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Catalysis Today 33 (1997) 251-261

CATALYSIS TODAY

Mechanistic study of NO reduction with methane over Co^{2+} modified ZSM-5 catalysts

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Abstract

NO reduction with methane over Co-ZSM-5 has been studied in an oxidizing atmosphere. Although the activity was reduced due to the poisoning of oxygen, NO decomposed over Co-ZSM-5 to nitrogen and oxygen in two different temperature ranges, 100–300°C and > 400°C. This suggests the presence of two types of Co^{2+} cations in ZSM-5. The adsorption of NO, NO_2 and CH_4, as well as the reduction of NO with methane in O_2 were studied with in-situ diffuse reflectance Fourier-transform infrared spectroscopy (DRIFT). NO and methane molecules were only weakly adsorbed on Co-ZSM-5, and would desorb completely at the reaction temperature. The presence of oxygen was found to enhance the NO interaction with Co-ZSM-5, leading to the formation of adsorbed NO_2 intermediates. The adsorbed NO_2 would activate methane molecules and yield hydrogen and methyl radicals, which could in turn react with NO_2 to generate nitromethane intermediates. A tentative reaction mechanism has been proposed to elucidate the production of N_2, N_2O, H_2O, formaldehyde and CO_2.

Keywords: Mechanistic study; NO reduction with methane; Co^{2+} modified ZSM-5 catalysts; ZSM-5 catalysts

1. Introduction

The development of effective catalysts for exhaust emission control is of increasing interest since fossil fuel combustion to supply energy contributed greatly to atmospheric pollution. Designing more effective boilers, gas turbines and engines, as well as controlling air/fuel ratio would help minimize the emission of CO and volatile organic compounds (VOC). Better hydrodesulfurization in fuel refinement would lead to reduced emission of SO_x in flue gas. To achieve better fuel efficiency, lean combustion is desirable but it involves higher temperatures which would generate more NO_x. Nitrogen oxides are regarded as atmospheric pollutants which cause acid rain. They also react with VOC to produce photochemical smog, leading to the depletion of ozone.

To avoid the generation of nitrogen oxides at high temperatures, combustion of fossil fuel in pure oxygen represents an alternative for power plants and boilers, but is inapplicable for automotive engines. Current efforts on NO_x removal have therefore been focused on post-remediation technologies, such as direct decomposition and selective catalytic reduction (SCR). Since most NO decomposition catalysts do not have a high, stable activity [1] or a resistance to the

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PII S0920-5861(96)00117-4

high water content present in the exhaust [2], much attention remains devoted to SCR development. In the early 1990s, Iwamoto and Hamada [3] discovered that NO could be selectively reduced to nitrogen over Cu-ZSM-5 catalysts by most hydrocarbons, except methane. Subsequently, a series of studies showed that many other metal oxides [4,5] and modified zeolites [6,7] were also very active towards NO reduction with hydrocarbons. However, reductants such as CO, H_2 or CH_4 were widely believed to be catalytically non-selective to NO reduction since they were more active towards catalytic combustion.

In 1992, Li and Armor [8,9] discovered that methane could selectively reduce NO to nitrogen over Co- or Mn-exchanged ZSM-5 catalysts with very high, stable activities over a broad temperature range. Oxygen, a poison to most of the NO decomposition catalysts, enhanced the catalytic activity in this reaction. They also reported that the Co-ZSM-5 was more resistant to water and dealumination compared to Cu-ZSM-5 [10]. Catalyst deactivation via formation and aggregation of cobalt oxides in Co-ZSM-5 was hardly noticed. This catalyst further demonstrated moderate tolerance to sulfur poisoning [11]. In addition to the efforts on metal-ion modified ZSM-5, Li and Armor [12] and Yogo et al. [13,14] found that Ga-, In- and even H-modified ZSM-5 also demonstrated a stable high activity towards selective NO reduction with methane. Unlike the transition metal cations, Ga, In and H cations lack variability in their oxidation states at mild reaction conditions. This suggests that there may be an alternative mechanism for catalytic NO reduction over these non-metal modified ZSM-5 catalysts, or that no direct electron transfer is required between the reactants and the active sites over these non-metal (Ga, In, and H) or transition metal (Co and Mn) modified zeolites discussed.

Mechanisms of catalytic NO reduction with hydrocarbons have been summarized by Burch and Scire [6]. For mixed metal oxide catalysts, oxygen defects appear to be responsible for generating hydrocarbon radicals for further NO reduction and hydrocarbon combustion [15]. For modified zeolitic catalysts and reductants with long hydrocarbon chains, formation of coke, hydrocarbonitrile or isocyanate intermediates is thought to lead to catalytic NO reduction [16–18]. The mechanistic study of NO reduction with methane or longer chain hydrocarbons as a reductant has been conducted by Witzel et al. [19], Lukyanov et al. [20], and Yasuda et al. [21]. Their studies suggested that the SCR of NO with hydrocarbons might be fulfilled through a homogeneous radical reaction at the external surfaces of the catalyst crystals, and the activation energy required for free radical generation was lowered over the catalyst. In this report, a mechanistic study of NO reduction with methane over Co-ZSM-5 was conducted using in-situ diffuse reflectance Fourier-transform infrared spectroscopy (DRIFT). It illustrates that NO interaction with cations in ZSM-5 is not crucial for reduction with methane. Rather, the adsorbed NO_2 intermediates play a critical role for catalysis with Co-ZSM-5 for activating the combustion of methane and the reduction of nitric oxide.

2. Experimental

Modified ZSM-5 catalysts were prepared by aqueous ion-exchange of Na-ZSM-5 ($Si/Al = 13.6$) (Davison Chemical Division of W.R. Grace Co., lot no. 11659-46A) with 0.001 M $Co(acetate)_2$ aqueous solution at 80°C. The as-prepared Co-ZSM-5 was then dried at 120°C for 24 h and stored in a desiccator. The atomic ratio of Co/Al in the as-prepared Co-ZSM-5 was determined to be 0.53 using a Perkin Elmer Plasma 40 inductively coupled plasma (ICP) spectrometer.

Studies of the catalytic decomposition of NO and the catalytic NO reduction with methane over Co-ZSM-5 catalyst were conducted in a microreactor consisting of a 1/8″ OD quartz tube with a quartz frit for holding powder samples. The composition of the feed gas was monitored by MKS (model 247-C) mass flow controllers, and the reaction temperature was maintained with an Omega programmable temperature controller. Powder sample (50 mg) pretreated in helium at 500°C for 2 h was used for the catalytic studies. The gaseous products were analyzed by a Perkin Elmer Autosystem gas chromatograph with a thermal conductivity detector using a 1/8″ diameter 10 ft packed 5A molecular sieves column. Nitric oxide reaction is presented as percent conversion to nitrogen.

The mechanistic study of NO reduction with methane was carried out on BIO-RAD FTS-60A spectrometer using a Harrick Scientific diffuse reflectance cell with KBr windows. The sampling stage is in the middle of a stainless steel rod in which both the heating cartridge and thermocouple are embedded. The electrical leads from the heating cartridge and high vacuum cell (HVC) ensure that heat loss from the sampling stage to the outer chamber body is minimized. Circulating water is used to prevent the cell from overheating. The gas stream was introduced from a manifold which consists of control valves and mass flow controllers.

3. Results

3.1. Catalytic activity measurements

To test the NO decomposition activity over Co-ZSM-5, a NO-He gas mixture was introduced to the Co-ZSM-5 catalyst which had been pretreated in He at 500°C. The results showed that even at 100°C, NO could be catalytically decomposed to N_2 (Fig. 1). However this initial activity was quickly lost. No oxygen was detected in the exhaust, which could be due to strong chemisorption of the oxygen produced on Co-ZSM-5 or reaction of O_2 with NO downstream of the reactor. Negligible NO decomposition was observed upon raising the reaction temperature to 200°C and 300°C. Further increase of the temperature to 400°C gave rise to 30% NO conversion which gradually decreased with time. Separate tests also showed that NO decomposition did not occur over a Co-ZSM-5 which had been pretreated in He at 100°C or in 5% O_2–He gas mixture at 500°C for 2 h. The selective catalytic reduction of NO with methane over Co-ZSM-5 was also investigated. The maximum reduction activity was found at 450°C in a gas mixture of 1000 ppm NO–1000 ppm CH_4–2.5% O_2–He whereby the ratio of methane oxidation to NO conversion to N_2 was ~ 1 as previously reported by Witzel et al. [19].

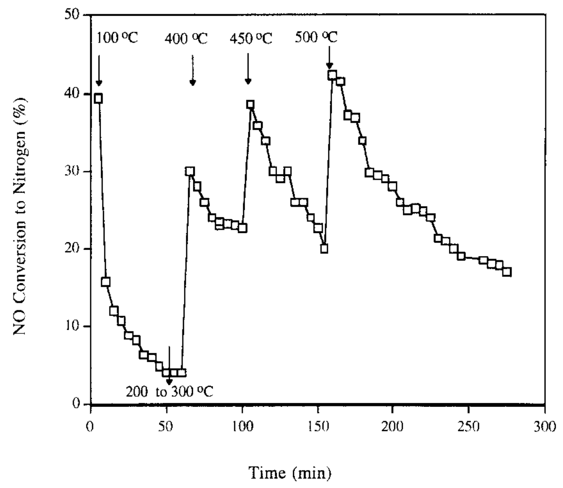
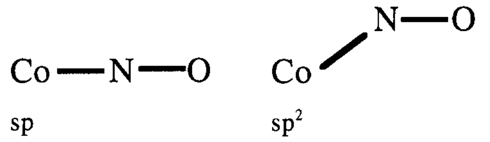


Fig. 1. NO decomposition to N_2 over Co-ZSM-5 as a function of time under increasing reaction temperatures. The as-prepared Co-ZSM-5 was pretreated in He at 500°C for 2 h before the catalytic testing. Reaction conditions: $W/F = 0.1$ g s/cc, 2250 ppm NO–He.

It has been proposed that NO reduction by hydrocarbons could proceed through NO decomposition over the active centers, followed by oxidation of hydrocarbons (by the oxygen species produced from NO decomposition) to regenerate the catalytic sites [22,23]. To examine the validity of this mechanism, the Co-ZSM-5 was exposed to NO at 450°C until the activity of NO decomposition was completely lost. The deactivated catalyst was exposed to 4670 ppm CH_4–He at 450°C for 2 h in attempt to 'regenerate' the NO decomposition active sites, and then purged with He for 1 h. No recovery of NO decomposition activity was noted over the Co-ZSM-5 catalyst regenerated with CH_4 by such procedure. Similarly, the deactivated catalyst could not be regenerated for NO decomposition by treatment with H_2–He at 450°C. These results indicated that CH_4 or H_2 would not act towards effective catalytic sites regeneration via the proposed reduction schemes for other hydrocarbons [22,23], confirming the findings of Witzel et al. [19].

3.2. DRIFT studies

The adsorption of NO on Co-ZSM-5 was examined in-situ with DRIFT at different temperatures. As illustrated in Fig. 2, three NO infrared bands emerged at 1812, 1865, and 1892 cm^{-1} as 2250 ppm of NO was introduced at 25°C to the Co-ZSM-5 sample which had been pretreated with He at 450°C. More importantly, the intensity of band at 1812 cm^{-1} was much stronger than that of the band at 1892 cm^{-1}. The 1865 cm^{-1} band is related to loosely bound NO in Co-ZSM-5 matrix since it is very close to the gaseous NO vibrational band of 1876 cm^{-1} [24]. The bands at 1892 and 1812 cm^{-1} have also been observed by Zhang et al. [25] in their transmission infrared study of NO adsorption on Co-ZSM-5 self-supporting wafer, and they were assigned to dinitrosyl adsorbates. The basis for their assignment was that the peak areas of these two bands underwent changes simultaneously, and NO temperature programmed desorption (TPD) study [25] also suggested the presence of dinitrosyl species since the ratio of the total amount of NO adsorbed species to Co in the sample was close to 2 (1.8–1.9). Closer examination of the infrared data of Ref. [25], however, reveals that the area ratio of the 1892 and 1812 cm^{-1} bands changed at different rates. In search of other possible assignments for these two bands, we note that the infrared study of NO adsorption on Cu-ZSM-5 [26] showed two bands at 1895 and 1807–1815 cm^{-1} which were attributed to adsorbed $NO^{\delta+}$ on Cu^{2+} and adsorbed $NO^{\delta-}$ on Cu^{+}, respectively. Dinitrosyls for Cu-ZSM-5 were associated with bands at 1824 and 1730 cm^{-1} [26]. The bands at 1892 and 1812 cm^{-1} in our study may therefore be more appropriately assigned to adsorbed $NO^{\delta+}$ and $NO^{\delta-}$ on Co^{2+} in ZSM-5. The 2:1 ratio of NO to Co can be related to the presence of loosely bound NO, evidenced by the NO band at 1865 cm^{-1}. Electron paramagnetic resonance (EPR) and X-ray photoelectron spectroscopy (XPS) studies of Co-ZSM-5 [27] have suggested that Co cations occupied two possible sites with low coordination symmetry in ZSM-5. The two infrared bands of NO are, hence, likely derived from the adsorption on these two different Co^{2+} with the following configurations with the structure constrained by the framework of ZSM-5:



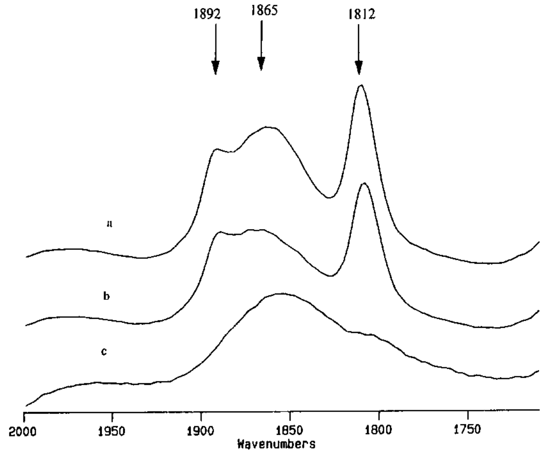


Fig. 2. DRIFT spectra of Co-ZSM-5 pretreated in He at 450°C for 2 h: upon exposure to a flowing NO/He mixture at a NO partial pressure of 0.23 torr under (a) 25°C, (b) 100°C, and (c) 450°C.

The adsorption of NO on Co-ZSM-5 was investigated at different temperatures. As illustrated in Fig. 2b and Fig. 2c, the NO bands decreased in intensity at 100°C, and almost disappeared as the temperature approached 450°C. This temperature effect on NO adsorption on Co-ZSM-5 is consistent with the TPD study reported by Zhang et al. [25] where two desorption peaks were observed at ca. 100 and 300°C, and all NO desorbed by 400°C. Therefore, it can be concluded that the NO adsorption on or interaction with Co-ZSM-5 is very weak at 450°C. Therefore, the adsorption of NO on Co-ZSM-5 cannot be a direct factor for attaining NO reduction with methane. Li and Armor [8] have also shown that the high activity of NO reduction with CH_4 could only be obtained as O_2 was added to the feed stream.

The oxygen effect on the characteristics of NO adsorption was also studied by DRIFT since the maximum NO reduction activity was noted only in the presence of O_2. The as-prepared Co-ZSM-5 was first pretreated with He at 450°C for 2 h, and then exposed to a gas mixture of O_2 and NO at 450°C. We noted that three new bands emerged at 1357, 1374, and 1410 cm^{-1} (see Fig. 3b–d) which could not be removed by flushing with He. These bands can be assigned to asymmetric and symmetric NO_2 bands adsorbed on Co cations as such bands have been observed in NO_2-cobalt complexes [28]. Even more interesting were the reduction of a band at 949 cm^{-1} and the appearance of a band at 652 cm^{-1} at a very fast rate as the $NO-O_2$ mixture was introduced to Co-ZSM-5. The band at 949 cm^{-1} has been assigned to a disturbed Si(Al)–O lattice vibration caused by the strong coordination perturbation of bonding-unsaturated Co^{2+} with framework oxygen in dehydrated Co-ZSM-5 [27]. Such strong interaction between cobalt and ZSM-5 disappeared upon catalyst exposure to the $NO-O_2$ mixture. The 652 cm^{-1} band is more likely due to Co–O vibration associated with the generation of a Co–oxygen complex, as discussed in [25]. In the higher frequency region, bands at 2411 and 2759 cm^{-1} appeared following the exposure of Co-ZSM-5 to the $NO-O_2$ mixture. These two bands were designated as the overtones of asymmetric and symmetric bands of adsorbed NO_2 on Co^{2+} since they were produced from $NO-O_2$ introduction and were found in many NO_2-containing organic compounds, such as nitromethane CH_3NO_2 [29].

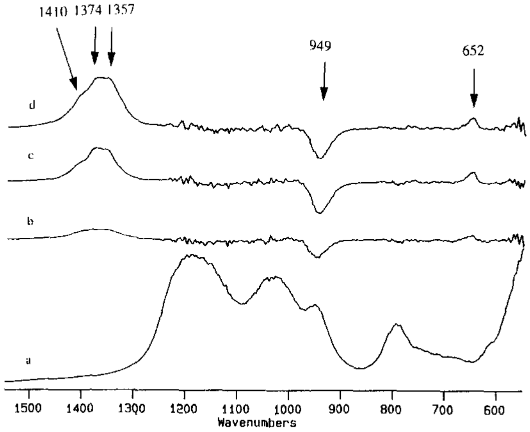


Fig. 3. (a) DRIFT spectrum of Co-ZSM-5 dehydrated in He at 450°C, and the difference spectra of adsorbed NO_2 on Co-ZSM-5 after exposure to a mixture of 1125 ppm NO–2.5% O_2–He at 450°C for (b) 5 min, (c) 15 min, and (d) 30 min.

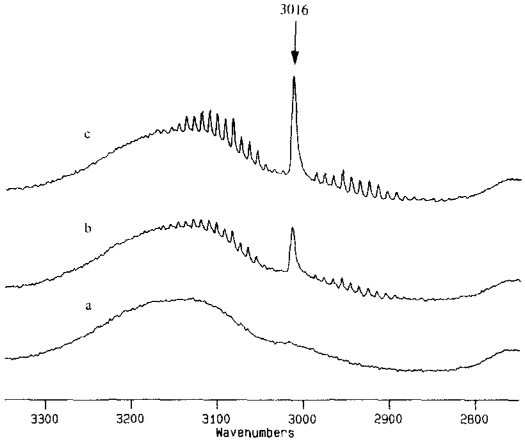


Fig. 4. DRIFT spectra of Co-ZSM-5 at 450°C (a) in flowing He, (b) in a flowing gas mixture of 2250 ppm CH_4–2.5% O_2–He, and (c) in a flowing gas mixture containing 4467 ppm CH_4 balanced with He.

The DRIFT spectra of methane adsorption on Co-ZSM-5 at 450°C are presented in Fig. 4b and Fig. 4c. The interesting feature was the symmetrically distributed and well-resolved rotational peaks by the sides of the sharp C–H stretching band at 3016 cm^{-1}. The intensities of these peaks increased in the absence of oxygen. The rotational side peaks might have arisen from the restricted rotation of methane in the zeolite matrix. There were no other bands noted which would indicate dissociative adsorption of methane on this catalyst, such as the C–H bending modes at 1300–1500 cm^{-1} which is infrared inactive for free CH_4 molecules. This suggested that there was no formation of longer chain hydrocarbons or chemically dissociated methyl groups from methane on the cobalt sites in ZSM-5 in the absence of NO and O_2.

At 450°C, the reaction intermediates were produced and consumed very rapidly so that they were difficult to be detected by infrared spectroscopy. Quenching has been frequently used to capture the reaction intermediates since many intermediates could not proceed to complete the reaction at a lower temperature. In this study, the DRIFT cell loaded with the catalyst under a gas flow of 1000 ppm NO–1000 ppm CH_4–2.5% O_2–He was cooled from 450 to 400°C for 1 h, then suddenly quenched down to room temperature. A DRIFT spectrum was obtained at 450, 400 and 25°C to illustrate the surface intermediates captured in this quenching experiment.

As illustrated in Fig. 5a, upon quenching to 25°C, adsorbed NO_2 bands at 1357, 1374 and 1410 cm^{-1} became more prominent, and a strong band at 1384 cm^{-1} and a very weak feature at 1308 cm^{-1} were noted. The 1308 and 1384 cm^{-1} bands could be associated with a NO_2 band with a different coordination with cobalt cations. In the range of 1450 to 1950 cm^{-1} (Fig. 5b), a band at 1860 cm^{-1} which is associated with physisorbed (or maybe gaseous) NO, and a strong 1634 cm^{-1} water bending mode were found. In addition, a weak band at 1760 cm^{-1} was detected, which is in the frequency range of dinitrosyl and carbonyl (C = O) adsorbed species. Since the corresponding symmetric vibration of the 1760 cm^{-1} band was not observed, we did not attribute this band to dinitrosyl species. One might argue that the band at 1860 cm^{-1} is the symmetric band for dinitrosyls, but this can be ruled out since the relative intensity of these two bands would not be consistent for such an assignment. Attribut-

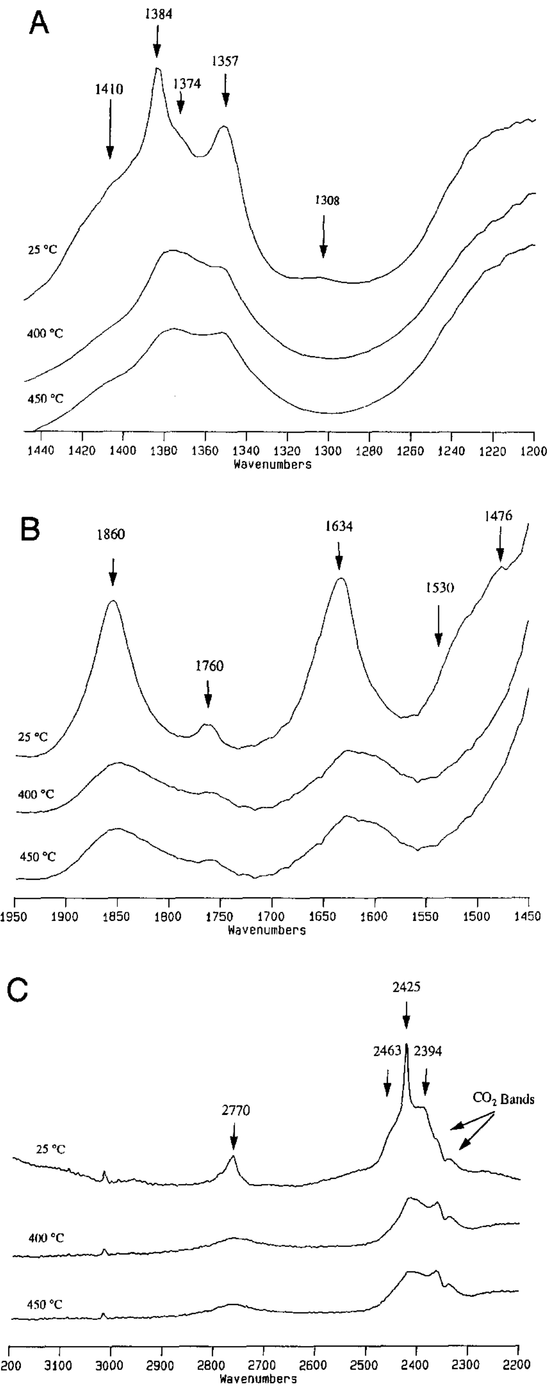


Fig. 5. DRIFT spectra of Co-ZSM-5 obtained under a gas flow of 1000 ppm NO–1000 ppm CH_4–2.5% O_2–He at the noted temperatures for frequency ranges: (a) 1200–1450 cm^{-1}, (b) 1450–1950 cm^{-1}, and (c) 2200–3200 cm^{-1}. The reaction temperature was lowered from 450 to 400°C for 1 h, and then rapidly quenched to 25°C.

ing the origin of this band to carbonyl group would also present a more consistent mechanism with the general understanding of NO reduction with methane over Co-ZSM-5, which is supported by an infrared study of Yasuda et al. [21]. The weak features around 1476 and 1530 cm^{-1} (Fig. 5b) have been reported as NO_2-cobalt complexes [28], so they may be assigned to NO_2 species coordinated to the Co^{2+} cations. Recently, Yasuda et al. [21] observed a broad feature at ~ 1560 cm^{-1} in their infrared investigation of catalytic NO reduction when nitromethane was introduced to Ce-ZSM-5 at 25°C. It is, therefore, more plausible to assign these weak features trapped from the quenching study to the reduction intermediate of NO reaction with methane since they were not observed at high reaction temperatures. This assignment was supported by the observation of nitrohydrocarbon bands in the range of 2200 to 2770 cm^{-1} as discussed in the following paragraph.

Four bands at 2394, 2425, 2463 and 2770 cm^{-1} were found in the quenched sample (see Fig. 5c). The bands at 2425 and 2770 cm^{-1} are the overtones of adsorbed nitrohydrocarbons [29]. The bands at 2394 and 2463 cm^{-1} only emerged from quenching the reaction intermediates. The similar shape and evolution of the 2300–2500 cm^{-1} bands to the 1300–1450 cm^{-1} bands suggest that the former are overtones of the latter. However, nitrogen-containing hydrocarbons, such as nitromethane CH_3NO_2, also possess infrared bands in the 2300–2800 cm^{-1} range [29]. The 2300–2500 cm^{-1} bands might, therefore, be related to the reaction intermediates between methane and adsorbed NO_2 on Co-ZSM-5.

4. Discussion

4.1. Nature and distribution of Co^{2+} in ZSM-5

Co^{2+} cations in ZSM-5 have been studied by EPR and XPS, and their +2 oxidation state was found to be very stable under both reducing and oxidizing atmospheres [27,30]. These results indicated that the redox characteristics of the cation should not be a key factor in the NO reduction with methane over the Co-ZSM-5 catalyst. Similar reasoning may also apply to explain the high activity on selective NO reduction over Ga-, In-, and H-ZSM-5 catalysts since all these cations cannot change their oxidation states during the reaction. The reaction pathway might be governed instead by the nature of interaction between the reactants and cations in ZSM-5 for these systems.

The NO decomposition results in Fig. 1 showed that Co-ZSM-5 has initial NO decomposition activity though the reaction is not a cyclic catalytic process since no oxygen was noted in the exhaust. The activity at low and high temperatures could be attributed to the two different low-symmetry Co^{2+} sites present in ZSM-5 found in the EPR and XPS studies by Sun et al. [27]. The decomposition activity could be associated with the presence of bonding-unsaturated Co^{2+} cations after the sample pretreatment in He at 500°C. The samples pretreated in He at 100°C or in O_2 at 500°C would not possess bonding-unsaturated Co^{2+} due to the strong adsorption of O_2 from the gas phase, and were found to be inactive towards NO decomposition. Our observation of NO decomposition without oxygen release confirms the speculation of Burch and Scire [6] that Co–oxygen species were formed when the dehydrated Co-ZSM-5 was treated in O_2-containing gas stream, causing the loss of NO decomposition activity. The interesting feature in O_2-poisoned Co-ZSM-5 was the high stability of the chemisorbed oxygen on Co^{2+} cations. The chemisorbed oxygen could not be removed by exposure to very strong reducing agents to regenerate the catalyst's NO decomposition activity.

4.2. Adsorption of reactants on Co-ZSM-5

The DRIFT spectra of NO adsorption at 25°C are very different for Co-ZSM-5 and Cu-ZSM-5.

No adsorbed NO_2, N_2O and dinitrosyl species were observed in the DRIFT spectra of NO-treated Co-ZSM-5. Despite the uncertainty in the assignment of 1812 and 1892 cm^{-1} bands, the DRIFT study showed that the intensity of NO bands did not vary with time, indicating that NO could not decompose at such a low temperature. The amount of NO adsorption decreased with temperature increase, and was negligible at 450°C where Co-ZSM-5 demonstrated the highest NO reduction activity with methane. This suggests that the interaction between NO and Co-ZSM-5 was very weak or that the equilibrium between NO adsorption and desorption was very rapid. This weak adsorption cannot activate NO decomposition after the Co-ZSM-5 was exposed to an O_2-containing gas stream.

The study of methane adsorption revealed that methane did not adsorb strongly on Co-ZSM-5, and that the rotation of methane molecule was hindered in the zeolite pore structures. The absence of C–H bending modes in the DRIFT spectrum of CH_4 adsorption was another indication of the weak interaction between methane and Co-ZSM-5 since strong chemical activation of methane molecule would have led to the cleavage of C–H bond, showing C–H bending modes in the range of 1300–1500 cm^{-1}. Our adsorption results thus indicated that NO or CH_4 individually could not be catalytically activated by Co-ZSM-5 below 450°C.

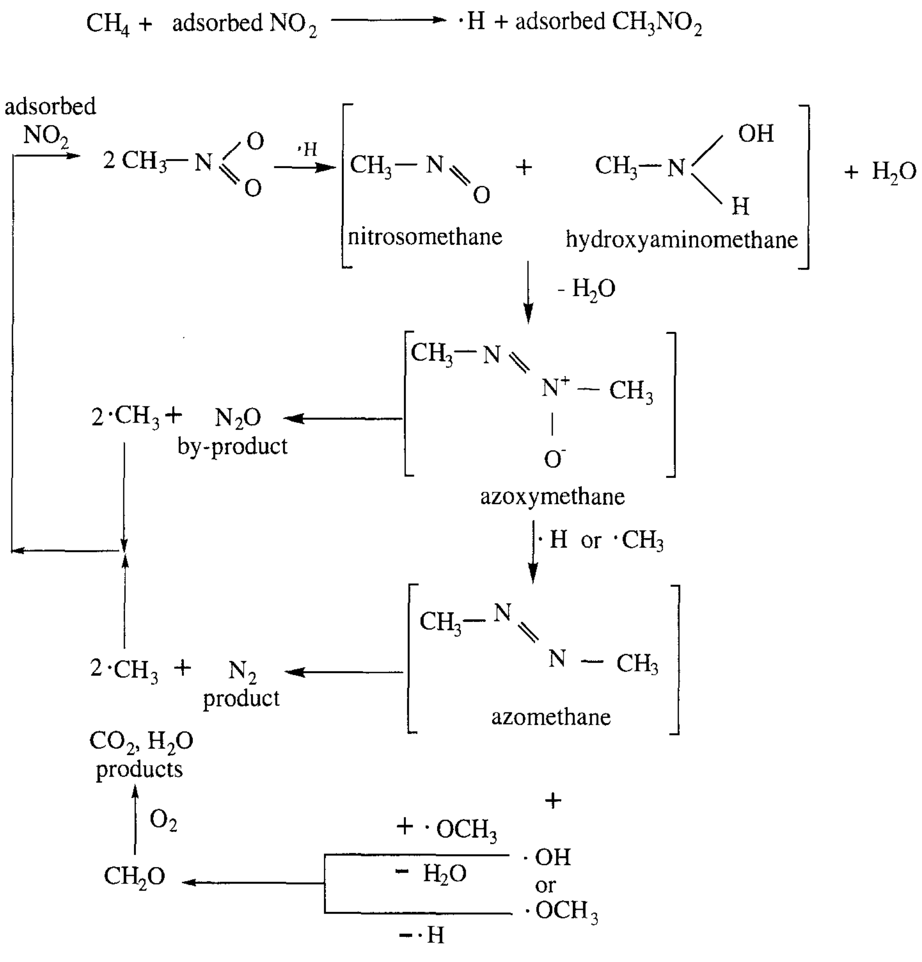
From studies on NO reduction with C_3 hydrocarbons over $Cu\text{-}ZrO_2$ and Cu-ZSM-5 catalyst, Bethke et al. [31] proposed that the adsorbed NO_2 on the metal active centers reacted with hydrocarbons to create nitrogen-containing surface intermediates, which further reacted with NO_2 or O_2 to form other intermediates, followed by NO reduction to N_2. Our DRIFT experiments manifested that the chemical nature of cobalt cations in ZSM-5 changed drastically when a gas mixture of NO and O_2 was introduced. The most prominent change was the interaction of Co^{2+} cations with zeolite framework oxygen. Both the disappearance of the perturbed Si(Al)–O band and the emergence of Co–O band upon exposure to a mixture of NO and O_2 indicated that Co^{2+} relaxed its coordination with the zeolite framework in the presence of NO–O_2 mixture, forming some structured NO_2 intermediates in ZSM-5. The creation of NO_2 intermediates in Co-ZSM-5 was further confirmed by the development of bands in the range of 1350–1400 cm^{-1}, which have also been observed in NO_2-containing cobalt salts [28]. The NO_2 intermediate on the surface of Co-ZSM-5 was found to be very stable, and could not be removed by flushing with pure He at 450°C. These adsorbed NO_2 species are very different from those found on the surface of Cu-ZSM-5 [26], and have lower vibrational energy. The lower frequency of NO_2 intermediates was another indication of the strong interaction between Co cations and the NO_2 species in ZSM-5. The DRIFT results agreed with the mechanism proposed by Bethke et al. [31], and suggested that the active species for NO reduction with methane in Co-ZSM-5 were the adsorbed NO_2 intermediates which modified the intrinsic nature of Co^{2+} in ZSM-5. They also confirmed the speculation by Burch and Scire [6] that the formation of Co–oxygen complex enhanced the interaction between Co-ZSM-5 and NO as the intermediate for NO reduction with methane.

4.3. Mechanism of NO reduction with methane over Co-ZSM-5

The methane and hydrogen regeneration experiments resulted in no recovery of NO decomposition activity. This indicates that NO reduction with methane over Co-ZSM-5 does not proceed via the NO decomposition mechanism, followed by regeneration of the deactivated decomposition sites with methane oxidation by the adsorbed oxygen species on the Co-ZSM-5 surface.

The observation of new infrared bands from the quenching experiments of NO reduction with methane over Co-ZSM-5 suggested the presence of carbonyl C = O band at 1760 cm^{-1}, a possible intermediate or a by-product of methane partial oxidation. A carbonyl band around 1725 cm^{-1} has been observed on Ce-ZSM-5 by Yasuda et al. [21], and was confirmed by their ^{15}NO isotope experiment. Lukyanov et al. [20] have reported that there was a 15–20% deficit in carbon balance for NO reduction with methane over Co-ZSM-5, and they attributed this to the formation of formaldehyde, which is consistent with our infrared observation. Since no band at 1760 cm^{-1} was present in the high temperature DRIFT spectrum, formaldehyde might have been the combustion intermediate of methane over Co-ZSM-5. This intermediate from the partial oxidation of methane might react with adsorbed NO_2 or O_2 in the gas phase to produce N_2, CO_2 and water, as Bethke et al. [31] proposed in their study of NO reduction with longer chain hydrocarbons over Cu-containing catalysts. However, it is more likely for formaldehyde to be further oxidized into CO_2 by oxygen.

Yasuda et al. [21] have studied the infrared spectrum of nitromethane over Ce-ZSM-5 and measured the reactivity of the adsorbed nitromethane with NO_2, O_2 or NO. They found that the intensity of a band ~ 1560 cm^{-1}, which was attributed to adsorbed nitrohydrocarbons, was reduced as the N_2 production in the exhaust increased, indicating that NO reduction with hydrocarbons proceeded through consumption of nitrohydrocarbon compounds. Bands at



Scheme 1.

~ 1500 and 2300–2800 cm^{-1} observed from our quenching experiments also suggested the formation of nitrogen-containing hydrocarbon intermediates, and the low intensity of the ~ 1500 cm^{-1} band confirmed that it was the residue of an unreacted intermediate trapped by the quenching. In contrast to the reports from Yukisu et al. [32], Yahiro et al. [33], and Bethke et al. [31], these nitrogen-containing hydrocarbon intermediates were not adsorbed NCO and CN since no band for NCO at ~ 2240 cm^{-1} was found in this study. The unique structure and chemistry of methane have to be considered in understanding the role of methane in NO reduction over Co-ZSM-5.

Combining all the information from this study and the other previous reports cited, the NO reduction scheme with methane over Co-ZSM-5 can be explained by the following scheme:

$$\mathrm{NO_2\ or\ NO + O_2}$$

$$\xrightarrow{\text{Co-ZSM-5}} \text{Adsorbed } \mathrm{NO_2} \text{ complexes on}$$

$$\text{Co-ZSM-5} \xrightarrow{\mathrm{CH_4}} \mathrm{CH_3NO_2} \text{ or } > \mathrm{C=O}$$

$$\xrightarrow{\mathrm{NO_2+O_2\ or\ NO+O_2}} \mathrm{N_2, CO_2, H_2O, N_2O}$$

In this proposed scheme, O_2 or $NO + O_2$ molecules will interact with bonding-unsaturated Co^{2+}, which is generated from dehydration of as-prepared Co^{2+}-exchanged ZSM-5, to form Co–oxygen complex. Such a complex will further interact with gaseous NO and O_2 to generate adsorbed NO_2 intermediates. As methane is introduced to the gas stream, it will react with the adsorbed NO_2 intermediate to form nitromethane intermediates. The nitromethane will finally react with NO_2 and/or a $NO + O_2$ mixture to produce nitrogen, water, and carbon dioxide. The NO reduction with methane over Co-ZSM-5 via the formation of nitrile or isocyanate intermediates is unlikely since Yasuda et al. [21] have demonstrated that the infrared bands related to these species were not diminished as the reaction proceeded. The nitrile or isocyanate species were, therefore, most likely the spectator by-products of the NO reduction. If nitromethane was the reaction intermediate, how were the $N=N$ bond and the product and by-product formed? A tentative reaction mechanism which may elucidate this issue is outlined in Scheme 1.

Methane has been found to readily produce $\cdot CH_3$ and $\cdot H$ radical species over metal oxides and zeolites [20,34,35]. In this proposed reaction pathway, we speculate that $\cdot CH_3$ and $\cdot H$ radicals are readily produced on the NO_2 modified Co^{2+} sites in ZSM-5 with lower activation energy, resulting in nitromethane intermediate species from reaction with NO_2 species. The nitromethane intermediates formed on the active sites of the catalyst desorb, diffuse into the gaseous phase, react with $\cdot H$ radicals to form nitrosomethane and hydroxyaminomethane. Azoxymethane and azomethane intermediates may then form through dehydration and reaction with $\cdot H$ or $\cdot CH_3$ radicals, respectively. These intermediates can be thermally decomposed to generate methyl radicals and N_2O or N_2. The $\cdot OH$ or $\cdot OCH_3$ radicals (produced along with azomethane) can react to produce formaldehyde, which can be easily oxidized by NO_2 and O_2 in the gas phase. In the proposed reaction pathways, only the nitrosomethane, hydroxyaminomethane, azoxymethane and azomethane have not been directly detected, and will be of interest for further investigation.

5. Conclusion

Results of NO decomposition study over Co-ZSM-5 indicated that Co^{2+} cations occupied two different positions in ZSM-5, and one was more accessible at lower temperature than the other, but both were active towards NO decomposition. The unsaturated bonding of Co^{2+} cations in He-pretreated ZSM-5 gave arise to the strong interaction between cobalt and oxygen to form Co–oxygen complex. DRIFT studies showed that little NO was adsorbed on Co-ZSM-5 at the reduction temperatures, but the interaction between NO and cobalt cations was greatly enhanced in the presence of O_2. DRIFT spectra of Co-ZSM-5 exposed to NO and O_2 also revealed the formation of adsorbed NO_2 species on the surface of Co-ZSM-5 catalyst. The experimental observations could be explained with a reaction scheme in which the adsorbed NO_2 species partially oxidize the methane molecule to form nitromethane. Such intermediates could readily form other nitrogen-containing hydrocarbons through reaction with $\cdot$H and $\cdot CH_3$ radicals, resulting in the final reduction products and by-products.

Acknowledgements

Support by National Science Foundation (CTS-9257223 and DMR-9400334) is gratefully acknowledged.

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