Selectivity-determining role of C_3H_8/NO ratio in the reduction of nitric oxide by propane in presence of oxygen over ZSM5 zeolites

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Received 13 January 1998; accepted 23 February 1998

The reaction of ($NO + C_3H_8 + O_2$) can result in selective formation of NO_2 over H-ZSM5, Cu,H-ZSM5, Ag,H-ZSM5, and Li,H-ZSM5 catalysts when the concentrations of NO and O_2 are 0.1 and 9%, SV $> 60{,}000$ h^{-1} (typical for automotive exhausts), and $C_3H_8/NO < 1$. Despite stoichiometric excess of reductant hydrocarbon below this limit, the *in situ* formed NO_2 *does not react* with C_3H_8, thus conversion of NO to N_2 is negligible. NO can be reduced by C_3H_8 selectively to N_2 *only* when $C_3H_8/NO \geqslant 1$. Contrary to many suggestions the reaction temperature, concentration of oxygen, space velocity, and type of exchange ions have minor influence on the selectivity for N_2. These parameters affect the rates of reactions ($NO + O_2$), ($C_3H_8 + NO_x$) and ($C_3H_8 + O_2$), therefore they also affect the production of N_2 in the HC-SCR process, but only when the ratio of C_3H_8/NO permits. The metal-exchanged zeolites were prepared *in situ* by solid-state ion exchange from H-ZSM5. Despite the low degree of copper exchange (63%), Cu,H-ZSM5 produces substantially more N_2 than H-ZSM5, Ag,H-ZSM5, or Li,H-ZSM5. However, the selectivity for N_2 is lowest over Cu,H-ZSM5, which also produces considerable NO_2 in the reaction of ($NO + C_3H_8 + O_2$) even at $C_3H_8/NO \geqslant 1$. Contrary to prior findings, the catalytic activity of Cu,H-ZSM5 for the oxidation of NO by O_2 to NO_2 in absence of hydrocarbon was comparable to that of H-ZSM5 at high space velocities (2.3 l g^{-1} min^{-1}). By replacing 30 and 40% of the protons of H-ZSM5 by Ag^+ and Li^+ ions in Ag,H-ZSM5 and Li,H-ZSM5, respectively, the catalytic activity for this reaction becomes negligible at temperatures $\geqslant$100 °C. Some mechanistic consequences of these experimental observations are discussed.

Keywords: lean NOx, SCR, reduction (selective catalytic), selectivity, nitrogen oxide, propane, ZSM5 catalysts

1. Introduction

The promising commercial potential of the selective catalytic reduction of NO by hydrocarbons (HC-SCR) for NO_x emission control in oxygen rich combustion exhausts is well known [1–3]. For not fully explored reasons, some ZSM5-type zeolites are the most active and selective HC-SCR catalysts at reaction conditions resembling those in the catalytic converters of automobiles [3,4]. Unfortunately, there are still many technical barriers that must be overcome before these catalysts can be commercialized.

An adequately understood reaction mechanism could facilitate the development of effective and durable catalysts. However, the HC-SCR process appears to be extremely complex. The selective conversion of a mixture of ($NO + O_2 + C_xH_y$) to ($N_2 + CO_x + H_2O$) includes several reaction steps and there is no agreement what are the initial and subsequent reactions. Furthermore, a large body of papers suggests that the HC-SCR process might follow several different reaction pathways. The actual sequence of reaction steps seems to depend on many factors, including the composition of catalysts, structure of hydrocarbons, concentration and ratio of reactants, space velocity, and reaction temperature. The overall subject of this paper is the comparison of the effect of some parameters on the yield of N_2 in the reaction of ($NO + C_3H_8 + O_2$).

The impact of reaction temperature and concentration of reactants on the production of N_2 in this reaction has recently been studied in details over a H-ZSM5 catalyst [5]. Despite a vast number of similar experiments over this catalyst before ([3,5–8], and references herein), this study demonstrated first that the reaction of ($NO + C_3H_8 + O_2$) can result in selective formation of either NO_2 or N_2. The selectivity for N_2 mainly depends on the ratio of C_3H_8/NO in the feedstock and other reaction parameters have only minor impact [5]. The importance of C_3H_8/NO ratio in the selectivity for NO_2 or N_2 is further examined here over Cu,H-ZSM5, Ag,H-ZSM5, and Li,H-ZSM5 catalysts at various reaction conditions. To contrast the catalytic effects of their exchangeable cations, these zeolites were prepared *in situ* by controlled solid-state ion exchange [9,10] from H-ZSM5. To emulate space velocities (SV) in the catalytic converters of automobiles [4,11], reactions were carried out at SV $= 64{,}000$ h^{-1} (2.3 l g^{-1} min^{-1}) instead of the previously used SV $= 9{,}600$ h^{-1} [5].

Cu-ZSM5 is the first and most studied active HC-SCR catalyst. This zeolite has been reported to be much more active for the catalytic oxidation of NO by O_2 to NO_2 at high space velocities than the H-ZSM5 [11]. Although many researchers believe that NO_2 is an important intermediate in the HC-SCR process over both zeolites [3,5,11–13], NO_2 production in presence of hydrocarbons has not been reported for Cu-ZSM5. Is it possible that this marked contrast to H-ZSM5 hints on some differences in the catalytic

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Table 1
Data for catalysts prepared by solid-state ion exchange from H-ZSM5 (Al: 0.859 mmol/g; Si: 15.424 mmol/g; protons determined by NH_4^+ exchange [5]: 0.424 mmol/g).

Catalyst	Salt added to 1 g H-ZSM5	Temperature of ion exchange (°C)	HCl evolved (mmol/g zeolite)	Exchanged H^+ (%)
Cu,H-ZSM5	0.85 mmol (0.114 g) $CuCl_2$	410	0.267	63
Ag,H-ZSM5	0.42 mmol (0.060 g) AgCl	700	0.169	40
Li,H-ZSM5	0.42 mmol (0.018 g) LiCl	400	0.126	30

function of H^+ and Cu^{2+} exchange ions? This issue is investigated here by focusing on the output of NO_2 in the presence and absence of C_3H_8. Numerous studies showed that the C_xH_y/NO ratio (e.g., $C_xH_y = C_3H_8$, i-C_4H_{10} or C_3H_6 [14–16]) affects the yield of N_2 in the HC-SCR of NO over Cu-ZSM5. Yet, the effect of this parameter on production of NO_2 has not been examined.

ZSM5 zeolites containing certain multivalent exchange ions, e.g., Cu^{2+}, Pt^{2+}, Co^{3+}, Ga^{3+}, or In^{3+}, are typically more active HC-SCR catalysts than those exchanged by monovalent cations. Among the few exceptions is Ag-ZSM5 which has been reported to be more active than Cu-ZSM5 for the HC-SCR of NO by C_2H_4 near 500 °C [17]. Little more is known about the catalytic activity of Ag-ZSM5 in HC-SCR related reactions [17,18]. The possible approach of HC-SCR process as a special combustion of hydrocarbons [5,7,12] and the well known epoxidation activity of silver are tempting to explore whether Ag-ZSM5 would promote the selective reduction of NO to N_2 when a saturated hydrocarbon, C_3H_8, is used as reductant or the effect of unsaturated ethylene is unique. Since Na-ZSM5 is only active for the reduction of NO_2 (but not NO) to N_2 and only when the reductants are unsaturated hydrocarbons [7,8,28], one could predict that the partial exchange of protons in H-ZSM5 by another alkaline ion, Li^+, will result in reduced N_2 production in the reaction of $(NO + O_2 + C_3H_8)$. Thus, Li,H-ZSM5 seemed to be appropriate to study how C_3H_8/NO affects the selectivity of H-ZSM5 for NO_2 or N_2 when its activity is suppressed. Except the known hydrocarbon radical producer, Li/MgO [19], lithium-containing catalysts have not been studied in the HC-SCR of NO. It is known that the oxidation of NO to NO_2 proceeds with comparable reaction rate over Li-ZSM5 and Cu-ZSM5 (but slower than over Na-ZSM5 and K-ZSM5) near 70 °C [20]. Li-ZSM5 has been found to be nearly inactive for this reaction above 200 °C but slightly active for the oxidation of C_3H_8 by O_2 near 600 °C [5,21].

2. Experimental

2.1. Catalysts and materials

H-ZSM5 zeolite was prepared by calcining an NH_4^+-exchanged ZSM5 sample from the PQ Corporation (Lot #ZN-9, 80% crystallinity, BET surface area ~460 m^2/g, total pore volume 0.28 ml/g, 0.002 mmol/g sodium, Si/Al ratio 18) at 550 °C for 24 h in air. The exchangeable proton capacity of this sample was found to be 0.424 mmol/g, i.e., roughly one-half of the total aluminum content (0.85 mmol/g) is associated with exchangeable protons. The procedure for determining the exchange capacity and some further properties of this zeolite have been reported elsewhere [5].

The Cu,H-ZSM5, Ag,H-ZSM5, and Li,H-ZSM5 samples were prepared *in situ* in the catalytic reactor (vide infra) from the H-ZSM5 zeolite by solid-state ion exchange [5,9,10,22–24] using 2 mol $CuCl_2$, 1 mol LiCl, and 1 mol AgCl per each mol exchangeable H^+ in the zeolite (table 1). The exchange level in these zeolites was determined in separate experiments by measuring evolved HCl during the synthesis. Appropriate amounts of H-ZSM5 and metal chlorides were thoroughly mixed, pressed, crushed, and sieved (see below). Approximately 1 g mixture was then placed between quartz wool plugs in a fused quartz tube (10 mm i.d.). The system was evacuated at room temperature and then heated to 400 °C (in case of Ag,H-ZSM5 to 700 °C) at a rate of 10 °C/min in 2 l/h flow of He. The end temperature was held until HCl evolution was observed (about 30–60 min). The effluent bubbled through two traps (each filled with 100 ml distilled water) to absorb evolving HCl. The solutions were continuously stirred by magnetic stirrers and neutralized with 0.1 N aqueous NaOH. The exchange level was calculated from the NaOH consumption. Results from repeated measurements agreed with each other within ±5%. Blank experiments with quartz powder instead of H-ZSM5 indicated some spontaneous evolution of Cl_2 (forming HCl or HOCl in H_2O) from $CuCl_2$ but not from the other salts. The corresponding roughly 10% $CuCl_2$ consumption was subtracted when the exchange of copper into the zeolite was calculated.

The reactants for the catalytic measurements were certified mastergases from Scott (0.1% C_3H_8 in He, and 0.1, 1 and 10% O_2 in He) and instrument grade gases from Linde (NO), Liquid Carbonic (He, 1% NO in He, 1% C_3H_8 in He), Union Carbide (C_3H_8) and Smith Welding Co. (O_2). 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 H-ZSM5 and mixtures of H-ZSM5 plus metal chlorides were pressed into pellets, crushed, and the 0.3–0.6 mm fraction was used for catalytic measurements. A 0.15 cm^3 (0.069 g) catalyst sample was placed on quartz wool in a fused quartz reactor (~4 mm i.d.) of the flow-through type and also covered with quartz wool. The Cu,H-

ZSM5 and Li,H-ZSM5 samples were pretreated in vacuum by increasing the temperature gradually to 110, 250, 400 and 600 °C and keeping these temperatures until material evolution (drop in vacuum) was observed. This procedure was used for the pretreatment of the other two zeolites except two differences: (1) to avoid the collapse of the zeolite lattice, H-ZSM5 was only evacuated up to 250 °C then calcined in He flow at higher temperatures; (2) to ensure ion exchange [23], Ag-ZSM5 was calcined up to 700 °C. Catalytic tests were made after cooling the catalyst to room temperature in vacuum, switching to helium flow (100 ml/min), reheating the catalyst to the reaction temperature, and setting the appropriate flows of reactants. Catalysts were kept in helium between runs. No further pretreatment was done during the catalytic tests.

Catalytic activity was measured by passing a mixture of (0.1% NO + x% O_2) (x = 0, 0.05, 0.1, 1, 1.75, 3, 5 and 8.75) or (0.1% NO + y% C_3H_8 + 8.75% O_2) (y = 0.05, 0.1 and 0.2) in helium carrier gas through the catalyst to achieve a total flow rate of 160 ml/min (SV = 64,000 h^{-1}) at 1 atm (1.0×10^5 Pa). These reaction conditions seem to be appropriate for simulating the conditions in commercial catalytic converters of automobiles. For example, a typical model exhaust from a fuel economic, lean burn, gasoline powered car engine might contain 200 ppm NO, 800 ppm C_3H_6, and 7% O_2 and a typical space velocity for laboratory experiments is 45,000 h^{-1} [4]. A TECO (Theall Engineering Co.) temperature controller was used to maintain constant reaction temperatures. The control thermocouple was attached to the inside wall of the furnace. The temperature of catalyst was measured using a separate type K thermocouple (24 gauge special accuracy) attached to the outer wall of the reactor ($\Delta T \sim 5$ °C). To avoid error in comparing the conversions of NO to the calculated equilibria of NO/NO_2 [21], the catalyst temperature was carefully maintained slightly (0–5 °C) above the desired reaction temperature. The estimated temperature difference between different points of the catalyst bed was less than ±3 °C. Flow rates were controlled by Brooks mass-flow controllers. The reaction system is constructed of stainless steel with bellows seal valves. Leaking rate is $\sim 5 \times 10^{-7}$ ml/s. Details of the system are described elsewhere [5,21,25].

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 NO. 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). All other products were analyzed by gas chromatography using a GOW MAC 550P type chromatograph equipped with TCD detector using He carrier gas [5].

The NO and NO_x concentrations were monitored continuously by passing the total effluent gas stream through the NO–NO_x analyzer. Steady-state NO conversion was attained (as detected by the NO/NO_x analyzer) before GC analysis was done. The reactor effluent was then connected to the GC system and a gas sampling valve (loop volume ~0.52 cm^3) was used to inject samples into the gas chromatograph. Further details for the analysis have been reported elsewhere [5,25].

3. Results

3.1. Degree of ion exchange

Results pertaining to ion exchange are summarized in table 1. The solid-state ion exchange (SSIE) of zeolites with metal chlorides (MCl_x) proceeds according to the equation Z–OH + MCl_x → Z–OMCl_{x-1} + HCl, where Z represents the zeolite lattice [9,10,24]. For chlorides of typically monovalent elements, such as LiCl and AgCl, one can safely assume that monovalent ions, such as Li^+ and Ag^+, enter the zeolite. Thus, each mol LiCl or AgCl participating in the SSIE process releases 1 mol HCl and the exchange level can be calculated by measuring the amount of HCl evolved. Based on these measurements, the exchange levels in Li,H-ZSM5 and Ag,H-ZSM5 were found to be 30 and 40%, respectively. These results imply that 70 and 60% of the exchangeable bridging OH groups of the original H-ZSM5 zeolite remained intact in the Li,H-ZSM5 and Ag,H-ZSM5 samples, respectively.

The number of HCl molecules released in the SSIE reaction from chlorides of multivalent elements, such as $CuCl_2$, can depend on several factors. For example, when the next nearest Z–OH groups are close enough to each other for being bridged with the multivalent exchange ion, Z–O–M–O–Z or Z–O–M–O–M–O–Z type bridges might form thereby two or more HCl molecules (depending on the valence and the number of OH neighbors) per reacted metal chloride molecule will be released. Such close Z–OH groups are typical for zeolites having low (<5) Si/Al ratios, such as the X or Y structures. However, the Si/Al ratio in our H-ZSM5 sample is 18 and measurements with NH_4^+ exchange indicate that only every second aluminum atom is paired with exchangeable Z–OH sites [5]. Thus, each Z–OH group is separated by 36 Si–O bonds which seems to be too big a distance for bridging with Cu^{2+} ions. Therefore, it is reasonable to assume that mainly $CuCl^+$ ions replace the protons of this H-ZSM5 sample in the course of solid-state reaction with $CuCl_2$. For this reason, 1 mol evolved HCl per mol reacted $CuCl_2$ was taken into account for calculating the degree of copper exchange into Cu,H-ZSM5. Thus, the exchange level for copper was found to be 63%, i.e., the Cu,H-ZSM5 sample retained 37% of the exchangeable protons from the starting H-ZSM5 zeolite.

It should be noted that several authors stress the possible formation of $[Cu–O–Cu]^{2+}$ type bridges in copper-

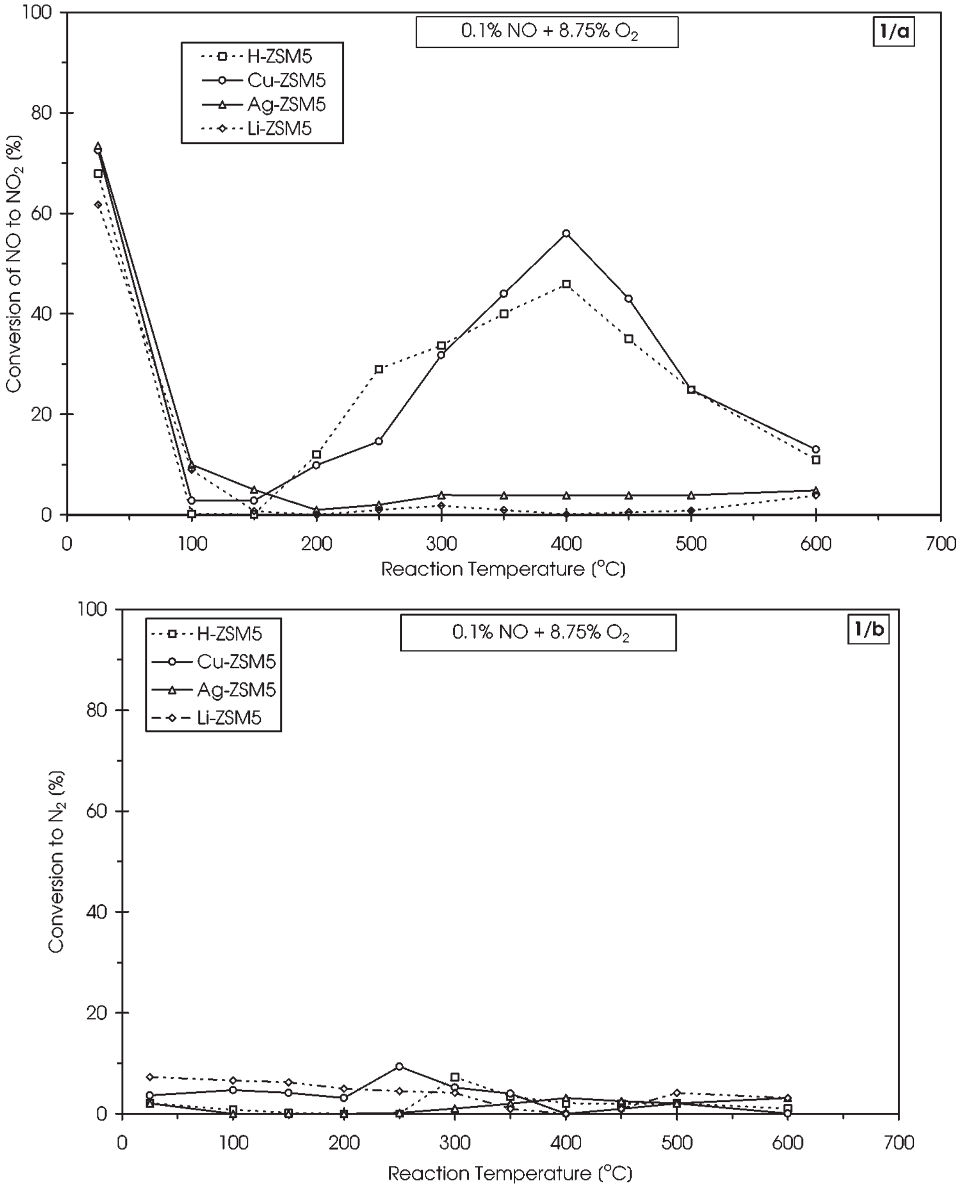

Figure 1. Temperature dependence of the conversion of NO to NO_2 (a) and N_2 (b) over various catalysts in the reaction of 0.1% NO and 8.75% O_2; total $P = 1 \times 10^5$ Pa; SV = 64,000 h^{-1}.

exchanged ZSM5 samples [26–28]. Since the diameter of double rings formed by 2 × 10 oxygen-bridged metal atoms (T atoms) at the intersections of the zeolitic channels is roughly 5.4 Å and the estimated linear O–Cu–O–Cu–O bond length is also 5.4 Å [39,40], it is possible that Z–O–Cu–O–Cu–O–Z bridges are formed between two opposite Al–O sites in these rings (four additional T atoms bind each double ring at the intersections, there are four such 24-T-atom rings per unit cell, and the diameters of the elliptical rings (channels) are 5.1/5.5 and 5.3/5.6 Å). The probability of such bridges is higher in those ZSM5 samples which have Si/Al < 24, because some of their double rings necessarily contain two or more Al–O units. If some copper atoms are bridged in our Cu,H-ZSM5 sample (Si/Al ~ 18), the level of exchanged copper is slightly lower than calculated above (63%), because in such cases two HCl molecules evolve from each reacted $CuCl_2$ (the 63% exchange level of protons remains intact).

It is also fair to note that, due to the partial ion exchange, the Cu,H-ZSM5, Ag,H-ZSM5, and Li,H-ZSM5 catalysts are mixed with 7.1, 3.5 and 1.2 wt% unreacted $CuCl_2$, AgCl, and LiCl, respectively. The catalytic activity of these chlorides is not known in reactions studied in this paper. However, the relatively low amounts and typically low specific surface areas of chlorides suggest that their impact on the catalytic activity of zeolites is probably negligible. Therefore, their potential catalytic effects have been neglected.

3.2. Oxidation of NO by O_2

The catalytic activities of H-ZSM5, Cu,H-ZSM5, Ag,H-ZSM5, and Li,H-ZSM5 for the oxidation of NO to NO_2

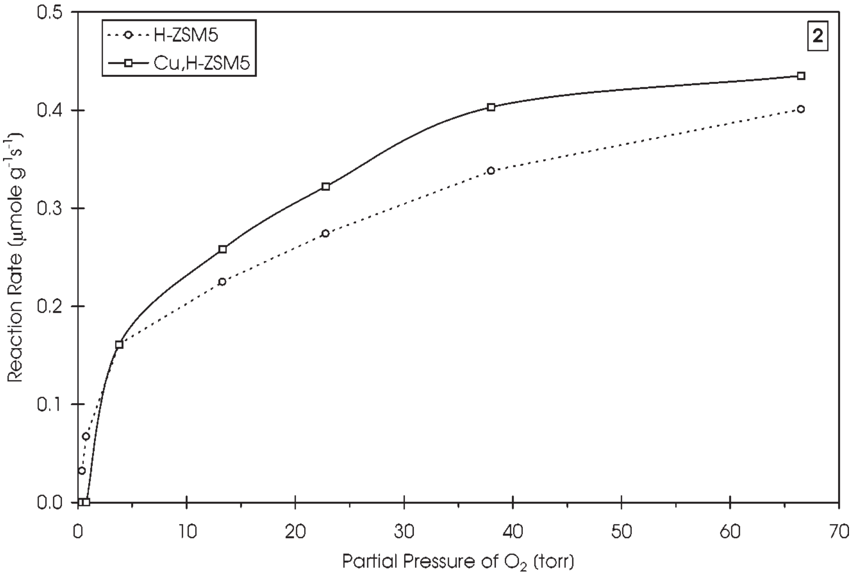

Figure 2. Effect of the partial pressure of oxygen on the reaction rate in the oxidation of NO to NO_2 over H-ZSM5 and Cu,H-ZSM5 zeolites at 500 °C; $P_{NO} = 0.76$ Torr; total $P = 760$ Torr (1×10^5 Pa); SV = 64,000 h^{-1}.

in absence of hydrocarbons were compared first. As expected [20,21], each ZSM5 sample showed substantial catalytic activity for this reaction near room temperature when ample oxygen was present in the feedstock. Using a mixture of 0.1% NO and various amounts of oxygen in He carrier gas, considerable conversion to NO_2 (>10%) only occurred when the concentration of O_2 exceeded about 1%, i.e., at molar ratios of O_2/NO > 10.

Figure 1(a) shows that the conversion of NO to NO_2 was around 70% over each catalyst in the reaction of (0.1% NO + 8.75% O_2) at 25 °C. This low-temperature reaction is probably due to a homogeneous-like reaction between physisorbed NO and O_2 molecules in the microporous solids [21]. Therefore, the exchange ions have only negligible effect on the reaction rate. Blank experiments indicated that measurable homogeneous or wall catalyzed reaction does not occur in absence of catalysts at any O_2/NO ratio or reaction temperature used in the present studies. Figure 1(b) shows that the decomposition of NO to N_2 remained below 10% over all zeolites, including the most active Cu,H-ZSM5 at the same reaction conditions as those in figure 1(a).

Figure 1(a) also indicates that only Cu,H-ZSM5 and H-ZSM5 have considerable catalytic activities for the oxidation of NO to NO_2 above 100 °C. The effect of oxygen concentration on the activity of these two catalysts is shown in figure 2. At these high space velocities (139 l/h total gas flow per gram zeolite), the catalytic activity of our Cu,H-ZSM5 sample (Si/Al ~ 18; exchanged Cu = 3.3%) was similar to that reported by Shelef et al. [11]. For example, figure 2 shows that the reaction rate is roughly 0.4 mmol(NO) g^{-1}(catalyst) s^{-1} when a mixture of 1000 ppm NO and 5% O_2 (38 Torr) with balancing He is passed through the catalyst at atmospheric pressure and 500 °C. Also at atmospheric pressure and 500 °C, Shelef et al. [11] passed a mixture of 600 ppm NO and 4.9% O_2 (balance nitrogen) at 160 l/h total gas flow per gram Cu,H-ZSM5 catalyst (Si/Al ~ 16; exchanged Cu = 2.4%), and found roughly 0.3 mmol(NO) g^{-1}(catalyst) s^{-1} reaction rate for the oxidation of NO.

However, these authors also reported that their H-ZSM5 sample (from different source as their Cu,H-ZSM5) was nearly inactive for the same reaction [11]. This finding is a frequently cited argument for explaining why Cu-ZSM5 is found to be more active than H-ZSM5 for the HC-SCR of NO by many hydrocarbons: NO_2 is a proposed reactive initial intermediate in the HC-SCR process for both catalysts, hence more NO_2 on Cu-ZSM5 would result in more N_2 over this catalyst than over H-ZSM5 [3]. Figures 1(a) and 2 clearly indicate that the catalytic activities of H-ZSM5 and Cu,H-ZSM5 for the oxidation of NO by O_2 are only slightly different from each other when their zeolite frameworks are the same. Consequently, the above argument is ambiguous.

In contrast to the nearly neutral effect of $[CuCl]^+$, the partial exchange of protons by Li^+ and Ag^+ ions substantially decreased the catalytic activity of H-ZSM5 for the oxidation of NO to NO_2 above 100 °C (figure 1). Since the shape of activity curves for H-ZSM5 and Li-ZSM5 strongly resemble those measured at SV = 9,600 h^{-1} [5,21], the same interpretation should be valid at this high (64,000 h^{-1}) space velocity as well (the equilibrium $NO + (1/2)O_2 \rightleftharpoons NO_2$ is attained near 400 °C).

3.3. Reaction of NO, O_2, and C_3H_8

Figures 3 and 4 show the temperature dependence of the conversion of NO to NO_2 and N_2 when various amounts of propane are added to the reaction mixture of (0.1% NO + 8.75% O_2) in balancing He. The space velocity of the total gas flow was 64,000 h^{-1} in each experiment, thereby results

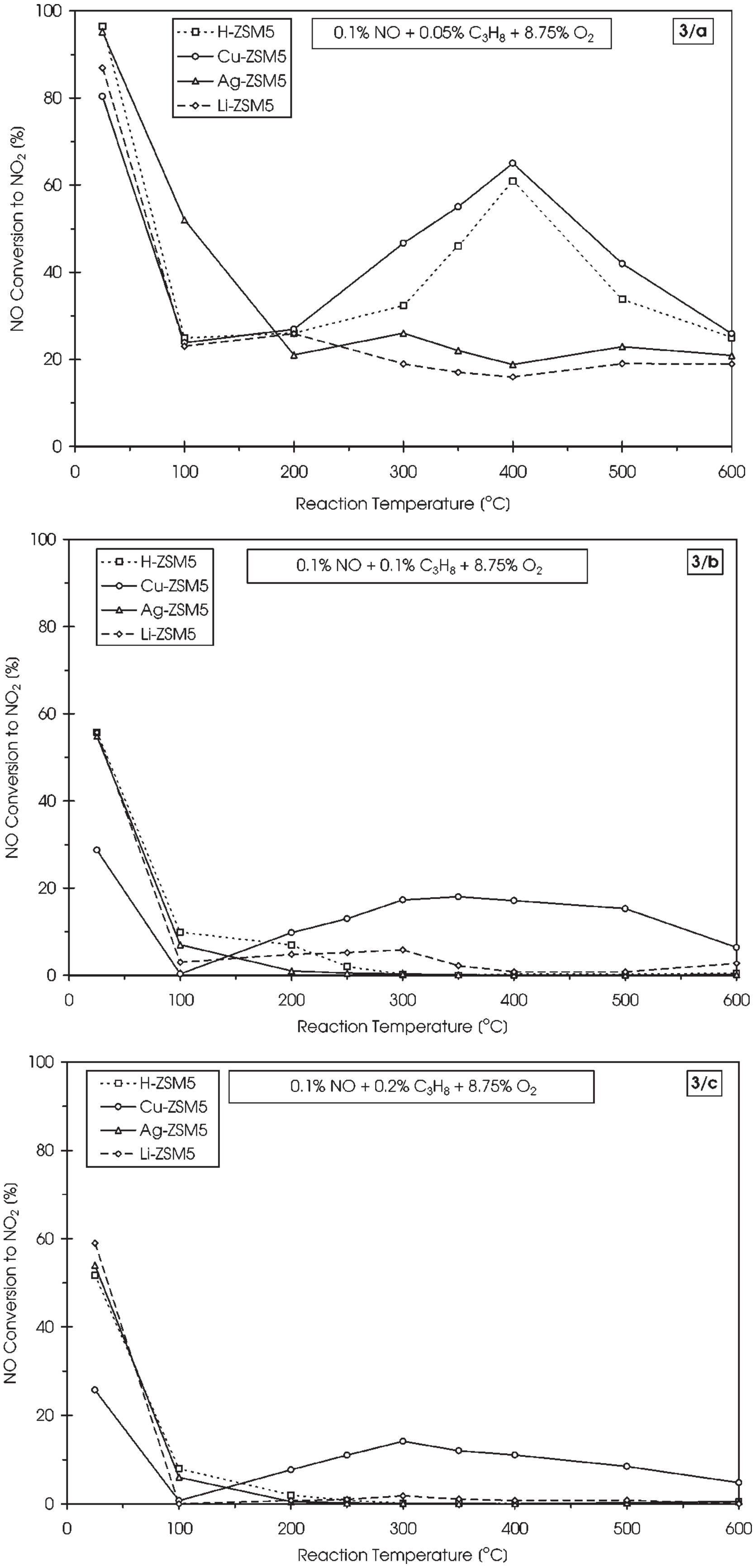

Figure 3. Conversion of NO to NO_2 in the reaction of (x% C_3H_8 + 0.1% NO + 8.75% O_2) over various zeolites. (a) $x = 0.05\%$; (b) $x = 0.1\%$; (c) $x = 0.2\%$; total $P = 1 \times 10^5$ Pa; SV = 64,000 h^{-1}.

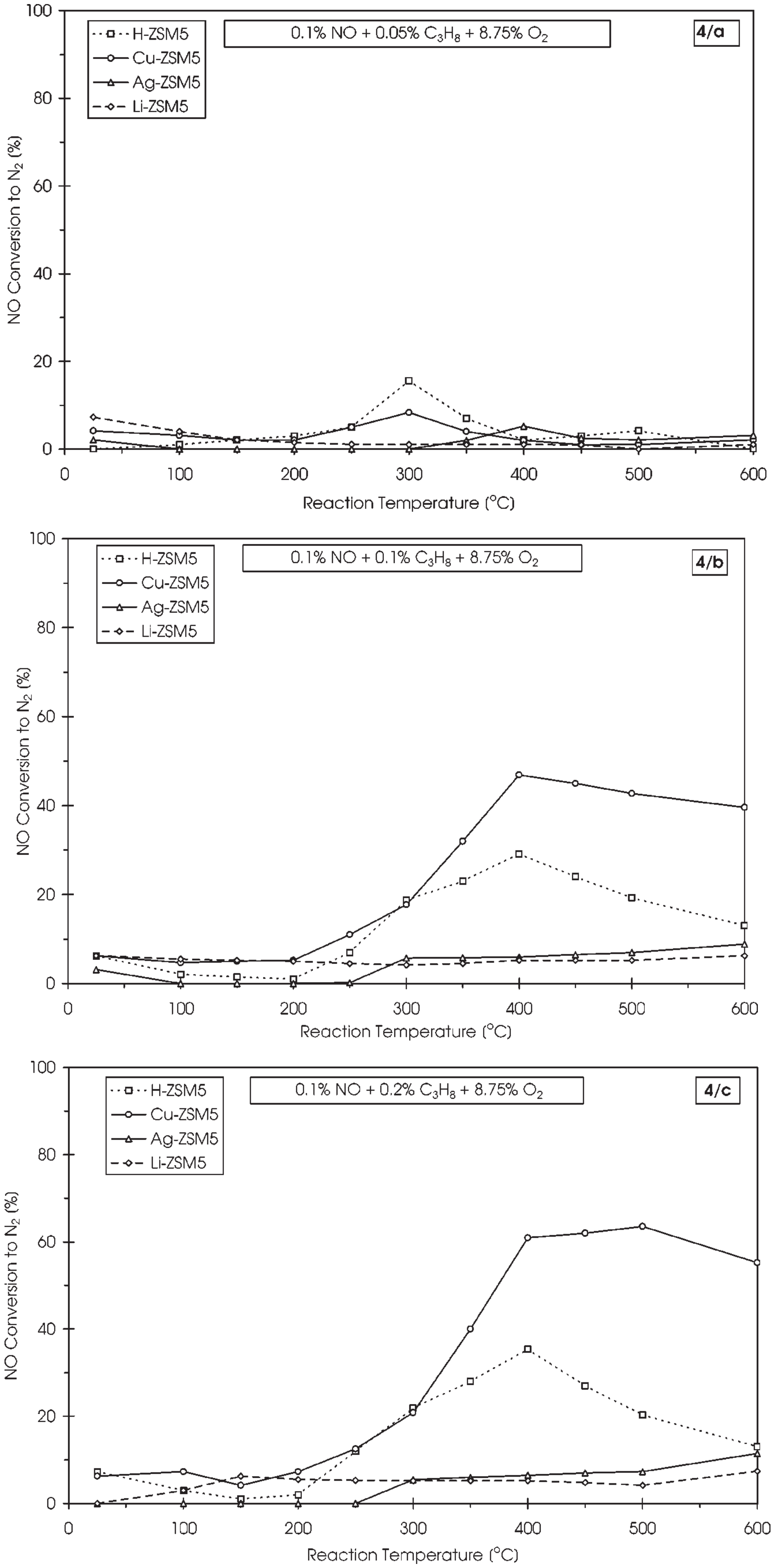

Figure 4. Conversion of NO to N_2 in the reaction of (x% C_3H_8 + 0.1% NO + 8.75% O_2) over various zeolites. (a) $x = 0.05\%$; (b) $x = 0.1\%$; (c) $x = 0.2\%$; total $P = 1 \times 10^5$ Pa; SV = 64,000 h^{-1}.

in figures 3 and 4 were obtained at comparable reaction conditions as those in figure 1.

As figures 3(a) and 1(a) indicate, the conversion of NO to NO_2 increases over each catalyst when as few as 0.05% C_3H_8 is added to the feedstock (i.e., $C_3H_8/NO < 1$). Figure 4(a) shows that, despite the presence of ample *in situ* formed NO_2, the production of N_2 is negligible at these reaction conditions. According to figures 1(b) and 4(a), the addition of 0.05% C_3H_8 generated a small increase in the conversion of NO to N_2 over the H-ZSM5 catalyst near 300 °C.

Probably due to the well known equilibrium limits [21], the increase in NO_2 formation over the most active H-ZSM5 and Cu,H-ZSM5 catalysts is negligible beyond 400 °C (figure 3(a)). Note, however, that the measured conversions of NO to NO_2 exceed the calculated equilibria at these high temperatures, perhaps because equilibria are calculated for closed systems and ours is an open, stationary, flow-through-type reactor. It is also possible that NO_2 is released from adsorbed N_2O_x dimers that presumably contribute to the pairing mechanism of nitrogen atoms over these catalysts [3,13,31–42]. Although the reasons are not understood, repeated experiments at carefully controlled conditions suggest that these data are not experimental errors. Many other papers contain similar data [11,43–45]. This issue will be addressed elsewhere [46].

Figure 3(a) shows two further surprising observations: (i) in presence of the small amount of hydrocarbon, the conversion of NO to NO_2 is by roughly 20% higher than that in the reaction of *only* $NO+O_2$ (figure 1(a)), regardless of the type of exchange ions in zeolites; (ii) this increase is independent of the reaction temperature. Since in absence of zeolite, only negligible (<5%) NO_2 is produced at these reaction conditions, a change in the sensitivity of the NO/NO_x analyzer can be ruled out. Hence the enhanced production of NO_2 is a catalytic effect.

Figures 3(b) and 4(b) indicate dramatic changes in both the total conversion of NO and the distribution of products when the partial pressure of C_3H_8 attains the partial pressure of NO ($C_3H_8/NO = 1$). Except on Cu,H-ZSM5 above 300 °C, the total conversion of NO decreases to a lower level than it was in the absence of C_3H_8 (figure 1 (a) and (b)) over each catalyst. Over Cu,H-ZSM5 and above 300 °C, the total conversion of NO is substantially higher than it was in the absence of C_3H_8. In agreement with plenty of literature data, the increased conversion is mainly due to production of N_2 which is much higher over the copper-exchanged zeolite than over any other catalyst (figure 4(b)). However, Cu,H-ZSM5 is the only catalyst which still produces considerable amounts of NO_2 above 100 °C (figure 3(b)). Parallel with the disappeared NO_2 at $C_3H_8/NO = 1$, increased production of N_2 was measured at temperatures above 300 °C on each catalyst (compare figures 1(b) and 4(b)). Nevertheless, the production of N_2 is still very low over the Ag,H-ZSM5 and Li,H-ZSM5 zeolites. Figures 3(c) and 4(c) indicate that further increase in the C_3H_8/NO ratio only results in minor changes in either the total conversion of NO or in the selectivity for NO_2 or N_2.

4. Discussion

As proposed before [5,7,12], the HC-SCR reaction can be viewed as the combustion of hydrocarbons:

$$C_nH_{2n+x} + a\mathrm{NO} + b\mathrm{O}_2 \rightarrow (a/2)\mathrm{N}_2 + n\mathrm{CO}_2 + c\mathrm{H}_2\mathrm{O}$$

where $b = (6n + x - 2a)/4$, $c = (n + (x/2))$ and $a \geqslant 1$, $b \geqslant 0.5$. For this reaction, a minimum of one oxygen atom must come from the nitric oxide even when all other oxygens come from the molecular oxygen and vice versa. Like in any combustion [47,48], a variety of radical intermediates can form (NO is already a stable free radical). Examples are NO_x [3,5,13,31,49], alkyl [3,5,11], alkoxy [50,51], nitroalkyl [3,25,52], and isocyanide [53] radicals. Their further homogeneous and heterogeneous reactions determine the ultimate products which might also include CO, NO_x, or other contaminants.

Since the direct reaction of C_nH_{2n+x} + NO is too slow over all known catalysts at the typical conditions of HC-SCR processes, two oxidations are widely considered as possible initial reaction steps: ($C_nH_{2n+x}+O_2$) and (NO + O_2). The best HC-SCR catalysts are only slightly active for the direct oxidation of saturated hydrocarbons by oxygen. This is evidenced by the low HC-SCR activity of the current three-way catalysts (TWC) of automobiles and the good HC-SCR performance of many ZSM5 zeolites which are poor hydrocarbon oxidation catalysts below 500 °C [3,5,8,12]. A plausible explanation for that could be that too fast burning prevents adequate secondary interactions with NO. (Effective HC-SCR catalysts are, however, active for the catalytic oxidation of NO to NO_2.) Since NO_2 can activate many hydrocarbons either by nitration or by oxidation below 500 °C [3,5,54–56], this reactant has been proposed to be an initial intermediate in low-temperature HC-SCR processes over most catalysts, including the here studied H-ZSM5 and Cu,H-ZSM5 [3,5,11,13].

Figures 1(a) and 2 indicate that these two zeolites are active catalysts for the oxidation of NO to NO_2. The activity minimum near 150 °C has been discussed for H-ZSM5 catalysts before [5,21]. It appears that the low-temperature reaction is due to a homogeneous-like reaction between physisorbed NO and O_2 molecules (another possibility will be proposed later) whereas the high-temperature reaction probably involves chemisorption on BA–OH sites. Similar explanation might be valid for the activity minimum of Cu,H-ZSM5. Several authors have postulated that extra-lattice oxygen radicals, ELO, might participate in the oxidation of NO over Cu-ZSM5 catalysts [33,57–59]. Recent studies [31,49,60] suggest that NO, a free radical, preferably adsorbs on the OH groups of both H-ZSM5 and Cu,H-ZSM5 zeolites. Thus, catalytic reactions of NO over Cu,H-ZSM5 might involve $[CuO]^+$, $[CuOH]^+$, and BA–OH active sites. Both $[CuO]^+$ and $[CuOH]^+$

are capable for autoreduction (e.g., $2[Cu^{2+}OH^-]^+Z^- \rightarrow Cu^+Z^- + [Cu^{2+}O^-]^+Z^- + H_2O$) [61–63] and can generate radicals, such as $^{\cdot}OH$ or O^- [26,62], which can be an important feature in the HC-SCR process. These considerations likely apply to our Cu,H-ZSM5 sample as well because the Cl^- ligands of the $[CuCl]^+$ exchange ions will quickly be replaced by O^- or OH^- ligands in the course of reactions when ample oxygen and water are present (e.g., $[CuCl]^+ + HOH \rightarrow [CuOH]^+ + HCl$). Independent FTIR, DTG, XRD, and catalytic studies [49,61,64] suggest that $[CuO]^+$ and $[CuOH]^+$ exchange ions form even when the Cu,H-ZSM5 catalysts are prepared via solid-state reaction of Cu(I)Cl and H-ZSM5. (While $[CuO]^+$ and $[CuOH]^+$ are thermodynamically stable [62], formation of Cu^+ ions can only be unambiguously confirmed when the catalysts are reduced by hydrocarbons or CO [61,65].)

Figure 1(a) shows that the partial substitution of protons by Li^+ or Ag^+ ions in H-ZSM5 virtually eliminates its catalytic activity for the oxidation of NO above 100 °C. This effect suggests that BA–OH groups are included in the active sites of H-ZSM5 at higher temperatures. Since only about 30 and 40% of the exchangeable protons were replaced by Li^+ and Ag^+ ions in the Li,H-ZSM5 and Ag,H-ZSM5 samples, respectively, the almost total loss of catalytic activity compared to that of H-ZSM5 is somewhat surprising yet not unique. It is well known that even a partial ion exchange (as low as 1%!) of H-ZSM5 by alkaline ions, such as Na^+ and K^+, can substantially decrease the catalytic activity of this zeolite in acid-catalyzed reactions [57,66]. Partial exchange by NH_4^+ has similar effect [57]. Currently there is no perceptible explanation for these effects. It is possible that different BA–OH sites exist on the surface of H-ZSM5 (e.g., OH groups associated with various numbers of Al atoms in the immediate neighborhood or OH groups surrounded with T sites having various T–O bond lengths and T–O–T bond angles [66]) and only those hydroxyls are catalytically active which are also most capable for ion exchange (either from liquid or solid phase). Another possibility is that a long-range electronic interaction exists between the metal ions (e.g., alkalines) and non-exchanged BA–OH groups [57], therefore the proton donating capability hence catalytic activity of BA–OH sites is suppressed.

Note that ESR studies indicate selective NO adsorption on the Lewis acid (LA) sites of H-ZSM5 at temperatures $\leqslant$25 °C [67,68]. Therefore, suggestion was made for considering LA active sites for the oxidation of NO on zeolite catalysts [3]. A number of studies indicate that metal ions, including Ag^+ or Li^+, are typical LA sites in zeolites [64,69–71]. Consequently, it is unlikely that LA sites alone are active for the oxidation of NO to NO_2 above 100 °C. However, they might be active sites for the low-temperature oxidation of NO. Figures 1(a), 3 (b) and (c) demonstrate that the conversion of NO to NO_2 near room temperature substantially decreases in the presence of C_3H_8 at $C_3H_8/NO \geqslant 1$. If LA sites are really needed at such low temperatures and C_3H_8 can also adsorb on these sites, the poisoning effect of C_3H_8 is understandable. In contrast, the effect of C_3H_8 is difficult to explain if only the widely assumed homogeneous-like ($NO + O_2$) reaction is considered [5,21,72].

Figure 4 shows that the reaction of ($NO + O_2 + C_3H_8$) does not result in considerable production of N_2 over Ag,H-ZSM5 or Li,H-ZSM5. Since NO_2 is an initial intermediate in the production of N_2 when this reaction is executed over H-ZSM5 [5], but partial exchange by Li^+ and Ag^+ prevents the formation of NO_2 (figure 1(a)), the low HC-SCR activities of Ag,H-ZSM5 and Li,H-ZSM5 can probably be ascribed to their inability to act for NO_2 production.

Currently, there is no clear explanation for the overwhelming formation of NO_2 from NO at $C_3H_8/NO < 1$ (figures 3(a) and 4(a)). One apparent possibility is that the reduction of NO to N_2 requires *adsorption* of C_3H_8 on the ZSM5 catalysts and adsorbed NO_x species prevent the adsorption of C_3H_8 until the partial pressure of NO exceeds the partial pressure of hydrocarbon. If so, the mechanism of the HC-SCR reaction over H-ZSM5 and Cu,H-ZSM5 must be different from those recently proposed reaction pathways which include reactions of *gaseous* hydrocarbons with either gaseous or adsorbed NO_2 [7,8,12,13,54]. Nevertheless, the increased NO_2 production in the presence of small amounts of C_3H_8 (figure 3(a)) compared to that in the reaction of ($NO + O_2$) (figure 1(a)) might include gas phase radical reactions. It is well known that low levels of hydrocarbons can promote the homogeneous oxidation of NO to NO_2 [73,74]. Since blank experiments indicated that this homogeneous reaction cannot proceed during the short residence time in an empty reactor, catalytic steps must be involved over zeolites. As proposed before [5], fast interaction of NO with alkylperoxy radicals forming in the catalytic oxidation of hydrocarbons ($RO_2 + NO \rightarrow RO + NO_2$) can be a conceivable key reaction.

Note that sometimes even low levels of C_3H_8 can prevent NO_2 production. Hamada et al. [43] have not observed NO_2 formation at any C_3H_8 content in the feed over their home-made H-ZSM5 (Si/Al ratio $\sim$ 17) catalyst and reported 28 and 38% NO conversions to N_2 at 0.25 and 0.5 C_3H_8/NO ratios, respectively (reaction temperature 400 °C; SV $\approx$ 0.6 $l\,g^{-1}$(catalyst) min^{-1}). Since this never occurred over our commercial H-ZSM5 (Si/Al ratio $\sim$ 17) sample, the different results imply that beyond the Si/Al ratio and type of exchange ions some unexplored, possibly preparation related intrinsic properties of zeolites can affect catalyst activity and selectivity. The difference is also reflected in results at $C_3H_8/NO > 1$ where both catalysts produced selectively N_2: Hamada et al. [43] found 19 and 49% conversions for NO to N_2 at 300 and 400 °C (SV $\approx$ 0.6 $l\,g^{-1}$(zeolite) min^{-1}), respectively; the corresponding conversions over our catalyst were 46% (SV $\approx$ 0.35 $l\,g^{-1}$(zeolite) min^{-1} [5]) or 20% (SV $\approx$ 2.3 $l\,g^{-1}$(zeolite) min^{-1}, figure 4(b)) at 300 °C and 45% (SV $\approx$ 0.35 $l\,g^{-1}$(zeolite) min^{-1} [5]) or 32% (SV $\approx$ 2.3 $l\,g^{-1}$(zeolite) min^{-1}, figure 4(b)) at 400 °C.

The promoting effect of hydrocarbon over the otherwise inactive Ag,H-ZSM5 and Li,H-ZSM5 (figure 1(a)) suggests that the hydrocarbon-assisted catalytic oxidation of NO by O_2 might proceed on LA sites. Such sites contribute to the strong ionization field of zeolite channels which is known to be able to generate a variety of radicals and ions, such as N_2O_4, NO_2^-, NO^+, NO_2^+, O_2^- and $C_3H_9^+$ [31,49,50,67,75,76]. All these species can contribute to the elevated NO_2 production in presence of small amounts of C_3H_8, hence much more detailed study is needed before major conclusions can be drawn.

In the light of plenty literature data, it is not surprising that the reaction of ($NO + O_2 + C_3H_8$) results in substantial N_2 over Cu,H-ZSM5 at $C_3H_8/NO \geqslant 1$ (figure 4 (b) and (c)). Many recent papers propose [3,5,11–13] that the formation of NO_2 initiates the HC-SCR process over both the H-ZSM5 and the Cu,H-ZSM5 catalysts. If, as frequently happens, the initial reaction step is rate determining and NO_2 activates C_3H_8 in a secondary reaction, one would expect similar N_2 yields over both zeolites because the supply of NO_2 is largely identical on both catalysts (figures 1(a) and 2). In contrast, figure 4 (b) and (c) clearly indicates that much more N_2 is formed over the Cu,H-ZSM5 than over the H-ZSM5 above 300 °C at $C_3H_8/NO \geqslant 1$. Why? A possible explanation is that the abstraction of hydrogen from the hydrocarbon is rate determining in the HC-SCR process [3,5,12,77–79] and this step might be faster over Cu,H-ZSM5 than over other zeolites above 300 °C. One must also consider the potential rate-determining effect of H_2O which forms as a combustion product of the hydrocarbon, especially at high C_3H_8/NO ratios. Differently exchanged ZSM5 catalysts can differently tolerate the effect of H_2O [7,55,80–83]. Moreover, the competition of NO_x and O_2 for the reductant hydrocarbon [7,55] might result in slightly different reaction mechanisms for the HC-SCR-type combustion over H-ZSM5 and Cu,H-ZSM5: the direct oxidation or oxidative dehydrogenation of C_3H_8 by O_2 to reactive carboneous or oxygenated intermediates might be a viable initial reaction over the Cu,H-ZSM5 while the adsorbed propane must be activated by NO_2 over H-ZSM5 (at least at temperatures $\leqslant$500 °C [5]). Such different reaction pathways coincide with Takeda and Iwamoto's [87] recently proposed different rate-determining steps for Cu-ZSM5 and Al_2O_3 because copious experimental evidence suggest similar HC-SCR mechanisms over Al_2O_3 and H-ZSM5 [5,51,88–90].

Whatever is the mechanism, the marked difference between the production of NO_2 and N_2 at $C_3H_8/NO < 1$ (figures 3(a) and 4(a)) and $C_3H_8/NO \geqslant 1$ (figures 3 (b), (c) and 4 (b), (c)) indicates that the ratio of C_3H_8/NO determines the selectivity for NO_2 and N_2 in the reaction of ($NO+C_3H_8+O_2$) over all four catalysts. Thus, the summarized results in figures 3 and 4 demonstrate that the impact of C_3H_8/NO ratio (relative partial pressures of the hydrocarbon and NO in the feedstock) on the selectivity for N_2 is stronger than the space velocity (at least in the case of H-ZSM5), the reaction temperature (above 200 °C), or the type of exchange ions of ZSM5 catalysts. These latter parameters affect the rates of the intermediate reaction steps ($C_3H_8 + O_2$), ($NO + O_2$), and ($C_3H_8 + NO_x$), therefore they also affect the yield of N_2, but only when the ratio of C_3H_8/NO permits its selective production. However, it is apparent that the total conversion of NO mainly depends on the exchange ions of zeolites. A general kinetic description of the HC-SCR process must be able to account for these issues.

5. Conclusions

(1) The reaction of ($NO+C_3H_8+O_2$) over H-ZSM5 and Cu,H-ZSM5 catalysts can result in the selective production of either NO_2 or N_2. When $C_3H_8/NO < 1$ in the feedstock, only selective formation of NO_2 occurs and the catalytic reaction of NO_2 and C_3H_8 is inhibited regardless the stoichiometric excess of reductant. The selectivity for N_2 becomes dominant at $C_3H_8/NO \geqslant 1$ above 200 °C, but the Cu,H-ZSM5 still produces substantial NO_2 (the amount varies from about 5 to 20% depending on the temperature and ratio of C_3H_8/NO). The space velocity, reaction temperature, and exchange ions of zeolites have only minor impact on the selectivity for N_2.

(2) Contrary to prior statements, the H-ZSM5 and Cu,H-ZSM5 (prepared by solid-state reaction from the H-ZSM5 sample and $CuCl_2$) show comparable catalytic activities for the oxidation of NO by O_2 to NO_2 at $SV = 64{,}000\ h^{-1}$ ($2.3\ l\,g^{-1}\,min^{-1}$) which approximates the typical values in catalytic converters of automobiles.

(3) The partial exchange of protons (63%) in H-ZSM5 by $[CuCl]^+$ ions and presumably their subsequent transformation into $[CuO]^+$ or $[CuOH]^+$ substantially increases the yield of N_2 in the reaction of ($NO + C_3H_8 + O_2$) at $C_3H_8/NO \geqslant 1$ molar ratios above 300 °C. At these conditions, the total conversion of NO is much higher than that in the ($NO + O_2$) reaction. Hence the direct oxidation of C_3H_8 by O_2 might be an initial step in the HC-SCR process over Cu,H-ZSM5. The extra-lattice anionic ligands of Cu^{2+} appear to be important for the HC-SCR activity of this zeolite but its BA–OH sites are not essential for this process. The oxidation of NO to NO_2 is a conceivable initial step in the HC-SCR process over H-ZSM5. Gaseous or adsorbed NO_x and adsorbed C_xH_y species are likely involved in the secondary reactions when $C_3H_8/NO \geqslant 1$ in the feedstock.

(4) 30 and 40% exchange of protons in H-ZSM5 for Li^+ and Ag^+ ions, respectively, virtually kills the catalytic activity for both the reaction of ($NO + O_2$) and the reaction of ($C_3H_8 + NO + O_2$) when $C_3H_8/NO \geqslant 1$ and the reaction temperature is $\geqslant$100 °C. Thus, BA–OH sites of H-ZSM5 are likely involved in the active sites for both reactions. When the partial pressure of NO exceeds the partial pressure of C_3H_8 ($C_3H_8/NO < 1$) in the feedstock, the conversion of NO to NO_2 is higher than in the absence of hydrocarbon over all four zeolites studied here.

Acknowledgement

The authors thank the Advanced Scientific Design, Inc., for supporting this research. We also thank Mr. Michael Lukitsch for measuring the extent of ion exchange.

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