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Catalytic reduction of nitrogen oxides with methane in the presence of excess oxygen: a review

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Abstract

Interest in new approaches to NO_x removal were stimulated by the discovery that certain zeolites were very active for NO decomposition and reduction by C_{2S} and C_{3S}. Initially, NO could not be reduced by methane with this early generation of zeolites. Later it was discovered that Co-ZSM-5 demonstrated uniquely high activity for NO_x reduction by methane in the presence of O_2. Given the world's plentiful supply of natural gas, methane would certainly be a hydrocarbon of choice to reduce NO. Since the breakthrough work with Co-ZSM-5, a number of other materials were reported to be catalysts for this reaction. This review summarizes the work in this topical area and attempts to relate the activities of all these potential catalysts. Direct comparisons regarding the relative performance of many of these newer catalysts are not always possible, often because rates are not reported and the data are collected under different conditions. With the current information at hand, it appears that the most active catalyst under simulated sulfur-free, wet exhaust conditions is Co-ferrierite.

Keywords: NO_x; Methane; Reduction; Zeolites; ZSM-5; Ferrierite; Cobalt; Gallium

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1. Introduction

The use of hydrocarbons as reducing agents for NO_x was first reported in the 70's [1,2]. Hydrocarbons could offer an attractive, alternative reductant to ammonia [3]. In the presence of O_2 and in the absence of a selective catalyst, these earlier catalysts generally resulted in hydrocarbon combustion as well, thus requiring the use of a large excess of hydrocarbons to remove the O_2. As a result, the use of NH_3 as a reductant [3] became a more attractive commercial solution [4], and NH_3 is still being used on a worldwide level. There are some undesirable features with the use of NH_3 as a reductant, such as the concern over NH_3 slip [3], and this has driven a continual search for a more effective means of NO_x removal. The discovery by Iwamoto et al. [5] that Cu-ZSM-5 was effective for NO decomposition and shortly thereafter that the same material was also much more effective than earlier catalysts for non-methane hydrocarbon reduction of NO_x generated new momentum for this field. 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 ([6,7] and other manuscripts within this special issue) discuss the use of hydrocarbons as reductants for NO_x. Initial patent applications in this area suggested that methane was also a suitable hydrocarbon, but this was not the case for many of the zeolites later tested, especially for Cu-ZSM-5. Until recently, little progress

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has been made on the use of CH_4 as a reductant. Much of the recent interest in methane activation has been focused on its use as a precursor to value added products (such as methanol, formaldehyde, C_{2S}, etc.). As a readily available commodity chemical, methane offers a rich source of hydrogen atoms, if one could activate the methane. Given the plentiful supply of CH_4 in the world, the use of CH_4 as a selective reductant would be desirable.

In 1992 we announced [8,9] a new catalytic technology that uses methane to reduce NO_x in the presence of excess levels of oxygen (methane deNO_x). Selected metal exchanged zeolites are effective catalysts for the novel, selective reduction of NO_x by CH_4 in the presence of excess O_2. A complete conversion of NO to N_2 is obtained over a Co-ZSM-5 catalyst at 400°C. This discovery provides a new, and perhaps an alternative approach for NO_x emission control for both stationary and mobile sources. The properties, performance, and operation of these catalysts in contrast to other potential catalysts for the reduction of NO by methane will be described below.

2. Use of methane as a reductant

With the development of the current three-way catalyst, scientists reduced their efforts at developing new approaches to NO_x reduction. There were early efforts, e.g., [10,11] to destroy NO_x by decomposition (Eq. 1) into its elements, but these early catalysts were readily poisoned by O_2 and less attractive versus other approaches for NO_x removal. The

$$2NO \rightarrow N_2 + O_2 \qquad (1)$$

breakthrough result of Iwamoto et al. [5], demonstrating that Cu-ZSM-5 was effective at NO decomposition, stimulated this field once again. Unfortunately, the Cu-ZSM-5 catalyst is at least an order of magnitude less active than necessary for commercial utility. Further the thermal and hydrothermal instability of Cu-ZSM-5 severely limit its utility for NO decomposition [12]. As later work began to emerge from Japan [7,12–17], it became apparent that one could also use hydrocarbons as reducing agents to remove NO_x (Eq. 2). While these early catalysts were effective with higher hydrocarbons, they exhibited little activity using methane as a reducing agent (Eq. 3). These and other potential catalysts would drive combustion (Eq. 4) at the expense of Eq. 3.

$$2NO_x + C_xH_y + O_2 \rightarrow N_2 + xCO_2 + yH_2O \qquad (2)$$

$$2NO + CH_4 + O_2 \rightarrow N_2 + CO_2 + 2H_2O \qquad (3)$$

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O \qquad (4)$$

There is now a huge amount of work being done with higher hydrocarbons (more than C_1), but very little with CH_4. Other hydrocarbons are much more easy to activate for NO_x reduction, hence that is where the bulk of the attention has been focused. Recently, Iwamoto and others have summarized the reduction of NO with a variety of hydrocarbons [12,16,17].

Methane differs fundamentally from other hydrocarbons. CH_4 is the most difficult hydrocarbon fuel to ignite; over Pt-, Pd- and Rh-catalysts preheat temperatures of 480–510°C are required [18]. With iron-silicate molecular sieves, Yogo et al. reported that ethylene and propene were much more reactive than methane, exhibiting light-off temperatures about 200°C lower than with CH_4 [19]. Nevertheless, natural gas (NG), which is principally CH_4, is widely available in many parts of the world (more so than the higher hydrocarbons) and is a common fuel used in stationary engines at the power plants which are producing NO_x during the combustion process. Thus, it would seem that NG is potentially quite attractive as a viable reductant for NO_x removal. Let us begin by comparing thermal versus the new catalytic approaches to methane deNO_x.

2.1. *Non-catalytic methane deNO_x*

There are commercial approaches which use CH_4 to remove NO_x [20], but they operate in the absence of O_2, which puts a severe and costly limitation on the use of this technology. Methane is conventionally regarded as a non-selective reducing agent for NO in the presence of O_2, because thermally it generally reacts with O_2 much faster than with NO. If any O_2 is present in the exhaust stream, excess methane must be added to remove the O_2 by combustion before NO_x can be removed by CH_4 in the reducing atmosphere. A John Zink NOxidizer unit is a thermal incinerator that destroys NO_x. Natural gas fired burners raise the incinerator temperature in excess of 1200°C where excess natural gas is added to remove O_2 and consume the NO_x. In municipal waste combustors, adding excess methane above the combustion gate also serves to generate a O_2 free atmosphere which promotes the thermal decomposition of NO_x by-products from waste combustion. Eventually, air is added downstream to remove the CO which is a by-product from the fuel rich NO_x removal section. This non-catalytic, thermal process demands large levels of CH_4, and the combustion operation will produce additional NO_x as well! In GRI's and IGT's, methane deNO_x for the thermal reduction of NO_x in oxygen, a large excess of methane (ca. 12% to remove ca. 100 ppm NO_x) is required [21,22]. This technology has now been demonstrated for controlling NO_x and CO emissions from a commercially operating municipal waste combustor. NO_x emissions are reduced from about 275 ppm to 75 ppm. This thermal Methane deNO_x technology offers advantages of no NH_3 slip, no visible NO_x plume, no potential hazards of NH_3 storage and handling, and simultaneous reduction of CO emissions while increasing boiler efficiency. However, since flue gas contains high levels of O_2, normally 5-15%, utility owners may not want to add very high levels of CH_4 to the flue gas.

2.2. Catalytic methane deNO_x in the presence of excess O_2

Several catalysts have been tested for catalytic NO_x reduction by CH_4; these were often precious metal based catalysts which in the absence of O_2 often produce CO, NH_3, and/or N_2O as undesirable by-products [23]. In the presence of O_2 these catalysts preferentially catalyze the combustion of methane. On the other hand, a preferred series of metal exchanged zeolites were very effective catalysts for the reduction of NO_x by CH_4 [9]. Since progress in this topical area has been rapid, this section will be sub-divided into zeolitic and non-zeolitic catalysts.

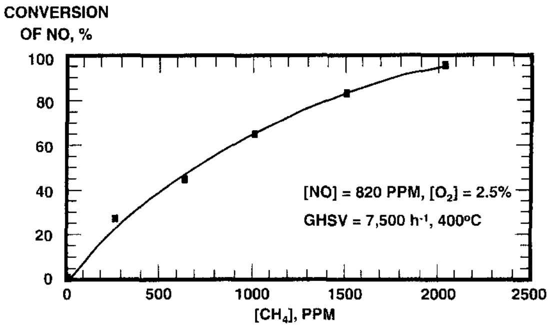

Fig. 1. NO_x removal as a function of methane levels. Co-ZSM-5 (4.0 wt.-% Co; Si/Al = 13.6; Co/Al = 0.70). Reproduced with permission from Ref. [9].

Use of transition metal zeolite based catalysts

With a Co-ZSM-5 catalyst, NO can be selectively reduced by methane in the presence of excess O_2. Fig. 1 illustrates the dependence of Eq. 3 upon the level of methane [9]. By operating in a slight excess of methane, one can achieve significant levels of control of NO_x. From the onset, we found metal exchanged zeolites containing cobalt, nickel, or manganese were particularly active catalysts. The stoichiometry of Eq. 3 was verified by monitoring all the possible reactants and products. At about the same time of our discovery, a similar observation was disclosed in a Japanese patent application [24], but no further record or elaboration of this work yet exists in the published journal literature. A recent article by Tabata et al. provides an exhaustive summary of catalysts for NO_x reduction by hydrocarbons including methane [16].

Table 1 describes a variety of cobalt based catalysts that were evaluated for this reaction [25]. One observes that certain zeolites are much more effective as a host than others, e.g., ZSM-5 vs. Y. In addition, adding cobalt by impregnation onto conventional oxide supports produces ineffective catalysts. H-ZSM-5 and Cu-ZSM-5 are also very

Table 1
Conversions[a] over cobalt exchanged zeolites and cobalt oxides

Sample	Si/Al	Me/Al	Metal loading (wt.-%)	Conversion to N_2		
				400°C	450°C	500°C
Co-ZSM-5	14.0	0.70	4.0	23	34	30
Co-FER	6.0	0.76	4.6	14	42	56
Co-MOR	5.3	0.47	5.6	17	27	24
Co-beta	12.9	0.42	2.3	9	16	23
Co-ZSM-11	26.6	1.15	3.5	11	17	21
Co-KL	2.9	0.18	3.5	7	9	11
Co-Y	2.5	0.67	11.8	nd	5	6
CoO/Al_2O_3			11	nd	nd	nd
CoO/TiO_2			2.6	nd	nd	nav
Co/TiO_2			10	nd	nd	nd
CoO/silicalite			1.6	6	5	nav
Co/SiO_2-Al_2O_3			3.0	nd	nd	nd
Co_3O_4			Bulk	nd	nd	nd

[a] All zeolite samples were tested at GHSV = 30 000, 0.1 g catalyst, 100 cm^3/min total flow, [NO] = 0.16%, [CH_4] = 0.10%, [O_2] = 2.5%.

[b] Co exchanged hydrous TiO_2 [25].

nd: Conversion not detected.

nav: Data not available.

NO percentage conversion on Co-zeolites and oxides of cobalt.

poor catalysts for Eq. 3 [9]. With Cu-ZSM-5, methane oxidation predominates (Eq. 4). This consumes the methane needed to reduce NO_x, hence the lower conversion of NO_x. This results in a bending over of the NO_x conversion profile at temperatures above 450°C. Water vapor serves as an inhibitor for the reduction of NO_x by CH_4 (see chapter 2.3).

Despite the competitive combustion of methane by excess O_2 over these metal exchanged zeolites, O_2 is required for enhanced NO_x reduction by CH_4. Some reaction occurs in the absence of O_2, but with a slight excess of O_2 (generally above a fraction of a percent) the reduction by CH_4 proceeds without exhibiting any strong dependence on larger levels of O_2 (up to 21%) [9]. This enhancement in activity and independence upon high levels of O_2 potentially has immense practical value. All over the world, stationary combustion engines produce NO_x in an O_2 rich exhaust. The injection of NH_3 is the currently preferred means of removing NO_x from these O_2-rich exhaust systems. These new cobalt ion based zeolite catalysts in O_2-rich streams potentially could have considerable practical value to the mobile engine manufacturers, because they would be able to run their engines in an O_2-rich mode, thus offering greater fuel economy.

Below a certain exchange level of Co^{2+}, the turnover frequency is independent of Co^{2+}. A single Co^{2+} cation is believed to be an active site. The ability to ion exchange the Co^{2+} into the zeolite allows one to generate a highly dispersed form of Co^{2+}, which maximizes the effectiveness of each Co^{2+}. Thus, in these catalysts one prefers to have as much ion exchangeable Co^{2+} as possible [25]. This can be achieved by lowering the Si/Al ratio. However, 'high alumina' zeolites are not readily achieved in many zeolite topologies. In addition, one has to realize that not all the exchangeable Co^{2+} may be available for selective reduction of NO_x by CH_4. With Co-ZSM-5, the best conversions are ca. 34% at 1640 ppm NO, 1025 ppm CH_4, and 2.5% O_2 at 450°C at 30 000 GHSV ($TON = 4.4 \times 10^{-4}\ s^{-1}$). Note in these systems excess O_2 does not alter the conversion, but conversion can be driven up by the level of methane and lower GHSV. Thus nearly 100% conversion of NO_x can be achieved at 820 ppm NO, 2.5% O_2 and 2000 ppm CH_4, at 400°C and at 7500 GHSV [26]. The same catalyst is also effective for the simultaneous oxidation of CO to CO_2 [27]. In addition, Co-ZSM-5 is very stable under high temperature, wet environments for more than 24 h [25].

The dramatic difference between Cu-ZSM-5 and Co-ZSM-5 for NO_x reduction by CH_4 is further indicated [26] in Table 2 and Fig. 2 and Fig. 3. While Cu-ZSM-5 is a poor catalyst for NO reduction by methane in the presence of O_2, it is much more effective than Co-ZSM-5 in the absence of O_2. O_2 is essential for cobalt to perform NO reduction. Interestingly, when propene is used (Table 2) in the presence of O_2, both copper and cobalt ZSM-5 have about the same activity. Also, from Table 2 one sees a dramatic difference between copper and cobalt for NO decomposition. One observes some initial instability with Cu-ZSM-5 for reduction by propene in the absence of

Table 2
NO_x removal over Cu-ZSM-5 vs. Co-ZSM-5

Catalyst	Reaction[a]			
	No decomp.	$NO+CH_4$	$NO+CH_4+O_2$	$NO+C_3H_6+O_2$
Cu-ZSM-5	17	55	9	52
Co-ZSM-5	4[b]	9[c]	26	48

[a] GHSV = 30 000; [NO] = 0.16%, $[CH_4]$ = 0.10%, $[C_3H_6]$ = 550 ppm, $[O_2]O$ = 2.5%, balanced by He, 400°C, conversion to N_2.
[b] The activity decreased with time, and the conversion was taken when t = 1 h.
[c] Impregnation of 0.4% Nb onto a Co(II)-ZSM-5 catalyst with oxidation pretreatment.
Reproduced with permission from Ref. [26].

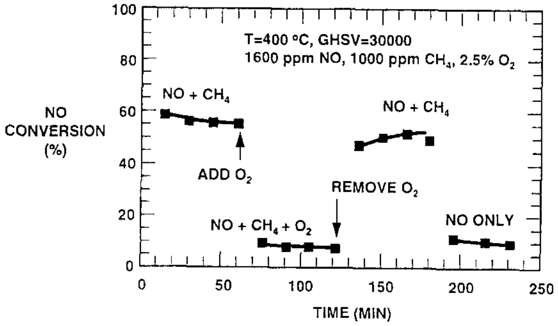

Fig. 2. NO reduction with methane over Cu-ZSM-5 with and without oxygen (Si/Al = 14; Cu/Al = 0.60; [NO] = 0.16%, O_2 = 2.5%, 400°C; GHSV = 30 000). Reproduced with permission from Ref. [26].

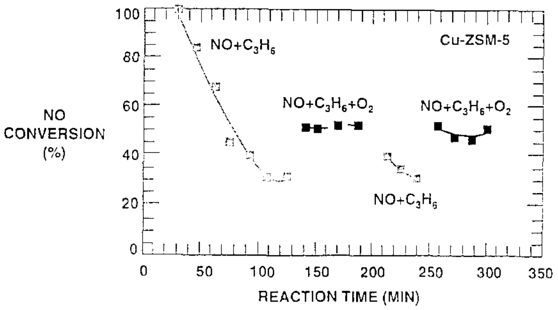

Fig. 3. NO reduction with propylene over Cu-ZSM-5 with and without oxygen (Si/Al = 14; Cu/Al = 0.60; [NO] = 0.16%, $[C_3H_6]$ = 550 ppm; O_2 = 2.5%, 400°C; GHSV = 30 000). Reproduced with permission from Ref. [26].

O_2. With O_2 added, the conversion actually increases. Clearly, only certain cations are preferred for NO_x reduction by CH_4.

Recently we announced [27,28] that ferrierite in place of ZSM-5 offers a dramatic increase in reactivity of the cobalt exchanged zeolite. Co-ferrierite (Co-FER) provides about twice [29] as much conversion (TON = 9.6×10^{-4} s^{-1} based upon the level of cobalt cations) at 500°C, 30 000 GHSV, CH_4 = 1015 ppm) of NO_x as Co-ZSM-5 (TON = 4.4×10^{-4} s^{-1}) (Table 1 and Ref. [28]). The ferrierite environment provides a much more selective use of CH_4. Previously, the Co-ZSM-5 used ca. 38% of the available methane for NO_x reduction, the balance being consumed by combustion. Ferrierite is more active because over 86% of the methane is now used for NO_x reduction! Once again, water suppresses the activity of the Co-FER catalyst (still reversibly). The dependence on cobalt loading is very different from that observed for the ZSM-5 topology. The added effectiveness of Co-FER must be associated with the availability of more sites for NO_x reduction; this must be associated with the difference in topology between these two classes of zeolites [30].

Nishizaka and Misono reported [31] in 1993 that Pd^{2+} exchanged H-ZSM-5 and Pd–H–Ce-ZSM-5 displayed activity for NO_x/CH_4 in the presence of O_2. Here acidity was indispensable for NO_x reduction. They report that Pd–Na-ZSM-5 was a very poor catalyst and suggest that the oxidation of NO to NO_2 is a key step in the process prior to reduction by CH_4 [32]. Although their reaction conditions were somewhat different, one can estimate the relative activity vs. Co-ZSM-5. At 1000 ppm NO, 2% O_2, in a dry system, with 2000 ppm CH_4 at 9000 GHSV (assuming 1 wt.-% Pd–H-ZSM-5 catalyst density of 0.5 g/cm^3), they obtain about 70% conversion of NO_x to N_2 at 450°C over Pd–H-ZSM-5. We have reported that Co-ZSM-5 gives ca. 100% conversion at 7500 GHSV at 400°C, and with Co-FER, we observed ca. 42% conversion at 450°C and at 30 000 GHSV with only about half of the level of methane (1015 ppm) [28]. In the absence of side-by-side experiments, it appears that Co-FER is more active than Pd–H-ZSM-5. As others have reported [31,33], Pt-ZSM-5 is an ineffective catalyst for NO_x reduction by CH_4.

A recent US Patent, issued to S. Hung of GE [34], claims that ZSM-5 impregnated with zinc and/or copper cations are catalysts for NO_x reduction by CH_4 in the presence of O_2. Once again, no comparative data to Co-ZSM-5 is provided, and the data are only reported with dry gases. Hung does plot his data vs. H-ZSM-5 and Cu-ZSM-5 (two relatively poor catalysts for NO_x reduction by methane), and in this regard, Zn-ZSM-5 only offers a modest improvement over H-ZSM-5. This new zinc based catalyst probably is still not sufficiently active to be of immediate commercial value.

Non-transition metal loaded zeolites

During the course of our studies with Co-ZSM-5, we observed [27,35] that gallium ion supported on H-ZSM-5 or on H-MOR was also a very active catalyst for this reaction between CH_4 and NO_x. Impregnation or traditional exchange of gallium salts into H-ZSM-5 appears to give similar activity. Further a synergism exists between the gallium species and the H^+. Interestingly, the interaction between NO and gallium ions is weaker than between NO and Co^{2+}. (No detectable NO adsorption occurs at room temperature.) It appears that the mechanism for these gallium based catalysts is different from that for Co^{2+}. Under a dry atmosphere at more than 500°C, Ga–H-ZSM-5 is more reactive and selective than Co-ZSM-5; unfortunately, the gallium loaded zeolites are much more sensitive to water (much more so than Co-ZSM-5) which makes them unattractive as a commercial catalyst. Independently, Kikuchi and coworkers reported similar activity with gallium zeolites [36].

Kikuchi and coworkers later reported that In-ZSM-5 showed higher conversion at 400°C [37]. Recently, they [38] reported that the reactivity of NO_2 with CH_4 in 2.5% O_2 in a dry feed follows the order: $In \approx Ga > Co$ (65% exchanged) $\approx H$ with ZSM-5 at about 450°C. While our conditions were not exactly the same, we have never seen a fully exchanged Co-ZSM-5 perform as poorly as H-ZSM-5. An incompletely exchanged cobalt catalyst is not as active as a fully exchanged material [25]. In the past, we also prepared In-ZSM-5 and observed that it was quite reactive in dry atmospheres [39] but exhibited a slow decay with time. More importantly, we observed the conversion dropped from 51% to 11% at 400°C with 2% water vapor added to the feed stream. Several attempts by us to prepare (via the same procedures used to prepare Ga-ZSM-5 [35]) In-ZSM-5 never gave a catalyst which was more effective than Co-ZSM-5 in a wet stream. In a wet stream we have never seen a Ga-ZSM-5 catalyst perform better than Co-ZSM-5; our relative reactivity in a wet stream is ($Co \gg Ga \gg H$)-ZSM-5 [40].

Yogo et al., recently described [41] the use of a variety of H-zeolites for reaction 3. At 1000 ppm CH_4 with 1000 ppm NO (a high level) in 10% dry O_2, they observed ca. 40% conversion at ca. 500°C at ca. 12 400 GHSV (assuming a catalyst density of 0.5 g/cm^3: 0.5 g catalyst and 100 cm^3/min). They reported that H-FER is more selective than H-MOR or H-ZSM-5. At three times the GHSV, we observed 46% conversion of NO with Co-FER [29]; thus suggesting that the H-FER catalyst is less active than Co-FER. Yogo and coworkers studies were done under dry conditions; we reported earlier [42] that H-ZSM-5, was very sensitive to even 2% water vapor. In an article focused on Pd–H-ZSM-5, Nishizaka and Misono also reported [32] relatively low activity for H-ZSM-5 (5.2% conversion of NO at 1000 ppm NO, 2000 CH_4, 2% O_2 with 0.5 g catalyst at 400°C). Recently, Kikuchi and Yogo reported that in 10% water vapor both Ga-ZSM-5 and H-ZSM-5 underwent a dramatic loss in activity over a wide range of temperatures [38].

Non-zeolitic oxides

SnO_2 is also reported [43] to be a catalyst for hydrocarbon reduction of NO_x. Teraoka et al., reported that SnO_2 was more active for ethylene reduction of NO_x than Cu-ZSM-5 because of the greater hydrothermal stability of SnO_2. Methane was much less effective providing only ca. 17% conversion of 4400 ppm NO with 4400 ppm CH_4 at ca. 1800 GHSV, at 500°C. Compared to Co-ZSM-5, SnO_2 is much less active using CH_4 as a reductant. No studies were reported in the presence of water and/or SO_2.

Zhang et al. have described [44] the use of a variety of other oxide catalysts for the reaction of NO_x with CH_4. Lithium promoted MgO was slightly more active than pure MgO (on a per g basis). Substantial selectivity (20–40%) to N_2O was also reported. Unlike Co-ZSM-5, O_2 is not necessary for NO_x (at low NO_x levels) conversion to N_2. The rate of reduction of NO_x at 820 ppm was ca. 130 times lower (at temperatures of ca. 100°C higher) than Co-ZSM-5 on a per g basis. Another methane coupling catalyst, La_2O_3, was even more active than Li/MgO [45]. Again, the temperature for comparable conversion is about 100°C higher than with Co-ZSM-5, and Co-ZSM-5 has about 13 times more activity on a per g basis (0.11 μmol/g-s at 500°C, 850 ppm NO, 1000 ppm CH_4) than La_2O_3 at comparable levels of NO (0.0084 μmol/g-s at 500°C, 820 ppm NO and 820 ppm CH_4) and O_2. At high levels of NO (2%), the activity of Co-ZSM-5 is about 44 times more active than La_2O_3 on a per g basis. Unlike the Li/MgO system, the La_2O_3 catalysts do demonstrate a strong dependence on the presence of O_2. In contrast to Co-ZSM-5, no bend over in the conversion of NO was observed with increasing temperature. With La_2O_3, Zhang et al. speculate that N_2O rather than NO_2 might be the reaction intermediate. The reactivity of these oxides is attributed to the formation of surface methyl radicals. None of these studies describe the impact (if any) of water on the performance of La_2O_3. The activity of these oxides at higher temperatures in dry systems may be appropriate to very hot exhaust streams.

Loughran and Resasco [46] recently reported that Pd supported on acidic, non-zeolitic supports display some activity for methane reduction of NO_x in excess O_2. In particular, Pd on sulfated ZrO_2 exhibited modest activity.

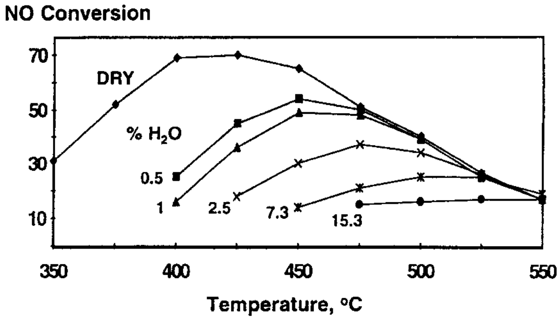

Fig. 4. NO reduction by methane in excess oxygen (3%) as a function of temperature and level of water vapor. Co-ZSM-5: GHSV = 7500, 500 ppm NO, 2000 ppm methane, Si/Al = 11.2. Reproduced with permission from Ref. [26].

2.3. Impact of water vapor on performance

As we continued our work in this area, we began to appreciate the importance of running reactions in the presence of water vapor [42]. During the combustion of NG, large amounts of water vapor (5–16%) are produced. Recall that one only needs to remove ppms of NO_x. Water, like NO_x, is a good Lewis base, and probably competes for the same sites on which NO_x reduction must occur. We recently reported [26,42] the impact of various levels of water (Fig. 4) upon the performance of Co-ZSM-5. The presence of water has a dramatic impact upon the rate law and kinetics of the reaction. With 10% water vapor, a dramatic loss in NO conversion to N_2 occurs. Fortunately, the inhibition in NO_x conversion appears reversible with Co-ZSM-5 (removing water from the feed, results in a return to the activity observed in a dry stream). Some of the inhibition caused by water can be regained by simply raising the reaction temperature. The initial bending over in NO_x conversion with increasing temperature (Fig. 4) is due to the impact of methane combustion (Eq. 4). With higher temperatures, the partial pressure of water on the surface of the catalyst is less (the equilibrium constant for water adsorption will be smaller at higher temperatures), thus the impact of water is less. Most of the inhibition occurs with low levels of water.

The dependence of the rate law upon water vapor, the dramatic differences in NO desorption [42], the limited hydrothermal stability of many of these zeolites, and the fact that commercially these catalysts must operate in very wet streams demands that more work needs to be reported using wet, simulated exhaust streams. Otherwise, scientists will continue to be led astray by the dramatic and important impact of water on the catalysts. For example, as described above, Ga–H-ZSM-5 is a more active catalyst under dry conditions than Co-ZSM-5, but in a wet atmosphere, Ga–H-ZSM-5 suffers a catastrophic loss in activity.

Interestingly, the presence of excess levels of water has a much more serious impact on the performance of the Cu-ZSM-5 catalyst for NO_x reduction by hydrocarbons. The copper system is simply not as thermally stable as the cobalt system in wet atmospheres. A number of engine tests [47–50] now describe the short term life performance of Cu-ZSM-5 catalysts in wet atmospheres at 500°C. On the other hand, Co-ZSM-5 (Si/Al = 12) can withstand (using N_2O decomposition as a test reaction) treatment in 2–7% water vapor for move than 72 h without a change in performance [51,52].

2.4. Impact of SO_2

Natural gas has trace levels of sulfur, hence, any catalytic system for NO_x removal must assess a catalyst's stability to low levels of sulfur compounds. We just released [53] some studies on the impact of SO_2 on the performance of these catalysts. SO_2 was chosen because it should represent the dominant form of sulfur under oxidizing conditions. Over a Co-ZSM-5 catalyst, in the absence of added water, the addition of 53 ppm SO_2 slightly decreased the conversion of NO at 500°C, but doubled the NO conversion at 550 and 600°C. In the presence of both SO_2 and 2% H_2O, a substantial decrease in the NO conversion was found at <500°C, but no change was seen at 600°C. Over a Co-FER catalyst, addition of 53 ppm SO_2 caused a sharp decrease in NO conversion! Thus the Co-FER catalyst is more sensitive to SO_2 than Co-ZSM-5. Interestingly, CH_4 selectivity for NO_x reduction was increased in the presence of SO_2. In summary, the effect of SO_2 is strongly related to the temperature of operation, the presence of water vapor, and the zeolite topology.

2.5. Related results and issues

Witzel et al. recently described the reactivity of a variety of hydrocarbons for NO_x reduction over Co-ZSM-5 and Co-FER [54]. By examining NO conversion at a constant flux of total carbon, they suggest that molecular sieving effects may become important with neopentane. While varying the hydrocarbon from CH_4 to substituted pentanes, plots of NO conversion to N_2 vs hydrocarbon oxidation appear to show comparable behavior. This suggests larger hydrocarbons may break up, and the fragments diffuse into the zeolite to react at the metal ion centers. Under dry conditions, Witzel et al. [54] reported somewhat higher activity for H-ZSM-5, which may be a result of the different reactant concentrations used.

In most of these studies of NO_x reduction by hydrocarbons, it is difficult to make direct comparisons among the various reports that seem to test catalysts at different conditions. It is preferable to run under conditions close to real exhaust compositions: more than 10 000 GHSV, NO ca. 50–800 ppm, O_2 ca. 10%, H_2O 12–16%, and minimal hydrocarbon. As Burch et al. have pointed out, differences in test results emerge at very high space velocities (60 000 GHSV), different levels and methods of loading the metal ion, and with the source of the zeolite. Also, we have found that it is unwise to extrapolate conversion data collected at high levels of NO to data collected at lower levels of NO.

There have been some recent reports that the catalytic reduction of NO_x by propene results in the formation of by-product HCN [55]. In all our studies with CH_4, we have never detected any HCN. We believe that significant HCN formation is not a concern when using CH_4 in place of higher olefins. Further, Spivey [56] recently reported that in their studies with oxygenates (alcohols) as reductants, no HCN was detected in the presence of excess levels of water vapor.

2.6. Mechanism

The mechanism for the use of methane as a reductant is probably quite different from that for other hydrocarbons. Further, the broad range of reactivity exhibited by widely varying catalysts (Co-ZSM-5, Ga-ZSM-5, SnO_2, La_2O_3, and H-ZSM-5) suggest that different mechanisms may be operable with different oxide catalysts [57]. Since Co-FER is still one of the most active catalysts, this author will focus the mechanistic discussion on that system in an effort to try to learn how to come up with improved catalysts.

A great deal of catalyst characterization was performed to aide in arriving at a detailed mechanism. TPD profiles of NO sorbed on Co-FER or Co-ZSM-5 indicate the presence of multiple types of adsorbed NO which appear from 100–400°C [25]. The dominant NO species adsorbed on Co-Y, Co-ZSM-5 and Co-FER is in a dinitrosyl form appearing at 1810 and 1897 cm^{-1} for Co-Y and 1810 and 1890 cm^{-1} (via FT-IR) for Co-ZSM-5 and Co-FER [29]. Upon exposure to O_2, nitrosyl species are converted at higher temperatures to NO_2 species. In situ IR measurements during a steady-state NO_2/CH_4 reaction at 400°C did not detect a measurable IR signal of any adsorbed species. This may be attributed to extremely small amounts of adsorbed molecules on the catalyst at these higher temperatures. Direct evidence for C–N bond formation during the NO_x/CH_4 reaction remains as a challenge and provides a basis for future research. Magnetic and XPS measurements indicate that the as prepared Co-FER catalyst contains Co^{2+}. The cobalt center appears to be coordinatively unsaturated [30]. NO_2 also reacts readily with CH_4 over these catalysts in the absence of any added O_2.

To address possible pathways for the NO reduction reaction, two important questions need to be asked: (a) how is CH_4 activated and (b) how is an N–N bond formed? As Burch and Scire [33] indicate, the formation of carbonaceous deposits is unlikely in O_2-rich feed streams. Drawing upon the results of our previous work, highlighted above, an earlier presentation [57], and a recent publication [30], a mechanistic scheme (Eqs. 5–12, below) was proposed which we believe best describes the NO_x reduction by CH_4 in the presence of excess O_2 involving the formation of $CH_3\cdot$ radicals as a key step and a nitro species as an intermediate. A less detailed scheme has been offered for In-ZSM-5 [38].

$$\text{Z-Co} + \text{NO} \rightarrow \text{Z-Co–NO} \quad (5)$$

$$\text{Z-Co–NO} + 1/2\ O_2 \rightarrow \text{Z-Co–NO}_2 \quad (6)$$

$$CH_4 + \text{Z-Co–NO}_2 \rightarrow CH_3 + \text{Z-Co–HNO}_2 \quad (7)$$

$$CH_3 + \text{Z-Co–NO}_2 \rightarrow \text{Z-Co–NO}_2\text{CH}_3 \quad (8)$$

$$\text{Z-Co–NO}_2\text{CH}_3 + \text{NO} \rightarrow N_2 + CO + H_2O + \text{Z-Co–OH} \quad (9)$$

$$\text{Z-Co–OH} + \text{NO} \rightarrow \text{Z-Co–HNO}_2 \quad (10)$$

$$2\text{Z-Co–HNO}_2 \rightarrow NO + NO_2 + H_2O + 2\text{Z-Co} \quad (11)$$

$$CO + 1/2\ O_2 \rightarrow CO_2 \quad (12)$$

(Z = zeolite)

The formation of an adsorbed NO_2 on Co^{2+} sites is a necessary step. Our TPD and IR studies suggest CH_4 does not adsorb on a 'bare' Co-zeolite at low temperatures. We also found that there was little CH_4 combustion when CH_4 and O_2 were fed over Co-zeolite catalysts at low temperatures. However, the presence of NO or NO_2 enhances the CH_4 conversion in a NO (or NO_2)/CH_4/O_2 feed [57]. Further, with Co-FER under differential reaction conditions at 400°C, CH_4 is consumed mainly for NO_x reduction instead of combustion. This suggests that NO_x plays a key role in activating CH_4. Cant and coworkers [58] studied NO reduction using CH_4 and CD_4 in the presence of excess O_2 over a Co-ZSM-5 catalyst and found that the ratio of CH_4 to CD_4 consumption is ca. 2.4 with a dry feed (1640 ppm NO, 2.5% O_2, 1040 ppm CH_4 or CD_4) at 375°C. These ratios are close to those expected for a primary kinetic isotope effect. They concluded that the rate determining step must include the breakage of a C--H bond in the CH_4 molecule. For catalysts that are known to generate methyl radicals (such as La_2O_3), it seems reasonable that methyl radicals must be involved in the mechanism of NO_x reduction. Our work suggests that this C–H bond breakage may be facilitated by surface NO_2 species. Perhaps CH_4 is catalytically activated by adsorbed NO_2 species through a cobalt bound NO_2 species, e.g., NO_2^-, forming $CH_3^\cdot$ radicals [56]. The $CH_3^\cdot$ radical may be formed by abstraction of a $H^\cdot$ from CH_4. In a series of fast steps, the $CH_3^\cdot$ radical could react further with a nitrito species forming CH_3NO_2 [30]. N_2 then forms by reacting the adsorbed CH_3NO_2 with a gas phase NO molecule (Eq. 9). Z-Co-HNO_2 formed from Eq. 7 can decompose readily to NO, NO_2 and H_2O or convert to HNO_3 [59]. CO formed from Eq. 9 is easily oxidized to CO_2 in an oxidizing atmosphere (Eq. 12), and Z-Co–OH may react with a NO molecule forming Z-Co–HNO_2 (Eq. 10). Alternatively, CH_3NO_2 can also be readily isomerized and subsequently decomposed on a catalyst. For our kinetic studies with Co-ZSM-5 and Co-FER, the rate determining step must include the cleavage of the C--H bond (Eq. 7), especially at low temperatures (350-450°C), whereas the formation of catalyst bound NO_2 (Eq. 5) can occur quite readily in this temperature range and is thermodynamically favored. The decomposition of a reaction intermediate (C--N species), e.g., CH_3NO_2 can also occur quite readily at moderate conditions and should not be a rate determining step. At high temperatures (more than 500°C), the reduced levels of NO_2 on the catalyst, due to desorption and conversion to NO, severely limits the overall reaction rate. Therefore, a slower increase in the NO_x conversion occurs with increasing temperature. A side reaction, i.e., CH_4 combustion, can proceed via a parallel path on separate Co^{2+} sites. This does not alter the rate determining step but decreases the effective concentration of CH_4, thus decreasing the NO_x reduction rate. Similarly, water has a significant impact on the NO_x reduction rate but does not affect the rate determining step; water simply reduces the sites available for NO_x reduction.

As indicated earlier, the dramatic difference in composition between Co-ZSM-5 and Ga-ZSM-5 and the very different dependence on water vapor is suggestive that a different mechanism may be operational with Ga-H-ZSM-5. Kikuchi and Yogo have recently [38] elaborated on their work with the Ga system and suggest that NO oxidation occurs on Brønsted acid sites, while the NO_2/CH_4 reaction occurs on the Ga sites. In order to explain the relative inactivity of Ga/alumina, they also point out that the Ga site on a zeolite is very different from that on alumina. With NO/CH_4, CO is an intermediate product, but with NO_2/CH_4, CO_2 is the primary product. Thus they suggest that a common intermediate from the reaction of NO_2 with CH_4 further reacts either with NO or NO_2 to produce CO or CO_2, respectively. They believe that both Ga and In-ZSM-5 operate by similar mechanisms. However, they believe In-ZSM-5 is much less sensitive to the presence of water.

3. Summary

For the catalytic reduction of NO_x by CH_4 in the presence of O_2, Co-ZSM-5 and Co-FER appear to be uniquely more reactive than other transition metal ions. A number of newer materials have recently been announced, but the comparative tests under wet atmospheres have not be completed by other investigators, which makes direct comparison difficult. It would appear that under simulated exhaust stream conditions, Co-FER is one of the better catalysts; however, in the presence of 2% water vapor and ppm levels of SO_2, both Co-ZSM-5 and Co-FER show comparable activity at 600°C. None of these catalysts are sufficiently effective in wet atmospheres. Under wet atmospheres, we estimate that Co-FER is about a factor of four too low in activity for commercial application in stationary engines. Versus traditional methods of NO_x removal with ammonia, this technology still has considerable potential, but the technology awaits another 'invention.' Progress in this field will accelerate if all investigators adopt comparable reaction conditions which mimic typical exhaust streams, especially with the addition of high levels of water vapor.

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