literature [34]. On the other hand, the solubility constant for $Ga(OH)_{3(s)}$ is very small; it is difficult to evaluate the concentrations of all gallium species in a solution in the presence of the zeolite. However, it is possible that the local concentrations of Ga^{3+} inside zeolite cages are high enough to cause $Ga(OH)_3$ precipitation.

It appears that Brönsted acidity in gallium catalysts is very important; Ga/H-ZSM-5 is active for the NO reduction but Ga/Na-ZSM-5 is not. The presence of Brönsted acidity or gallium oxide alone is much less active than the combination of both. Yet, the exchange or impregnation by gallium ions does not significantly alter the Brönsted acidity. There must be some synergistic effect [26] between the gallium species and the H^+ in the zeolite. Possibly, the role of gallium is to enhance the activation of CH_4 with the NO reduction occurring on H^+ sites, or vice versa. A referee has pointed out that the role of gallium could depend on the specific nature of the gallium phase, its dispersion, and/or interaction with zeolite acid centers. For enhancing light paraffins aromatization, only well a dispersed gallium phase is responsible for the catalysis [35,36]. The synergism we observe may be analogous to that suggested [37,38] in propane aromatization reaction on Ga-H-ZSM-5, where C_3H_8 is dehydrogenated on the gallium phase to form the $C_3H_7^+$ carbenium ion, which subsequently reacts with the Brönsted acid sites of the zeolite. Price and Kanazirev [39] have also noted that for light paraffin aromatization major differences in activity for Ga/H-ZSM-5 exist vs. Ga/Na-ZSM-5 which they attribute to a more highly reduced state of gallium in Ga/H-ZSM-5. This disparity may be complicated by differences in oxidation state of gallium with different acidity.

Water vapor has a dramatic and deleterious effect upon the NO reduction activity. The NO conversion decreased from 40% to 13% upon addition of 2% H_2O at 500°C, and 16% conversion was obtained at 550°C in the presence of H_2O. [On a Co-ZSM-5 catalyst, however, the NO conversion decreases from 53 to 28% and from 40 to 35% at 450 and 500°C, respectively upon addition of 2% H_2O to the feed (GHSV = 30 000, 800 ppm NO, 1000 ppm CH_4 and 2.5% O_2).] From practical point of view, the tolerance of water vapor by a de-NO_x catalyst is very important because flue gas streams contain high levels of water vapor. The dramatic sensitivity of Ga based catalysts to water may be related in some way to the different mechanistic pathways for Ga-H-ZSM-5 vs. Co-ZSM-5 and/or to different degrees of hydrolysis of the two elements. For the moment, the cobalt based zeolite catalysts are more effective in the presence of water vapor than those incorporating gallium.

It appears two different mechanisms may be operating for the NO reduction over Co-ZSM-5 vs. Ga-ZSM-5, and this difference is probably related to their very different active centers. Over Co-ZSM-5, NO adsorbed at room temperature, and all the NO desorbed at $T < 400$°C in a He flow as determined by TPD [20]. The NO adsorption is essential to its reduction by CH_4. On Ga-H-ZSM-5, however, there is no appreciable NO adsorption at room temperature or at elevated temperatures. Therefore the interaction between NO and Ga must be very weak. Unlike Co-ZSM-5, on which NO conversion decreases with increasing NO partial pressure in a dry feed, the NO conversion on Ga-H-ZSM-5 is constant with NO partial pressure, which means that NO reduction on Ga-H-ZSM-5 is first order in NO. The peculiar dependence of NO conversion on CH_4 partial pressure suggests that gallium catalysts are capable of effectively activating CH_4, which is the key for the high selectivity of this reaction for gallium catalysts. However, on a gallium catalyst, increasing the CH_4 concentration in the feed can only enhance the NO conversion to a certain point.

At about the same time that Li and Armor were working with the Ga-ZSM-5, Kikuchi et al. were also working [23,24] on this same system. They reported similar activity for the reduction of NO by CH_4 over the range of temperatures indicated in Fig. 1. They also reported the same relative effect of various zeolites and added Ga-ferrierite to the list of effective catalysts. They attributed the observed decrease in CH_4 selectivity above 500°C to CH_4 combustion. Later Tabata et al. [40] reported evidence for the adsorption of CH_4 by Ga-ZSM-5 even at room temperature. Tabata et al. also showed that Ga-ZSM-5 can adsorb methane dissociatively, but Ga-ZSM-5 did not adsorb O_2. This was further supported by work with CD_4.

Recently Kikuchi and Yogo summarized [30,41] their studies on CH_4 reduction and suggested a mechanism [Eqs. (3)–(7)]. Since NO reduction occurred under conditions where CH_4 could not be activated solely by O_2, they suggest that NO_2 is involved in the selective reduction. Further there was no appreciable difference in the level of NO_2 conversion between the NO_2/CH_4 and $NO/O_2/CH_4$ systems, suggesting the predominant species under reaction conditions is NO_2. They observed that CO was the primary product of the reduction on NO, but CO_2 is the primary product of the reduction of NO_2. Thus they propose that NO_2, oxidized on zeolitic acid sites, activates CH_4 and forms a reaction intermediate, X [Eq. (4)]. This intermediate can react with gaseous NO or with NO_2. In this same article, they also acknowledged the significant impact of water vapor upon the performance of the Ga loaded catalysts.

$$NO + \tfrac{1}{2}O_2 \rightarrow NO_2 \quad \text{on acidic zeolite sites} \tag{3}$$

$$NO_2 + CH_4 \rightarrow X + nH_2O \quad \text{on Ga sites} \tag{4}$$

$$X + NO \rightarrow N_2 + CO + mH_2O \tag{5}$$

$$X + NO_2 \rightarrow N_2 + CO_2 + mH_2O \tag{6}$$

$$CO + O_2\,(\text{or } NO_2) \rightarrow CO_2 \tag{7}$$

With the Co-ZSM-5 catalysts, no CO intermediate is detected nor do H^+ sites appear to enhance catalyst activity, thus the proposed mechanism is somewhat different and incorporates the role of methyl radicals [42].

4. Use of sulfated zirconia with gallium loaded catalysts

A recent report by Feeley et al. described [43] the use of various gallium loaded catalysts supported on sulfated zirconia or post treated with sulfates. A wide variety of catalysts were evaluated, including gallium supported on zirconia or sulfated zirconia, gallium supported onto a wide variety of other amorphous oxides, Ga exchanged ZSM-5, Zr loaded ZSM-5, Ga and Zr loaded ZSM-5, sulfated Ga exchanged ZSM-5, sulfated Zr loaded ZSM-5, and sulfated Ga and Zr loaded ZSM-5. Some synergism appears to exist between gallia and zirconia on S-GaZr/ZSM-5. Of several zeolites tested, only ZSM-5 was enhanced by sulfation of the zirconia. Propane, propylene, and methane were evaluated as reducing agents, and compared with Cu-ZSM-5. Ga/S-ZrO_x was found to be effective for the reduction of NO_x in a lean environment and more active than S-ZrO_x or Ga/ZrO_x. Adding ZSM-5 to the formulation, i.e. S-GaZr/ZSM-5 increased the NO_x reduction activity, especially at lower temperatures. For ZSM-5, the combination of sulfation with Ga and Zr produced the most active catalyst. Unlike Cu-ZSM-5 which was most active with propylene, Ga/S-ZrO_x and S-Ga/Zr/ZSM-5 were more active with propane than with propylene. As with Co-ZSM-5, the S-Ga/Zr/ZSM-5 catalyst was also active with CH_4. Although Ga/S-ZrO_x and S-Ga/Zr/ZSM-5 are more hydrothermally stable than Cu-ZSM-5, their activities decreased significantly at high space velocities or with significant levels of water vapor present in the feed stream. The authors concluded that these last two factors make these sulfated zirconia catalysts impractical for mobile or stationary engine applications.

5. Role of acidity

Since Hamada's early work [13] which demonstrated the importance of acid catalysts for the reduction of NO_x by higher hydrocarbons, others have reported the importance of some acid sites for this reaction. As described above, Li and Armor [26], Yogo et al. [22,27], and Feeley et al. [43] reported the importance of the combination of Brönsted acid sites and gallium ions on ZSM-5. However, with Co-ZSM-5 there was no improvement in activity with the replacement of some cobalt sites by protons [20]. Recently, a more intensive study was completed by Satsuma et al. [44], who compared Ga-MOR with a variety of ion exchanged cations and H-ZSM-5. Ga-ZSM-5 was the most active catalyst at the higher temperatures [> 400°C], but with the complete consumption of propylene. At 300°C the reduction of NO_x by propylene followed the order: CaHMOR > SrHMOR = BaHMOR > LaHMOR = GaHMOR > H-ZSM-5 = H-MOR. Using NH_3 TPD, these zeolites could be classified into three groups of activity: those like HMOR, LaHMOR, and GaMOR having only strong acid sites; H-ZSM-5 having only one kind of acid site, but weaker than those of the first group; and alkaline earth ion-exchanged mordenites having moderate and strong acid sites. The activity for NO_x reduction increased with increasing total acidity. In addition some carbonaceous deposits were observed on the spent catalysts. With regard to the selectivity of NO_x reduction by the propylene [the efficiency of the hydrocarbon usage], they conclude that acid properties of these zeolites are not major factors determining the reduction of NO_x. The activity is dependent upon the amount of acidity, not just its strength. All this work with acidity, seems to suggest again that different mechanisms may be operational with gallium loaded vs. transitional metal exchanged zeolites. In some cases, certain catalysts are enhanced by the presence of Brönsted acidity, while others are not, suggesting the presence of alternative mechanistic pathways for these reactions.

6. Molecular dynamics

Miyamoto et al. recently described [45] computational studies using molecular dynamics and computer graphics techniques on active catalysts for NO removal. Various gallium species such as Ga^{3+}, GaO^+, $Ga(OH)_2^+$, and $Ga(OH)^{2+}$ were simulated inside ZSM-5. In this regard, gallium behaves similarly to copper ions since it appears to migrate to the T12 site where Al is substituted. Unlike the six coordination in bulk Ga_2O_3, there is low coordination for gallium in Ga-ZSM-5. The GaO^+ cation appears to be more dynamic than the hydroxylated gallium ions. Water appears to undergo preferential adsorption on GaO^+ and $Ga(OH)^{2+}$ to form $Ga(OH)_2^+$. This hydration appears to increase the coordination number around gallium, thus making NO sorption more difficult. Their simulations also suggest that the oxygen atoms on gallium have high mobility which offers easier access by NO or hydrocarbons to the Ga center.

7. Summary

A wide variety of gallium loaded catalysts have been used for the reduction of NO_x by methane and higher hydrocarbons. These include gallia exchanged or impregnated ZSM-5, gallium in mordenite or ferrierite, gallium with sulfated zirconia or sulfated ZSM-5, and combinations of gallium with zirconium on sulfated and unsulfated ZSM-5. In most cases it appears that Brönsted acidity promotes the activity of these catalysts. Given that gallium is not expected to perform like a transition metal, it is interesting to note that for dry feed streams, these gallium catalysts are quite active or better than the comparable transition metal loaded catalysts. Unfortunately, the gallium centers are drastically affected by the presence of water vapor, which limits their ultimate utility for NO_x removal, since large levels of water vapor are always present when combustion and NO_x formation occur.

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