Active sites of H-ZSM5 catalysts for the oxidation of nitric oxide by oxygen

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The catalytic activities of H-ZSM5-18, H-ZSM5-150, Li-ZSM5-18, and H-Mag (numerical suffixes mark the Si/Al ratios of zeolites, H-Mag is the proton exchanged form of the layered sodium silicate, magadiite) were compared for the oxidation of NO by O_2 at different ratios of reactants at reaction temperatures from 25 to 600°C. H-ZSM5-18 typically has activity maxima near 25 and 400°C at most O_2/NO reactant ratios. Regardless of the partial pressures of reactants, $NO + \frac{1}{2}O_2 \rightleftharpoons NO_2$ equilibria are attained at 400°C and above. The H-ZSM5-150 and Li-ZSM5-18 zeolites are only active at temperatures near 25°C. H-Mag is practically inactive at the reaction conditions used. Results indicate that Lewis acidic lattice aluminium ions and silanol hydroxyls are not active in the oxidation of NO to NO_2 over H-ZSM5 zeolites. Brønsted acidic bridging hydroxyls are probably active sites for this reaction at temperatures above 200°C.

Keywords: nitric oxide; oxidation of nitric oxide; H-ZSM5 catalyst; selective catalytic reduction of nitric oxide; pollution abatement; automotive emissions; active sites of H-ZSM5 catalyst

1. Introduction

Mounting experimental evidence indicates that the oxidation of nitric oxide to nitrogen dioxide might be the first step in the selective catalytic reduction (SCR) of NO by NH_3 [1–5] or hydrocarbons [6–14] over many catalysts. Hence, understanding the mechanism of the oxidation of NO over these catalysts is important for elucidating the overall reaction pathway of the environmentally important SCR processes.

Certain mordenite (M) [1–3] and ZSM5 [6–14] zeolites are among the most studied SCR catalysts, for which the intermediacy of NO_2 has been proposed. However, only scarce and contradictory data have been published pertaining to the mechanism of the NO oxidation over these catalysts. One impediment to exploring the mechanism of this catalytic reaction is the limited information on the nature of the catalytically active sites of zeolites. According to several studies [15–17], the exchangeable cations of zeolites usually affect their catalytic activities for the oxidation of NO. In contrast, studies of the active sites of mordenites for the SCR of NO by NH_3 led to the conclusion that Lewis acidic lattice aluminum ions (L-Al) are responsible for the formation of NO_2 intermediates [1–3]. This conclusion is largely based on three experimental observations. (i) The reaction rates over three active mordenite catalysts increase in the sequence of H-M < Fe-M < Cu-M for the SCR reaction but decrease in the sequence of H-M > Fe-M > Cu-M for the oxidation of NO by O_2. (ii) L-Al sites were identified on the surface of dehydroxylated H-M. (iii) Increasing degrees of dealumination decrease activities of H-M zeolites for the oxidation of NO.

Not much is known about the active sites of ZSM5 zeolites in the oxidation of NO. A recent paper suggested that the copper cations of Cu-ZSM5 catalysts may be part of the active site ensemble because their catalytic activities for this reaction are much higher than those of the H-ZSM5 catalysts at temperatures near 400°C [11]. These experiments were done with a mixture of 500 ppm NO and 4.9% O_2 (balance N_2) using contact times of less than 0.015 s. Other papers indicate that identical NO conversions can be attained over both catalysts above 300°C when a contact time of 2 s is used for the reaction of 1032 ppm NO and 10% O_2 [7], and the catalytic activity of H-ZSM5 is higher for the reaction of 1000 ppm NO and 6% O_2 at 70°C than that of Cu-ZSM5 when the contact time is 0.5 s [16]. By analogy to H-M, a suggestion was made [14] that L-Al sites may be catalytically active in H-ZSM5, which also has favorable medium-pore structure to contact the reactants. This description is in line with the facts that the surface acidity of H-ZSM5 has been found to be quite similar to that of H-M and NO can adsorb on L-Al sites in H-ZSM5 at room temperature [18,19]. However, the active sites of ZSM5 zeolites for the oxidation of NO by O_2 to NO_2 have not been studied.

The present paper focuses on H-ZSM5 for several reasons. (i) For many metal exchanged ZSM5 zeolites, the formation of NO_2 is believed to be the initial step in the SCR of NO by hydrocarbons although other theories have also been advanced [20–22]. However, this has never been questioned over H-ZSM5. (ii) Although the effects of the inlet concentrations of NO and O_2 on the outcome of the SCR reaction are well documented, their effect on the catalytic formation of NO_2 intermediates has not been studied. (iii) Unlike most other ZSM5 catalysts, the only exchangeable cations of H-ZSM-5 are protons that form the well-characterized Brønsted acidic bridging hydroxyls (BA-OH). Therefore, if extra lattice sites are active in the catalytic oxidation of NO, they can only be BA-OH groups. (iv) It is conjectured that numerous metal exchanged ZSM5 zeolites that are active catalysts for the SCR of NO by hydrocarbons (e.g. Cu-ZSM5, Ga-ZSM5, and Pd-ZSM5) are bifunctional, i.e., the BA-OH sites and metal ions are both involved in the catalytic process [14,23–26]. Consequently, results pertaining to the catalytic role of BA-OH in H-ZSM5 may be pertinent to the role of BA-OH in a broad variety of ZSM5-based catalysts. (v) Recently, we have shown that homogeneous autocatalytic radical reactions are involved in the SCR of NO by propane over H-ZSM5 [27]. An SCR mechanism involving free radical chemistry has also been very recently proposed by Witzel and co-workers [13]. It is of interest to know if the intermediate step of NO_2 formation is a homogeneous non-catalytic reaction or a heterogeneous catalytic reaction over this zeolite at reaction conditions resembling those for the SCR of NO.

2. Experimental

2.1. CATALYSTS AND MATERIALS

ZSM5 zeolites are designated by a prefix to show their exchange cations, and a suffix to show their Si/Al ratio. For instance, H-ZSM5-18 is a proton exchanged ZSM5 sample having a Si/Al ratio of 18.

H-ZSM5-18 was obtained by calcining a sample of NH_4-ZSM5-18 (obtained from the PQ Corporation, lot # ZN-9, 80% crystallinity, 0.002 nmol Na/g, BET surface area ~ 460 m^2/g) for 24 h in air. Li-ZSM5-18 was prepared from the H-ZSM5-18 by solid state ion exchange according to the method of Beyer et al. [29]. Briefly, appropriate amounts of H-ZSM5-18 and LiCl at an equimolecular ratio of Li/Al were thoroughly mixed, pressed, crushed and sieved (see below). The mixture was then placed in a catalytic reactor, evacuated at 100°C, and then heated to 600°C at a rate of 20°C/min in 2 ℓ/h flow of He. The product Li-ZSM5-18 was finally cooled in He and kept in the reactor for the catalytic measurements. H-ZSM5-150 was purchased. (Grace Co., sample # S-115, 90% crystallinity, 0.006 mmol Na/g). The proton exchanged magadiite, H-Mag, is a crystalline silicic acid ($H_2Si_{14}O_{29}\cdot 5H_2O$) with a layered structure [30–32] and was synthesized in the Hungarian Hydrocarbon Institute (0.048 mmol Al/g, 0.015 mmol Na/g, BET surface area ~ 80 m^2/g).

Reactants were certified mastergases from Scott (0.1, 1, and 10% O_2 in He) and instrument grade gases from Linde (pure NO), Smith Welding Co. (pure O_2), and Liquid Carbonic (pure He and 1% NO in He). Except for helium, which was passed through a General Electric Go-Getter purifier, all gases were used as received.

2.2. ACTIVITY MEASUREMENTS AND ANALYSIS

The powdered samples were pressed at a pressure of 6.9×10^7 Pa (688 atm) into pellets, crushed, and 1 cm^3 (~ 0.5 g) of the 0.3–0.6 mm diameter fraction was selected for catalytic measurements. The catalyst samples were placed on a porous quartz frit of a fused quartz reactor (10 mm i.d.) of the flow-through type and covered with quartz wool. Prior to the first catalytic experiments, all samples were evacuated at 250°C for 2 h and pretreated in a flow of He (100 ml/min) for 2 h at 600°C. No further treatment was done during the catalytic tests. Catalysts were kept in helium overnight.

For catalytic measurements, appropriate amounts of oxygen and nitric oxide were mixed with a balance of helium to achieve a total flow rate of 160 ml/min (space velocity, SV = 9600 h^{-1}) at 1 atm (1.0×10^5 Pa). Flow rates were controlled by Brooks mass flow controllers. The reactor system is constructed of stainless steel with bellows seal valves and is leak free. Details of the system are described elsewhere [33–37].

Separate measurements of the nitric oxide and total NO_x contents in the reactor effluent were made using a Beckman model 951 chemiluminescent NO–NO_x gas analyzer and were compared with the nitric oxide contents at the reactor inlet to calculate the conversion of nitric oxide. The analyzer was calibrated with different concentrations of known gases. Due mainly to the error of reading an analog meter, it is estimated that the accuracy of the conversion is ±5% (repeatability plus linearity error). Repeated measurements on the same catalyst (after miscellaneous intervening reactions) gave a repeatability of ±10% (includes hysteresis of catalyst).

3. Results and discussion

To compare the activities of catalysts for the oxidation of NO by O_2 to form NO_2 and to screen the effect of reactant concentrations on the activities, three different series of reactant mixtures containing 0.1, 0.5, and 0.2% NO were studied. The concentrations of oxygen were varied from zero to 35% in order to attain comparable O_2/NO ratios at each NO concentration in the feed. Experiments were done at temperatures from 25 to 600°C at space velocities of 9600 h^{-1}. A typical (they can vary widely) concentration of NO in an automobile exhaust is 0.1%, a typical O_2/NO ratio is 5, and a typical space velocity is 50 000 h^{-1}.

Figs. 1 and 2 show typical temperature dependencies of NO conversions over the H-ZSM5-18 catalyst at various molar ratios of reactants for feeds containing 2 and 0.1% NO, respectively. The O_2/NO molar ratio is shown in boxes; the stoichiometric ratio (for complete reaction and no excess reagents) is 0.5. Dashed lines show the corresponding equilibrium conversions for the reaction $NO + \frac{1}{2}O_2 \rightleftharpoons NO_2$ [38,39]. Conversions above the equilibrium value are due to NO_2 formation in the cold parts of the system. Blank experiments in the absence of catalyst indicated significant homogeneous (or wall catalyzed) reaction between the nitric oxide and oxygen when the feed was 2% NO and the ratio of O_2/NO was high, fig. 3. The homogeneous oxidation is negligible when the NO concentration is 0.1% or the O_2/NO ratio is low.

The effect of the cold reaction on reactions done with 2% NO can be most easily

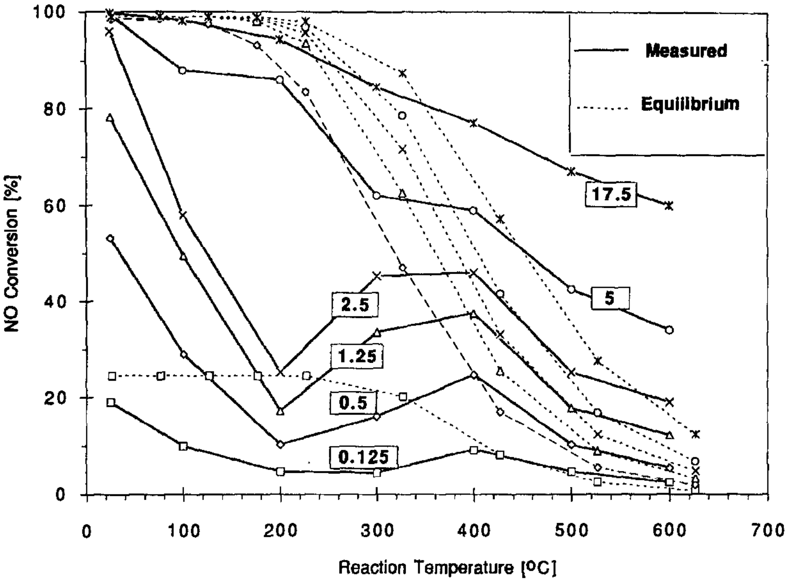

Fig. 1. Conversions of NO over H-ZSM5-18 at various reaction temperatures and O_2/NO molar ratios (shown in boxes) with feeds containing 2% NO; total $P = 1 \times 10^5$ Pa; SV = 9600 h^{-1}; dashed lines show the equilibrium conversions for the reaction NO + $\frac{1}{2}O_2 \rightleftharpoons NO_2$ and have the same symbol for plotting as the corresponding experimental curves.

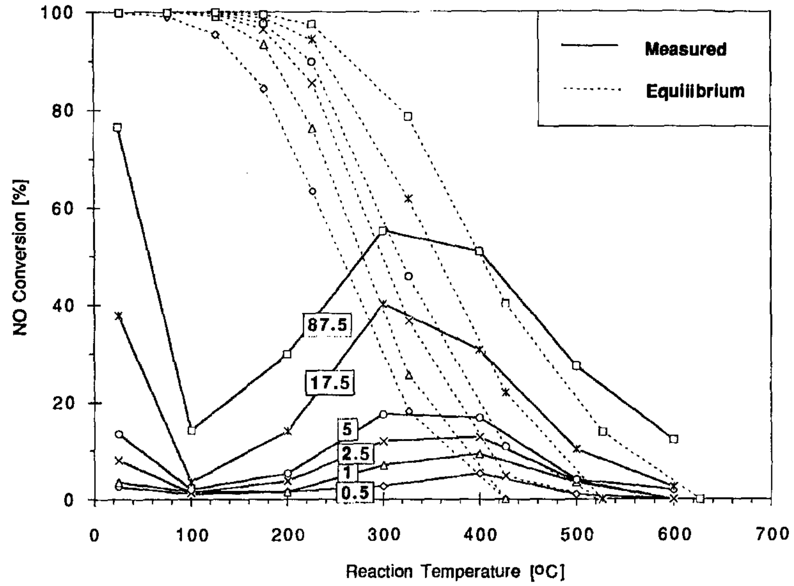

Fig. 2. Conversions of NO over H-ZSM5-18 at various reaction temperatures and O_2/NO molar ratios (shown in boxes) with feeds containing 0.1% NO; total $P = 1 \times 10^5$ Pa; SV = 9600 h^{-1}; dashed lines show the equilibrium conversions for the reaction NO + $\frac{1}{2}O_2 \rightleftharpoons NO_2$ and have the same symbol for plotting as the corresponding experimental curves.

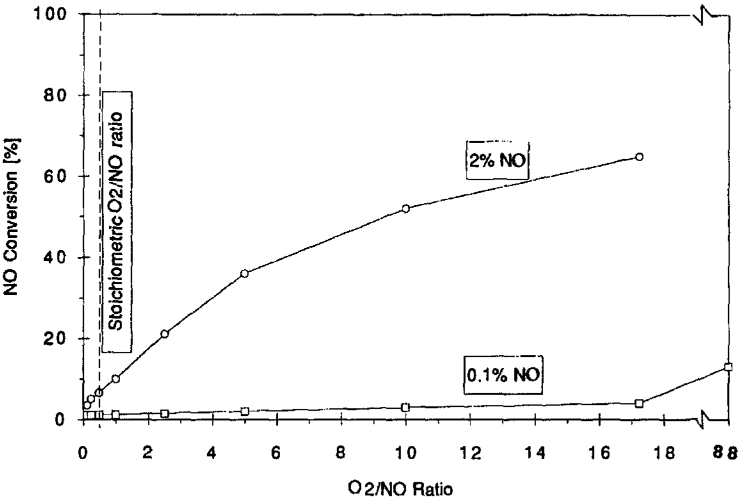

Fig. 3. Conversions of NO at various O_2/NO ratios in the absence of catalysts. NO concentrations in feeds: 2 and 0.1%; total $P = 1 \times 10^5$ Pa; SV = 9600 h^{-1}.

discerned by comparing the data of fig. 3 to the data of fig. 1 at room temperature. For example, at an O_2/NO ratio of 5, fig. 3 shows that the cold reaction gives a conversion of about 35%. The amount which occurs before and after the reactor is not known, but it is probably roughly equal, about 20% conversion in each part of the tubing. However, even though the residence time in a reactor is only about one-tenth that in the cold part of the tubing, fig. 1 shows that at room temperature the conversion is 100%. Hence, even at room temperature the catalyst gives a large conversion relative to the cold reaction. At a temperature of 600°C the catalyst would presumably give an equilibrium conversion, which is about 10%. Thus, the conversion is probably higher than this going into the reactor due to the cold reaction, the conversion drops to 10% in the catalyst bed, and then the conversion again rises to the observed value of about 35% due to the cold reaction downstream of the reactor. Thus, conversions exceeding the equilibrium value (based on the reactor temperature) can be observed. Consistent with this, the NO conversions in fig. 3 are virtually independent of the reactor temperature. For example, a feed of 2% NO with an O_2/NO ratio of 17.5 gave conversions of 65 and 75% at (empty) reactor temperatures of 25 and 600°C, respectively. The dependence of the amount of cold reaction on the feed stock also agrees with kinetic results for the homogeneous gas phase oxidation of nitric oxide, for which the rate of reaction shows a second-order dependence on the nitric oxide partial pressure and a first-order dependence on the oxygen partial pressure [4].

Comparing the data of figs. 1 and 2, one can conclude that the partial pressures of NO and O_2 at the inlet of the reactor have a stronger impact on the conversion of NO than their stoichiometric ratios. For example, at an O_2/NO ratio of 5 and a temperature of 300°C, the turnover frequency (based on the number of BA-OH sites) is 3.6×10^{-3} and 5.1×10^{-5} s^{-1} for feeds of 2% NO and 0.1% NO, respectively. At temperatures below 400°C, nearly equilibrium conversions are only obtained at 2% NO and at O_2/NO ratios of 17.5 and 5. At higher reactor temperatures, the conversion exceeds the equilibrium value in the reactor due to the cold reaction downstream of the reactor. For all feed stocks, equilibrium conversion is observed near 400°C (the solid and dashed lines cross). Thus, above 400°C, the reaction rate over H-ZSM5-18 is presumably high enough to reach equilibrium in the reactor for all ratios of O_2/NO and at NO concentrations of both 2 and 0.1%. These high reaction rates suggest (but do not rigorously prove due to additional sequential reactions) that equilibrium is also achieved during the SCR reaction. This in turn indicates that the oxidation of NO to NO_2 is not the rate determining step in de SCR reaction, since if it were then the aforementioned equilibrium would not be obtained. Also, if the formation of NO_2 were the rate limiting step, then other catalysts probably could not be more active than H-ZSM5, since it can give equilibrium conversion. However, many papers indicate that some metal exchanged ZSM5 zeolites are more active for the SCR reaction than H-ZSM5. The proposed free radical mechanisms [13,27] agree with this conclusion.

Except for the highest O_2/NO ratios in fig. 1, the activity curves in figs. 1 and 2 have two maxima. The minima near 100–200°C suggest that the oxidation of NO may proceed through two different reaction pathways below and above this temperature range. Diffusion control cannot play a significant role at the reaction conditions used since the Thiele modulus is less than 0.4. "Physical catalysis", i.e., homogeneous-like reaction between physisorbed NO and O_2 molecules, has been proposed to explain the high reaction rates at low temperatures [4,16,17] and the drop in activity with increasing temperature could be due to the declining number of adsorbed molecules with increasing temperature. A drop in the activity for the oxidation of NO to NO_2 with increasing temperature below 200°C has been observed over many ZSM5 catalysts [16]. However, others have not studied the reactions over a wide enough temperature range to observe the minimum reported here. Numerous studies [1,16,18,19,40–44] indicate that both NO and O_2 can adsorb on the surface of proton exchanged zeolites near room temperature forming measurable amounts of O_2^-, O^-, and NO^+ species coupled to Lewis acidic or basic surface sites. The decrease of adsorbed NO at increasing temperatures has also been reported [1,16,19,42,45]. A drop in the conversion with increasing temperature has also been reported for other catalytic reactions, the classic example being the hydrogenation of ethylene [28]. An increase in temperature results in an exponential increase in the activity *per covered site*, as determined by the *true* activation energy. However, the coverage of the surface can drop exponentially, as determined by the heat of adsorption. Thus, the overall *observed* activation energy can be negative. It is noteworthy that this is likely to only occur if the activation energy of the reaction is very low, as is the case for both olefin hydrogenation and NO oxidation (see figs. 1 and 2). Thus, it is probable that the declining number of adsorbed reactant molecules with increasing temperature is responsible for the drop in activity at temperatures below about 200°C.

At temperatures above 200°C, a different mechanism might be involved. Very recent results [46] indicate that NO may interact with the BA-OH sites of H-ZSM5 in this temperature range. Thus, the active sites for the activation of NO above 200°C may involve BA-OH groups.

To determine which sites are catalytically active on the surface of H-ZSM5, comparative experiments were done with zeolites containing significantly less L-Al sites (H-ZSM5-150) and BA-OH sites (H-ZSM5-150 and Li-ZSM5-18) than the H-ZSM5-18. Relative to H-ZSM5-18, Li-ZSM5-18 has zero concentration of BA-OH sites and the same concentration of L-Al sites, and H-ZSM5-150 has 1/8 the concentration of both BA-OH and L-Al sites. To see whether the shape of the zeolite lattice and/or its weakly acidic silanol groups (Si-OH) are of importance in the catalytic oxidation of NO by O_2, the activities of the non-zeolitic, crystalline, silicic acid, H-Mag, were also measured. Typical results are shown in fig. 4. Several conclusions can be drawn. (i) At 400°C, H-ZSM5-18 is the only catalyst that shows appreciable catalytic activity (above the homogeneous plus wall background level). (ii) Since Li-ZSM5-18 has the same concentration of L-Al sites but lower activity than H-ZSM5-18 at 400°C, the L-Al sites of ZSM5 catalysts are not the dominant active sites for this reaction at 400°C. (iii) Since H-ZSM5-150 has less L-Al sites but the same activity as H-ZSM5-18 at 25°C, the L-Al sites are not the dominant active sites at 25°C [18,19]. (iv) BA-OH groups might be active sites for the oxidation of NO near 400°C, because the catalytic activity of H-ZSM5-18 is higher than that of Li-ZSM5-18 and H-ZSM5-150, each of which has less BA-OH sites. (v) BA-OH

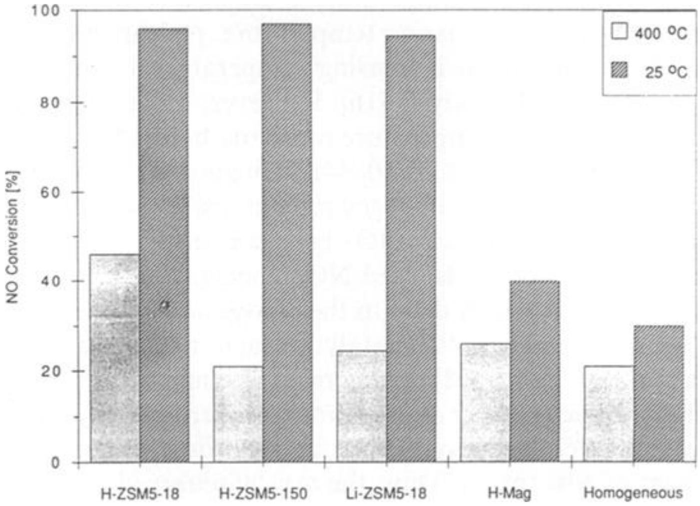

Fig. 4. Comparison of the catalytic activities of various catalysts for the oxidation of NO at 25 and 400°C; feed: 2% NO + 5% O_2 (O_2/NO ratio = 2.5) in helium; total $P = 1 \times 10^5$ Pa; SV = 9600 h^{-1}.

groups are probably not active sites for the oxidation of NO at 25°C, because the catalytic activity of H-ZSM5-18 is similar to that of Li-ZSM5-18 and H-ZSM5-150. (vi) Since the Si-OH groups of the slightly acidic H-Mag are virtually inactive for the oxidation of NO, they are probably also inactive on the surface of ZSM5 zeolites. However, the difference in activity could be partly due to the roughly six-fold difference in the specific surface areas of H-ZSM5 and H-Mag. (vii) The channel system of zeolites or the associated high specific surface area is an important requirement for the high catalytic activity at room temperature. The low activity of H-Mag at 25°C resembles the "physical catalytic" effect of silica gel and other non-zeolite oxides that has been known since the thirties [47].

The above results imply that at least one catalytic function of the BA-OH groups of H-ZSM5 catalysts during the SCR of NO by hydrocarbons is the formation of NO_2. This result is relevant to the possible catalytic role of BA-OH sites in other ZSM5 zeolites. Most proposed mechanisms for the SCR of NO by hydrocarbons assume that the activation of hydrocarbons via proton donation can be the sole catalytic function of BA-OH on zeolites [14,20,25,48,49]. An alternative mechanism is proposed here, in which HNO_2-type surface species, formed by the oxidation of NO over BA-OH active sites, are assumed to initiate the activation of saturated hydrocarbons in the SCR of NO over the H-ZSM5-18 catalyst. This proposal is consistent with a postulated homogeneous–heterogeneous formation of alkyl nitroxy intermediates in the SCR reaction over this zeolite [27].

At high space velocities ($\sim$ 160000 h^{-1}), Cu,H-ZSM5 is a more active catalyst than H-ZSM5 for both the oxidation of NO and the SCR of NO by hydrocarbons [11,14]. Consequently, accelerating the NO_2 formation can be one of the catalytic effects of copper cations in Cu,H-ZSM5. In contrast, the catalytic activity of Pd,H-ZSM5 has been very recently reported to be lower than that of H-ZSM5 for the oxidation of NO to NO_2 [26], although Pd,H-ZSM5 is a more active catalyst than either Cu,H-ZSM5 or H-ZSM5 for the SCR of NO by methane [26,50]. Since the initial formation of NO_2 is involved in the proposed mechanism of the SCR process over these catalysts, their relative activities suggest that the oxidation of NO proceeds over the BA-OH sites of the bifunctional Pd,H-ZSM5. It is conjectured [26] that a likely function of Pd is to activate methane. This picture supports our earlier notion pertaining to the possible importance of a combined dehydrogenation effect of the metal atoms of bifunctional catalysts and of O_2 (or NO_2) in the SCR of NO by saturated hydrocarbons [27].

4. Conclusions

(1) The oxidation of NO by O_2 to NO_2 is heterogeneously catalyzed at a much faster rate than the background (homogeneous plus wall) reaction near 25 and 350°C. Above 400°C the heterogeneous rate is probably fast enough to reach equilibrium at all reaction conditions studied here. At temperatures of about 200°C

(2% NO) or 100°C (0.1% NO) the observed conversion gives a minimum and is about the same as the background conversion, indicating low catalytic activity in this temperature regime. This suggests that the heterogeneous reaction might occur by a different mechanism below and above this temperature.

(2) Equilibrium is attained over H-ZSM5-18 for the reaction $NO + \frac{1}{2}O_2 \rightleftharpoons NO_2$ at 400°C and above at all reaction conditions used. This suggests that equilibrium is also achieved during the SCR reaction which would indicate that the oxidation of NO to NO_2 is not the rate determining step in the SCR reaction. Hence, to be more active for SCR than H-ZSM5, other catalysts must be more active for a reaction step subsequent to the formation of NO_2.

(3) The L-Al and the Si-OH sites of H-ZSM5-18 are probably not active sites in the catalytic oxidation of NO.

(4) BA-OH groups are probably active sites for the oxidation of NO over the H-ZSM5-18 at high temperatures but not near room temperature.

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