JOURNAL OF CATALYSIS **161,** 359–372 (1996)
ARTICLE NO. 0193

Catalytic Activity and Selectivity of H-ZSM5 for the Reduction of Nitric Oxide by Propane in the Presence of Oxygen

Istvan Halasz,* Alan Brenner,* K. Y. Simon Ng,† and Ying Hou†

*Departments of *Chemistry and †Chemical Engineering, Wayne State University, Detroit, Michigan 48202*

Received October 23, 1995; revised January 22, 1996; accepted January 29, 1996

The reactions of NO, C_3H_8, and O_2 were studied over a H-ZSM5 catalyst at various conditions. The reaction can result in the formation of either NO_2 or N_2. The selectivity for N_2 mainly depends on the ratio of NO/C_3H_8 in the feedstock; the reaction temperature and the concentration of O_2 have only minor influence. When the concentration of NO is 1000 ppm (which is typical for automotive exhausts) and NO/$C_3H_8 > 1$, the oxidation of NO to NO_2 dominates, but the NO_2 does not react significantly with C_3H_8 at these reaction conditions. NO can be reduced by C_3H_8 selectively to N_2 at NO/$C_3H_8 \leq 1$ when oxygen is present. Results suggest that the selective catalytic reduction (SCR) of NO can proceed via two different reaction pathways below and above 500°C. At low temperatures, the oxidation of NO by O_2 to NO_2 might be the initial reaction step. Below 500°C, this reaction is much faster than other possible reactions in the mono- or bimolecular mixtures of the three reactants. At 500°C, the reaction rate of the oxidation of C_3H_8 by O_2 is comparable to that of the NO oxidation. At 600°C, the oxidation of C_3H_8 is faster than other reactions in the mono- or bimolecular mixtures of reactants. Thus, probably the combustion of propane initiates the SCR process above 500°C. The rates of both initial reactions depend on the concentration of oxygen and the reaction temperatures, but contrary to common belief these parameters have little effect on the yield of N_2 in the SCR process. It appears that the active sites for the reactions of NO + O_2, C_3H_8 + O_2, and C_3H_8 + NO_2 are similar to each other, probably involving the Brønsted acidic bridging hydroxyls of H-ZSM5. When NO/$C_3H_8 > 1$, adsorbed NO_x species may prevent the adsorption of C_3H_8 since propane barely reacts with the other reactants. At NO/$C_3H_8 \leq 1$, the SCR of NO to N_2 probably proceeds via the secondary reactions of NO_2 + C_3H_8 (below 500°C) or $C_xH_yO_z$ + NO_x (above 500°C). Radicals are likely involved in both the initial and the secondary reaction steps. At 300°C, the probable overall stoichiometry of the SCR process is $2C_3H_8 + 6NO + 4O_2 \Rightarrow 6CO + 8H_2O + 3N_2$. At higher temperatures, CO_2 also appears in the products and the efficiency of propane to form N_2 decreases. © 1996 Academic Press, Inc.

INTRODUCTION

The selective catalytic reduction (SCR) of NO to N_2 by hydrocarbons at net oxidizing conditions is a complex process which can be used for air pollution control. Although much knowledge has been accumulated about this reaction during the past several years (1), the reaction route is still elusive even over the most intensively investigated ZSM5 catalysts. Despite several attempts (1–9) to outline some feasible general features of the mechanism, only few mechanistic issues have been settled.

Little is known about the active sites of SCR catalysts. Since most active ZSM5 zeolites contain exchangeable multivalent cations, such as Cu^{2+}, Co^{3+}, Ce^{3+}, Ga^{3+}, or Pt^{2+}, it is expected that these cations are active sites for the SCR reaction. The adsorption of NO_x and O_x species on Cu-ZSM5 catalysts has been well documented (1). However, access to the multivalent cations is mostly blocked by large extra lattice anions (e.g., OH^-, O^{2-}, or O_{2-}) in these high Si/Al zeolites (10–12). Therefore, the *direct* interaction of the reactant molecules (O_2, C_xH_y, and NO) and the cations is unclear. The role of the extra lattice anionic ligands in the SCR process has barely been studied. Likewise, little attention has been paid to other potential active sites, such as the oxygen, aluminum, and silicon ions of the zeolite lattice (1, 13–16). Moreover, the multivalent metal cations usually occupy only 20 to 50% (occasionally up to 75%) of the exchangeable positions in the ZSM5 catalysts. The rest is most frequently occupied by sodium ions and protons. Since the catalytic activity of Na-ZSM5 for the SCR of NO to N_2 is low (3, 7, 19), Na^+ ions are probably not active sites for this reaction. In contrast, the possible catalytic role of protons has received increasing experimental support recently (1, 2, 17–19). Although some active ZSM5 samples may not contain protons (20–22), the Brønsted acidic bridging hydroxyl (BA-OH) groups are likely involved in the SCR process over the proton exchanged H-ZSM5 catalysts (1, 8, 17–19, 23).

Recent studies indicate that the BA-OH groups of H-ZSM5 are probably active sites for the oxidation of NO by O_2 to NO_2 above 200°C (23). Many researchers agree that NO_2 might be an important initial intermediate in the SCR process (1–4, 7–9, 23–26). Others assume that this is only valid for the acidic H-ZSM5 and Al_2O_3 catalysts and the oxidation of hydrocarbons is the initial step over other catalysts (5, 6, 21, 27). Many subsequent intermediates have been proposed to participate in the SCR process, in which the ultimate products are N_2, CO_x, and H_2O. Examples are carbonaceous deposits (1, 28–30), ammonia (31), N_2O_3 (32),

0021-9517/96 $18.00

and alkyl (1, 2, 4), alkoxy (6, 7, 14, 33), nitoalkyl (1, 3, 7, 34), cyanide (35–37), and isocyanide (3, 36, 37) radicals. It appears that the rate determining step of the overall SCR process is either the oxidation of NO to NO_2 (1, 3) or the dehydrogenation of hydrocarbons (2, 23, 38, 39).

There is a good chance that the different mechanisms do not contradict each other. A large body of papers demonstrate that the ultimate reaction course may depend on several factors including the composition of catalysts, the reaction temperature, the space velocity (SV), the relative concentrations of reactants, and the structure of the reductant hydrocarbons. Consequently, different mechanisms may be valid at different reaction conditions and a general mechanism for the SCR of NO by hydrocarbons may not exist. In order to systematize the diversified and seemingly contradictory results, it is desirable to perform further studies over carefully characterized catalysts at systematically varied reaction conditions.

Present experiments explore some details of the SCR of NO to N_2 by propane over a H-ZSM5 catalyst at various reactant concentrations and temperatures. Among the active ZSM5 zeolites, H-ZSM5 is the simplest catalyst. Since protons are its only exchangeable cations, complications associated with multivalent exchangeable cations can be avoided but the possible catalytic role of BA-OH sites can be studied. A better understanding of the reaction pathway over H-ZSM5 should facilitate the understanding of the SCR process over more complex catalysts.

Numerous papers have reported SCR studies over H-ZSM5 (1, 2, 8, 17–19, 21, 22, 33, 34, 40–48). Most of these studies concentrate on the comparison of the activities and selectivities of H-ZSM5 samples with those of other catalysts by varying the reductants, reaction temperatures, and space velocities. Hence, experiments are usually made at constant concentrations of the three reactants, NO, C_xH_y, and O_2, typically near 0.1, 0.1, and 10%, respectively. While such comparative experiments with constant reactant mixtures are important, their significance is limited because the concentrations of reactants strongly impact the yields of N_2 and CO_x over many catalysts (8, 17, 21, 39, 41–48). Not much is known about the reasons for these changes. It appears that their magnitude varies with the composition of catalysts, space velocities, and reaction temperatures, but there are insufficient data to elucidate why. To get more information on this subject over the H-ZSM5 catalyst, a wide range of reactant concentrations is used in the present work.

SCR experiments at various oxygen and hydrocarbon concentrations have already been reported over H-ZSM5 (21, 33, 41–44). However, several aspects have not been investigated. For example, the effect of oxygen has only been examined in a feed containing 1000 ppm NO and 323 ppm C_3H_8 (balance He). By passing this mixture through a H-ZSM5 catalyst ($SV = 1800\ h^{-1}$), Hamada and co-workers (21, 33, 41, 44), who first reported the SCR activity of H-ZSM5 (40), demonstrated that there is no reaction between the two reactants at 400 and 500°C unless oxygen is also added to the feed. Since similar observations were also made over other catalysts, the universal importance of oxygen to initiate the SCR process seems to be well established (1).

In the presence of 1% O_2, about 50% of the NO and 50% of the C_3H_8 was converted to N_2, CO_2, and H_2O over the H-ZSM5 catalyst at 400°C (21, 33, 41, 44). By reacting the same mixture at 500°C, roughly 40% NO conversion and 90% C_3H_8 conversion was observed. These results indicate that higher temperature accelerates the combustion of hydrocarbons and slightly slows the reduction of NO to N_2. An increase in the concentration of oxygen from 1 to 10% did not significantly affect the production of N_2 and CO_x (33, 44). By contrast, a similar change in the concentration of oxygen considerably increased the yields of N_2 and CO_x over an Al_2O_3 catalyst (21, 41). This is surprising, because it is conjectured that the primary role of oxygen is to convert NO into more reactive NO_2 over both catalysts (1, 33, 41, 44, 45, 48). Moreover, the reaction rate of the oxidation of NO by O_2 to NO_2 is much faster over H-ZSM5 than over Al_2O_3 (33, 41) and the production of NO_2 can be considerably enhanced over H-ZSM5 by increasing the concentration of oxygen (23). It is not known what happens to the elevated NO_2 production at high oxygen concentrations over H-ZSM5 when C_3H_8 is present. It is possible that the oxidation of NO by O_2 is suppressed in the presence of propane over this catalyst, or perhaps unreacted NO_2 remains despite the presence of the hydrocarbon. It is also reasonable to assume that less than 1% O_2 can initiate the SCR reaction, but how much less is not known. It is further unclear, what happens when the absolute and relative concentrations of NO and C_3H_8 are changed. For example, should oxygen be in excess compared to the nitric oxide, to the hydrocarbon, or to both of them? These matters are examined in this study.

The effect of the hydrocarbon concentration on the N_2 production over H-ZSM5 has been studied by using a feed containing about 1000 ppm NO, 10% O_2, and different amounts of C_3H_8 (21, 33, 41–44). It was found that the NO conversion to N_2 roughly doubles (e.g., from 25 to 50% at 400°C and $SV = 18{,}000\ h^{-1}$) when the concentration of C_3H_8 increased from about 300 to 1300 ppm. This positive effect of the hydrocarbon concentration is similar to those reported for Cu-ZSM5 (8) and Co-ZSM5 (48). In contrast, the N_2 production changed little when the concentrations of hydrocarbons over a Ga-ZSM5 catalyst were changed (17, 43, 46). The reasons for these differences are not clearly understood. There are several unanswered questions regarding the concentration effect of hydrocarbons over the H-ZSM5 catalyst as well. For example: (i) Is this effect still valid when the concentration of oxygen is lower than 10%?

(ii) What happens when NO is in excess compared to C_3H_8? (iii) Is 300 ppm the minimum propane concentration that can initiate SCR reaction with 1000 ppm NO? According to the reaction $C_3H_8 + 10NO \Rightarrow 5N_2 + 3CO_2 + 4H_2O$, even 300 ppm C_3H_8 represents a threefold stoichiometric excess compared to 1000 ppm NO. If, as very recently proposed (2, 48), the combustion of hydrocarbons by NO_2 and/or NO is a major driving force in the SCR process, it is expected that excess NO_2 or NO is desirable to accelerate the combustion.

Some of the above questions regarding the mechanism of the SCR of NO by C_3H_8 over H-ZSM5 are addressed in this paper. Several problems regarding to the stoichiometry of this reaction are addressed as well. To check what happens when one of the three reactants, NO, C_3H_8, and O_2, is limiting or excess compared to the others, it is important to know what is their stoichiometric ratio in the overall SCR process. Since this information is not available, the determination of the probable stoichiometry for the SCR of NO by C_3H_8 was investigated.

The compositions of the actual exhaust gases of spark ignition engines and the reaction conditions in the catalytic converters of automobiles are complex and can vary widely. For example, various concentrations of CO, H_2, N_2, O_2, H_2O, NO, soot, and several hydrocarbons can be simultaneously present in a typical exhaust and the space velocity over a TWC catalyst randomly changes between 20,000 and 100,000 h^{-1} (62). These and many other factors have to be taken into account when practical applications are considered. It has also been shown that the SCR activity of ZSM5 catalysts is significantly suppressed in the presence of 10% H_2O which easily occurs in real exhausts (90). Hence, the model reactions presented here of the three reactants, NO, C_3H_8, O_2, at roughly 10,000 h^{-1} space velocity have been selected to elucidate certain features of the SCR reaction and the results cannot be directly used to define the best operating conditions for an automotive SCR process.

EXPERIMENTAL

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. According to the weight loss up to 800°C (measured by TGA in nitrogen), the catalyst contained 2.0 mmol/g (0.036 ml/g) adsorbed water. Li-ZSM5 was prepared by solid-state reaction of H-ZSM5 and LiCl as described elsewhere (23). The powdered zeolites were pressed into pellets, crushed, and the 0.3- to 0.6-mm fraction was used for catalytic measurements.

To measure the density of BA-OH groups in the H-ZSM5 sample, NH_4^+-exchange was carried out three times by stirring 4 g zeolite with 100 ml aqueous 1 *M* NH_4Cl (plus 5 ml 25% NH_4OH to maintain pH > 7) in a glass flask at 80°C overnight. The sample was thoroughly washed five times with 100 cm^3 distilled water and dried in air. Then, 0.5 g of the dried NH_4-ZSM5 was placed in a quartz reactor and heated in flowing N_2 (∼10 ml/min) to 600°C at a rate of 10°C/min. The effluent bubbled through two traps (each filled with 100 ml distilled water) to absorb evolving NH_3. The solutions were continuously stirred by magnetic stirrers and neutralized with 0.1 *N* aqueous HCl by using methyl orange indicator. Acid consumption was detected only in the first absorber, indicating full NH_3 absorption. Repeated experiments with different zeolites proved that the described method assures roughly 100% NH_4^+-exchange and the error in determining the lattice aluminum (BA-OH) content is less than ±5%.

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.

Activity Measurements and Analysis

A 1 cm^3 (0.46 g) catalyst sample was placed in a fused quartz reactor (10 mm i.d.) of the flow-through type. The catalyst was supported on a porous quartz frit and covered with quartz wool. Prior to the first catalytic experiment, the catalyst was 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 pretreatment was done during the catalytic tests. The catalyst was kept in helium between runs.

For catalytic measurements, appropriate amounts of oxygen, nitric oxide, and propane were mixed with a balance of helium to achieve a total flow rate of 160 ml/min ($SV = 9600\ h^{-1}$) at 1 atm (1.0×10^5 Pa). To cover the entire range of possible stoichiometries (Table 1) and also the reactant ratios used most frequently in the literature, NO/C_3H_8 ratios of 0.5, 0.7, 1, 2, 4, and 20 and O_2/NO ratios of 0.13, 0.25, 0.5, 2.5, 5, 17.5, and 87.5 were used for the present studies. All permutations of these two ratios were studied, so the corresponding O_2/C_3H_8 ratios varied from 0.065 to 1750. Typical NO/C_3H_8, O_2/NO, and O_2/C_3H_8 ratios (they can vary widely) in an automotive exhaust are 1.4, 4.9, and 6.8, respectively (61). The concentrations of O_2 were varied from 125 ppm to 34%, that of C_3H_8 from 50 ppm to 2%, and the concentration of NO was either 0.1 or 2%. Experiments were carried out at reaction temperatures from 25 to 600°C and at constant ($SV = 9600\ h^{-1}$) space velocity. Flow rates were controlled by Brooks mass flow controllers. The reaction system is highly leak tight and is constructed of stainless steel with bellows seal valves. Details of the system are described elsewhere (23, 34, 51–55).

TABLE 1

Feasible Formal Stoichiometries for the SCR of NO by Propane When (i) Both NO and O_2 Contribute a Minimum of One Oxygen Atom to the Oxidation of C_3H_8, (ii) a Single Oxygen Atom Reacts with Only One Hydrocarbon Molecule, and (iii) the Formation of CO and N_2O Is Not Significant

	Stoichiometric ratios			Expected
Possible reactions	O_2/NO	NO/C_3H_8	O_2/C_3H_8	N_2/C_3H_8
1. $2C_3H_8 + 2NO + 9O_2 \Rightarrow 6CO_2 + 8H_2O + 1N_2$	9/2 = 4.50	2/2 = 1	9/2 = 4.5	0.5
2. $2C_3H_8 + 4NO + 8O_2 \Rightarrow 6CO_2 + 8H_2O + 2N_2$	8/4 = 2.00	4/2 = 2	8/2 = 4.0	1.0
3. $2C_3H_8 + 6NO + 7O_2 \Rightarrow 6CO_2 + 8H_2O + 3N_2$	7/6 = 1.17	6/2 = 3	7/2 = 3.5	1.5
4. $2C_3H_8 + 8NO + 6O_2 \Rightarrow 6CO_2 + 8H_2O + 4N_2$	6/8 = 0.75	8/2 = 4	6/2 = 3.0	2.0
5. $2C_3H_8 + 10NO + 5O_2 \Rightarrow 6CO_2 + 8H_2O + 5N_2$	5/10 = 0.50	10/2 = 5	5/2 = 2.5	2.5
6. $2C_3H_8 + 12NO + 4O_2 \Rightarrow 6CO_2 + 8H_2O + 6N_2$	4/12 = 0.33	12/2 = 6	4/2 = 2.0	3.0
7. $2C_3H_8 + 14NO + 3O_2 \Rightarrow 6CO_2 + 8H_2O + 7N_2$	3/14 = 0.21	14/2 = 7	3/2 = 1.5	3.5
8. $2C_3H_8 + 16NO + 2O_2 \Rightarrow 6CO_2 + 8H_2O + 8N_2$	2/16 = 0.13	16/2 = 8	2/2 = 1.0	4.0
9. $2C_3H_8 + 18NO + 1O_2 \Rightarrow 6CO_2 + 8H_2O + 9N_2$	1/18 = 0.06	18/2 = 9	1/2 = 0.5	4.5

Note. The ratio N_2/C_3H_8 is [mol produced N_2/mol reacted C_3H_8] provided the combustion of C_3H_8 by O_2 is negligible.

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). The ammonia content was analyzed by its reoxidation to nitric oxide as described elsewhere (51). All other products were analyzed by gas chromatography using a GOW MAC 550P type chromatograph equipped with TCD detectors using He carrier gas. A stainless steel column (2.5 feet × $\frac{1}{8}$ inch) packed with 5A molecular sieve at 60°C separated NO, N_2, O_2, and CO. Hydrocarbons (C_1–C_4), CO_2, N_2O, and H_2O were separated at 105°C on a stainless steel column (6.5 feet × $\frac{1}{8}$ inch) packed with Poropack Q.

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 and analysis of NH_3 were 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. The total product composition was obtained by two injections on the two different GC columns. To avoid the condensation of water, the sample loop and the gas lines were heated to about 100°C. Despite this precaution, we were unable to separate and measure quantitatively the water and propane content in products when the hydrocarbon conversion exceeded roughly 30%. Therefore, the total CO_x production was used to calculate the conversion of propane. Possible NH_3 formation was occasionally checked whenever the oxygen content in the reactant mixture was low but measurable NH_3 was not detected at our reaction conditions.

RESULTS

Stoichiometry and Selected Reactant Ratios

There is substantial experimental experience that considerable reduction of NO to N_2 occurs only when all three reactants, NO, O_2, and C_nH_{2n+x}, are simultaneously present in the feed (1). Hence, neglecting that some N_2O and CO may appear at certain reaction conditions, the general SCR reaction can be described as

$$C_nH_{2n+x} + a\mathrm{NO} + bO_2 \Rightarrow (a/2)N_2 + nCO_2 + cH_2O,$$

where $b = [(6n + x - 2a)/4]$, $c = [n + (x/2)]$, and $a \geq 1$; $b \geq 0.5$. One can consider this reaction as the combustion of hydrocarbons (2, 48). For this special combustion, a minimum of one oxygen atom must come from the nitric oxide even when all other oxygens come from the molecular O_2 and vice versa. Consequently, depending on the ratio of NO to O_2 molecules participating in the combustion, several stoichiometric equations can exist for a single hydrocarbon molecule.

Table 1 shows some feasible equations for the SCR of NO by propane. Provided that a single oxygen atom (either from NO or from O_2) does not react with more than one hydrocarbon molecule, one of the nine reactions in Table 1 must be close to the overall stoichiometry of the SCR process regardless of the catalyst used. Since there are no chemical reasons to prefer any of these equations, all corresponding reactant ratios must be considered as possible stoichiometry when experiments with different concentrations of reactants are designed. Note that the limits of these stoichiometric ratios (Table 1) remain valid when the possible production of some CO or N_2O is also taken into account.

By determining the ratio of [produced N_2/reacted C_3H_8] (Table 1) when the direct combustion of C_3H_8 by O_2 is negligible, the stoichiometry of the SCR process can be elucidated. This ratio also describes the efficiency of propane to produce N_2, which is an important practical factor (1). According to the calculated values in Table 1, the minimum efficiency of propane must be near 0.5 when significant side reactions do not occur. Higher efficiencies can be expected when more than one nitric oxide molecule can react with one hydrocarbon. Hence, Table 1 suggests that maintaining high NO/C_3H_8 and low O_2/C_3H_8 and O_2/NO ratios could be favorable to improve the efficiency of propane. In contrast, considerable N_2 yields over H-ZSM5 have only been reported by selecting $O_2/C_3H_8 \gg 10$ and $O_2/NO \gg 10$ ratios (2, 8, 17–19, 21, 22, 33, 34, 40–48). The corresponding NO/C_3H_8 ratios were mostly close to 3 or 0.8 (2, 21, 33, 40–44) and in a few experiments near 2, 1.5, and 1 (22, 41, 43).

BA-OH Coverage

Based on the HCl consumption, the NH_4^+-exchange capacity of H-ZSM5 was 0.424 mmol/g. Since the Si/Al ratio of 18 (calculated from the total Si and Al content of the zeolite sample) would correspond to 0.85 mmol/g lattice aluminum atoms, the NH_4^+-exchange capacity of H-ZSM5 indicates that only one-half of the total aluminum content is associated with exchangeable protons (BA-OH groups).

Reactions with One or Two Reactants

To get information about the possible initial steps of the SCR process, reactions with feeds containing only one or two of the three reactants, NO, O_2, and C_3H_8, were studied first. The reaction parameters of these experiments were the same as those used for the SCR reactions.

In agreement with prior findings (34, 41), the conversions of NO or C_3H_8 remained below 3% in all possible reactions of the mono- or bimolecular mixtures except for the oxidations of NO and C_3H_8 by O_2. Only the oxidation of NO to NO_2 proceeds with measurable conversion below 400°C. Figure 1 shows the effects of oxygen concentrations and reaction temperatures on the conversion of NO in reaction mixtures containing 0.1% NO. The shape of the activity curves for feeds containing 2% NO are similar to those in Fig. 1, but, due to a second-order dependence of the rate of reaction on the nitric oxide partial pressure (56), the conversions are somewhat higher than those in Fig. 1. Details of these processes have been discussed elsewhere (23). Figure 2 illustrates two earlier observations that are relevant here (the homogeneously formed NO_2 (23) has been subtracted): (i) the conversion of NO declines after reaching a maximum at around 350°C because the equilibrium $NO + 1/2O_2 = NO_2$ is attained; (ii) the BA-OH groups of H-ZSM5 are probably active sites for this reaction above 200°C (but not near room temperature) because the conversion of NO vanishes at high temperatures when the protons are replaced by Li^+ ions in this zeolite.

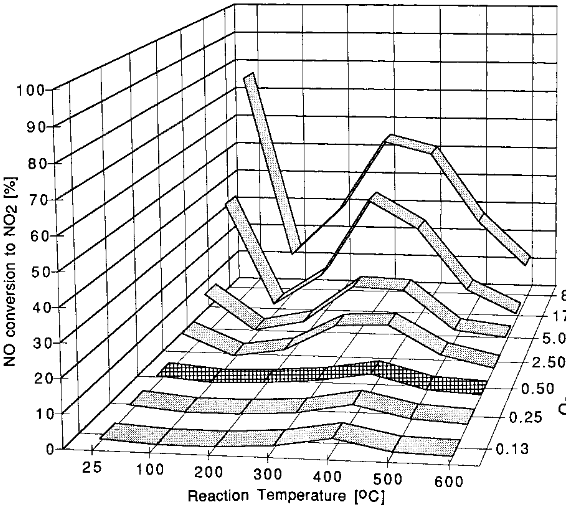

FIG. 1. Conversions of NO at various reaction temperatures and O_2/NO molar ratios with feeds containing 1000 ppm NO and variable O_2; total $P = 1 \times 10^5$ Pa; $SV = 9600\ h^{-1}$. Cross-hatched line is the stoichiometric ratio for $2NO + O_2 \Rightarrow 2NO_2$.

Figure 3 shows the oxidation of C_3H_8 by O_2. When only 50 ppm propane is in the feed (Fig. 3a), the combustion starts above 400°C. By increasing the concentration of propane to 1000 ppm (Fig. 3b), the "light-off" temperature decreases to 300°C and the conversions (at identical O_2/C_3H_8 ratios) go up. The light-off temperature remained above 300°C when the concentration of propane was increased to 2%.

Figure 4 shows an example for the effect of the concentration of C_3H_8 on the reaction rates of propane combustion in the presence of 10% O_2. (BA-OH groups are assumed active sites, *vide infra*.) This oxygen concentration would

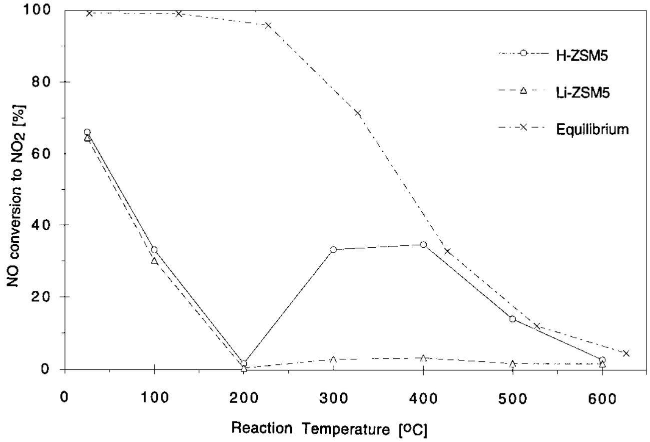

FIG. 2. Comparison of the catalytic activities of H-ZSM5 and Li-ZSM5 to the equilibrium conversion for the oxidation of 2% NO by 5% O_2 at various temperatures; total $P = 1 \times 10^5$ Pa; $SV = 9600\ h^{-1}$.

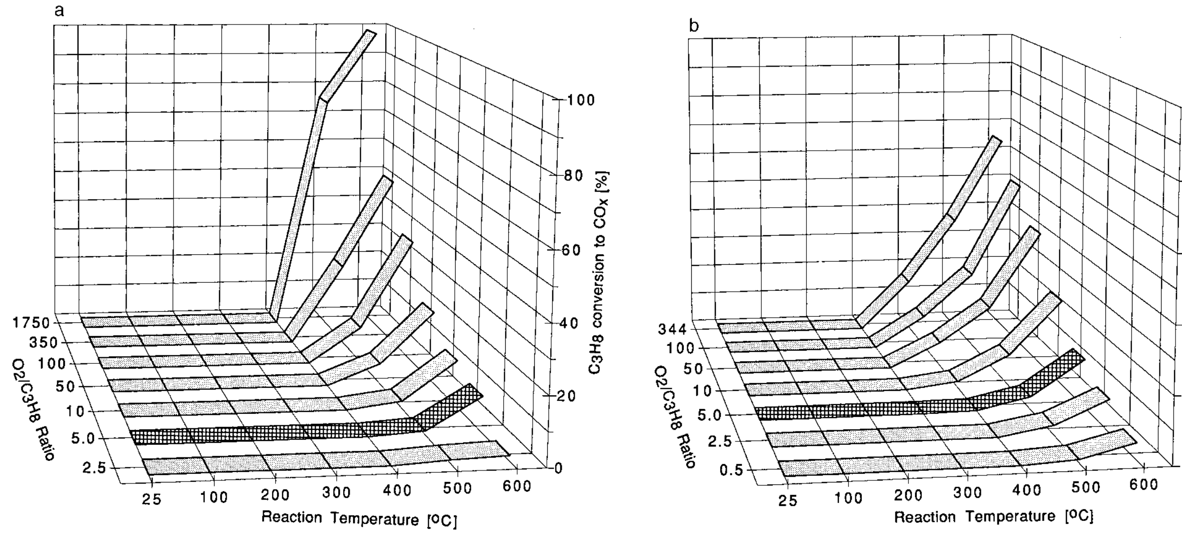

FIG. 3. Conversions of C_3H_8 to CO_x at various reaction temperatures and O_2/C_3H_8 molar ratios with feeds containing 50 ppm (a) and 1000 ppm (b) C_3H_8 and variable O_2; total $P = 1 \times 10^5$ Pa; SV = 9600 h^{-1}. Cross-hatched line is the stoichiometric ratio for $C_3H_8 + 5O_2 \Rightarrow 3CO_2 + 4H_2O$.

correspond to O_2/C_3H_8 ratios of 2000 and 100 in Figs. 3a and 3b, respectively.

Similar to other reports (48), significant CO production was observed at all reaction conditions studied. Figure 5 shows an example for the CO and CO_2 distributions at the reaction conditions of Fig. 3b. For feeds containing from 0.05 to 2% C_3H_8, the CO/CO_2 ratios were similar to those in Fig. 5 at identical O_2/C_3H_8 ratios and reaction temperatures. The combustion of propane over H-ZSM5 is a heterogeneously catalyzed reaction because less than 3% propane conversion was measured when blank experiments were carried out in an empty reactor at the reaction condition described above. Figure 6 illustrates that the conversion is also much lower when Li-ZSM5 catalyst is used instead of H-ZSM5.

Figure 7 compares the reaction rates of the oxidation of C_3H_8 and NO by O_2 at various temperatures. The combustion of propane is about 10 times slower at 400°C and about 10 times faster at 600°C than the oxidation of NO. Data in Figs. 1, 3, and 7 indicate that excess oxygen compared to the stoichiometric ratios of reactants (checked lines in Figs. 1 and 3) can significantly enhance the reaction rates in both reactions.

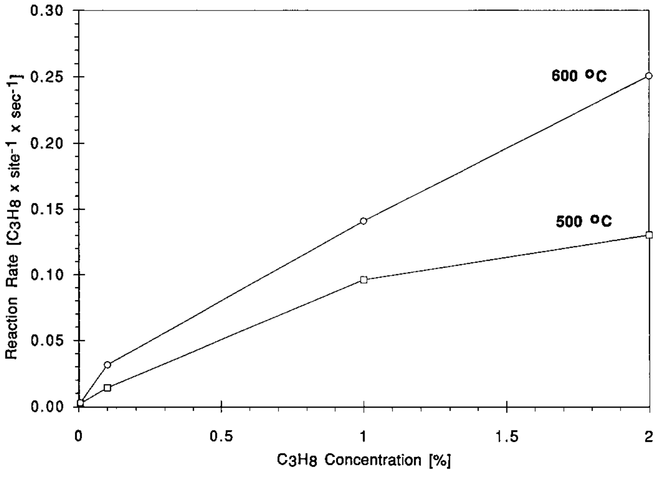

FIG. 4. Effect of the concentration of C_3H_8 on the turnover frequency in the oxidation of propane by oxygen with feeds containing 10% O_2 at 500 and 600°C; total $P = 1 \times 10^5$ Pa; SV = 9600 h^{-1}. The number of active sites was determined from the BA-OH density (0.424 mmol/g).

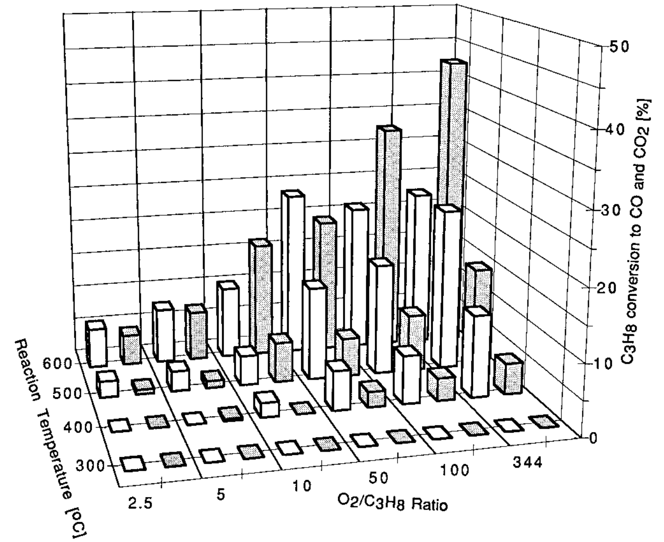

FIG. 5. CO (□) and CO_2 (▨) production in the oxidation of C_3H_8 by O_2. The reaction conditions are the same as in Fig. 3b.

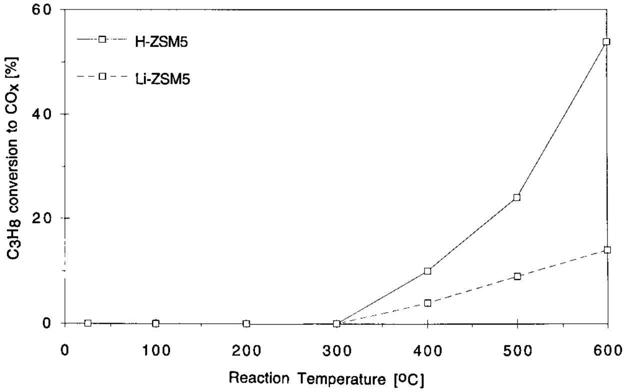

FIG. 6. Comparison of the catalytic activities of H-ZSM5 and Li-ZSM5 in the oxidation of 0.1% C_3H_8 by 9% O_2 at various temperatures; total $P = 1 \times 10^5$ Pa; SV = 9600 h^{-1}.

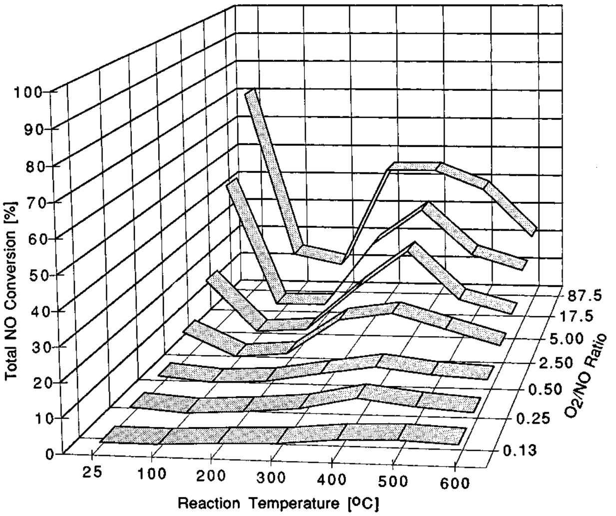

FIG. 8. Effect of the concentration of oxygen on the total conversions of NO in the presence of C_3H_8 at various reaction temperatures. Feed composition: 1000 ppm NO, 1000 ppm C_3H_8, and variable O_2. Total $P = 1 \times 10^5$ Pa; SV = 9600 h^{-1}.

Reactions with Three Reactants

Figure 8 shows the total conversions of NO for a reactant mixture of 0.1% NO, 0.1% C_3H_8, and 0.01–9% O_2 at various temperatures. Except that the feed also contained propane, the reaction conditions in Fig. 8 are the same as those in Fig. 1. There are only minor differences between the two figures: the high temperature maxima are ~50°C higher in Fig. 8 and the conversions in Fig. 8 are somewhat lower than those in Fig. 1 at temperatures below 400°C but somewhat higher at temperatures above 400°C.

Figure 9 shows the conversions of NO to NO_2 and N_2 at the same reaction conditions as Fig. 8. As expected, mainly N_2 is formed in the presence of propane and considerable NO_2 (the only product in Fig. 1) only appears when the reaction temperature is low. Experiments in Fig. 9 were carried out at a constant ratio of $NO/C_3H_8 = 1$. According to Table 1, this is the lowest stoichiometric value for the SCR process. Therefore, SCR reaction was also carried out at different NO/C_3H_8 ratios. For these measurements, the highest oxygen concentration (8.75%) was selected from Fig. 9 because this corresponds to the maximum N_2 production.

The rather surprising results of these experiments are summarized in Fig. 10. Despite many suggestions to the contrary, this graph indicates that the formation of NO_2 alone is not enough to initiate the SCR of NO to N_2 regardless of the temperature. Although ample NO_2 is present to react with the hydrocarbon when $NO/C_3H_8 > 1$, noticeable N_2 production occurs only when $NO/C_3H_8 \leq 1$. Above 100°C,

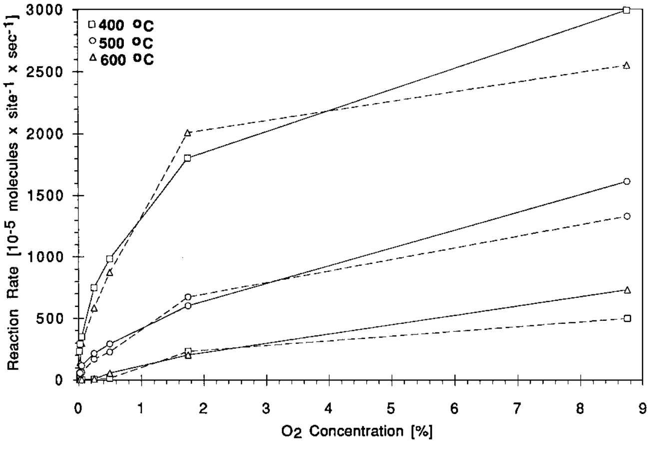

FIG. 7. Effect of the concentration of oxygen on the turnover frequencies in the oxidation of 0.1% NO (solid lines) and 0.1% C_3H_8 (dashed lines) by O_2 at 400, 500, and 600°C; total $P = 1 \times 10^5$ Pa; SV = 9600 h^{-1}. The number of active sites was determined from the BA-OH density (0.424 mmol/g).

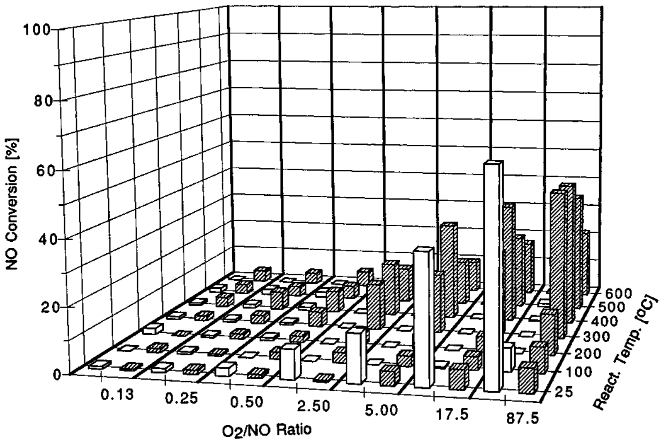

FIG. 9. Conversions of NO to NO_2 (☐) and N_2 (▨) at the same reaction conditions as those in Fig. 8.

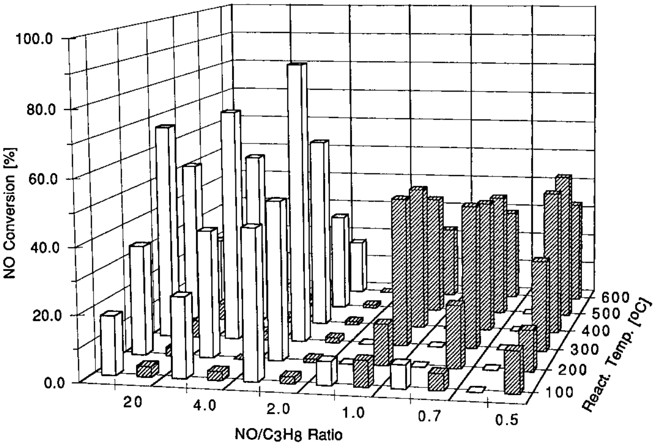

FIG. 10. Effect of the concentration of propane in the presence of O_2 on the conversions of NO to NO_2 (☐) and N_2 (▨) at various reaction temperatures. Feed composition: 0. 1% NO, 9% O_2, and variable C_3H_8. Total $P = 1 \times 10^5$ Pa; SV = 9600 h^{-1}.

the reaction temperature seems not to affect significantly the selectivity for N_2.

Figures 11–13 show the effects of the ratios O_2/NO and NO/C_3H_8 on the total conversion of NO and on the selectivity to NO_2 or N_2 at various temperatures and NO concentrations. For comparison, some data regarding the NO + O_2 reaction are also included in these figures.

Figure 11 summarizes results for the reaction of 0.1% NO with different amount of O_2 and C_3H_8 at 300°C. Similar to Fig. 10, the ratio of NO/C_3H_8 = 1 clearly divides results into two groups. Whenever the concentration of oxygen is high enough to generate noticeable reaction between the NO and the O_2 (line "Cat."), NO conversion also occurs in the full SCR mixture. At NO/$C_3H_8 > 1$, the total conversion of NO (in the presence of C_3H_8) is higher than in the NO + O_2 reaction (in the absence of C_3H_8, line "Cat.") but still NO_2 is the main product. At NO/$C_3H_8 \leq 1$, the total conversion of NO drops and N_2 forms selectively. Similar to the results of Fig. 9 at different reaction temperatures, the concentration of oxygen (O_2/NO ratio) affects the total conversion of NO but has no significant influence on the selectivity for N_2.

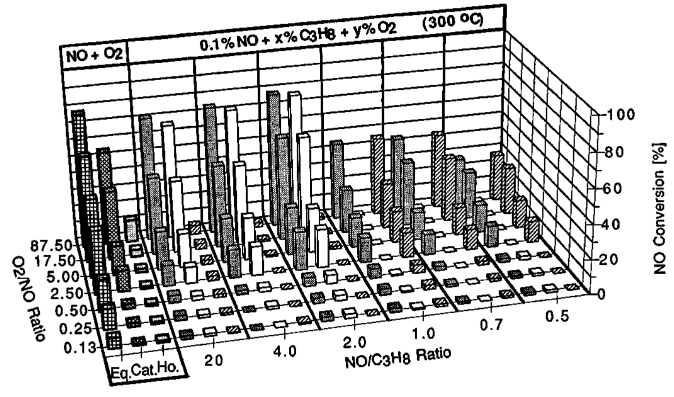

FIG. 11. Effect of the concentrations of propane and oxygen on the conversions of NO (total ▦, to NO_2 ☐, and to N_2 ▨) at 300°C. Feed composition: 0.1% NO, variable C_3H_8 and O_2. Total $P = 1 \times 10^5$ Pa; SV = 9600 h^{-1}. The first three lines are the conversions of NO in the absence of C_3H_8: Eq., equilibrium conversion of NO for the reaction NO + 1/2 $O_2 \Rightarrow NO_2$; Cat., conversion of NO over H-ZSM5 catalyst; Ho., blank conversion of NO in an empty reactor.

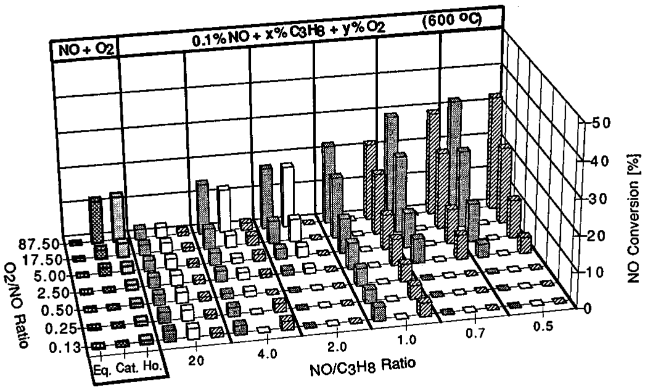

FIG. 12. Effect of the concentrations of propane and oxygen on the conversions of NO (total ▦, to NO_2 ☐ and to N_2 ▨) at 600°C. Except for the temperature, conditions are the same as in Fig. 11.

Results at 400°C were very similar to those shown in Fig. 11. Results at 500°C were rather similar to those at 600°C, which are shown in Fig. 12. Although the NO/C_3H_8 ratio still determines whether NO_2 or N_2 is produced at 600°C, the trends in Fig. 12 are different from those in Fig. 11. In Fig. 12, the conversion of NO monotonically increases with decreasing NO/C_3H_8 ratios (increasing C_3H_8 concentrations).

Figure 13 shows that the conversion of NO increases when the reactant mixture contains 2% NO instead of 0.1%

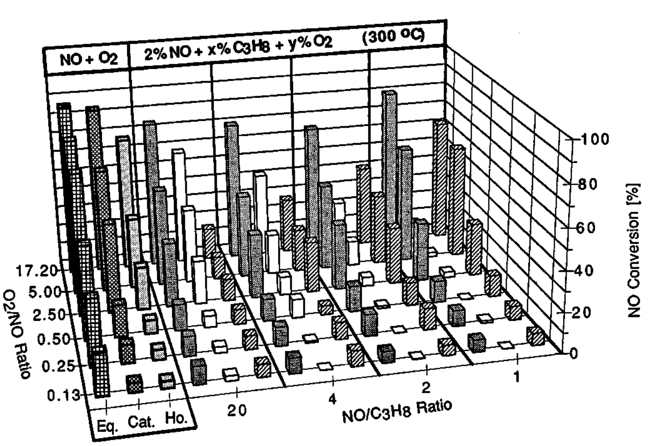

FIG. 13. Effect of the concentrations of propane and oxygen on the conversions of NO (total ▦, to NO_2 ☐, and to N_2 ▨) at 300°C. Except for the concentration of NO being 2%, conditions are the same as in Fig. 11.

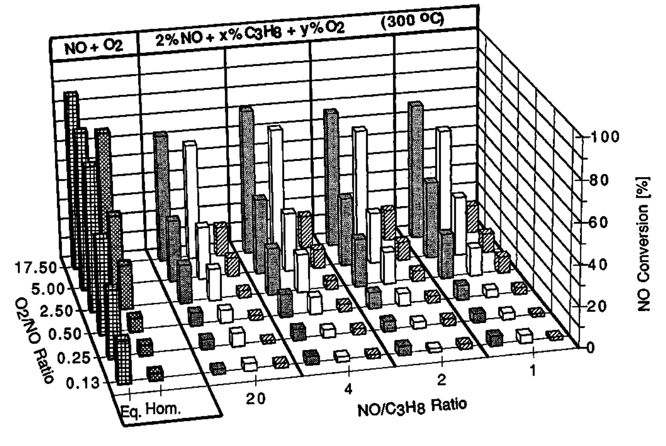

FIG. 14. Effect of the concentrations of propane and oxygen on the conversions of NO (total ▦, to NO_2 ☐, and to N_2 ▨) in an empty reactor. Conditions are same as in Fig. 13.

(Fig. 11). This increase is largely due to a significant homogeneous (or wall catalyzed) NO_2 formation (line "Ho.") (23). Despite this possibility, the NO/C_3H_8 ratio still primarily controls the selectivity. At these high concentrations of reactants, NO_2 is able to activate propane even at ratios $NO/C_3H_8 > 1$. However, the production of N_2 becomes selective only when the partial pressure of C_3H_8 approximates the partial pressure of NO. Figure 14 demonstrates that at $NO/C_3H_8 < 20$ less N_2 forms homogeneously in an empty reactor at the same reaction conditions as in Fig. 13. Thus, the reaction of NO_2 and C_3H_8 is mainly heterogeneously catalyzed even at these high partial pressures of reactants. As demonstrated before (34), the process is largely homogeneous at these high reactant concentrations near 600°C.

Figures 15 and 16 illustrate results for the combustion of propane by O_2 in the presence of NO. Figure 15 shows that the NO/C_3H_8 ratio has a strong impact on the conversion of propane to CO_x: there is no significant propane combustion when $NO/C_3H_8 > 1$, no matter how much oxygen is present at 500°C. Similar trends were observed at all temperatures from 300 to 600°C. This result confirms that NO_2, which is the chief product at these conditions (Figs. 10–12), does not react with C_3H_8 until the partial pressure of C_3H_8 attains or exceeds the partial pressure of NO. Figure 15 also illustrates that, akin to the bimolecular oxidation of propane by O_2 (Fig. 5), a significant amount of CO is formed when the ratio of NO/C_3H_8 is ≤ 1. At the highest concentrations of oxygen (8.75% or 87.5 O_2/C_3H_8 ratio) the average ratio of CO_2/CO was roughly 1/100, 1/2, 1/1, and 2/1 at 300, 400, 500, and 600°C, respectively.

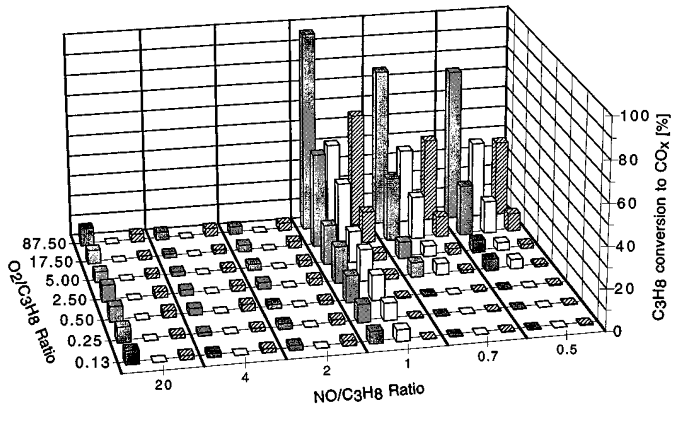

FIG. 15. Effect of the concentrations of propane and oxygen on the conversions of C_3H_8 (total ▦, to CO ☐, and to CO_2 ▨) at 500°C. Feed composition: 0.1% NO, variable C_3H_8 and O_2. Total $P = 1 \times 10^5$ Pa; SV = 9600 h^{-1}.

Figure 16 shows the total conversions of C_3H_8 to CO_x in the SCR reaction at temperatures and O_2/NO ratios similar to those in Fig. 3. Comparison of Fig. 16a and Fig. 3a indicates that NO inhibits the combustion of propane at all reaction temperatures when $NO/C_3H_8 \gg 1$. In contrast, comparison of Fig. 16b and Fig. 3b indicates that the combustion of propane is significantly accelerated between 200 and 500°C (but not at 600°C) when $NO/C_3H_8 = 1$.

Hydrocarbon Efficiency and SCR Stoichiometry

The number of N_2 molecules formed per consumed C_3H_8 (N_2/C_3H_8 in Table 1) was calculated from the total CO_x production. Since the measurements have an accuracy of $\pm 2.5\%$ in determining the conversions of NO or C_3H_8, efficiency data were only calculated when the conversions of both NO and C_3H_8 exceeded 5%. Figure 17 shows the efficiency ratio, N_2/C_3H_8, at various reaction conditions. As expected, the efficiency decreases with increasing temperatures and oxygen concentrations. The efficiency also decreases when the NO/C_3H_8 ratio goes below 1 because it is unlikely that a single NO can react with more than one C_3H_8 molecule. Figure 17 also indicates that the best efficiency for the SCR of NO by C_3H_8 to N_2 over the H-ZSM5 catalyst at the reaction conditions studied is about 1.5; i.e., one C_3H_8 forms 1.5 N_2, which indicates that it has reduced three NO molecules.

DISCUSSION

Experiments with mixtures of one and two of the three reactants, NO, O_2, and C_3H_8, indicate that the oxidation of NO by O_2 and the oxidation of C_3H_8 by O_2 are the only significant reactions at temperatures from 25 to 600°C. Since concerted trimolecular reactions have low probability, one of these oxidations probably initiates the SCR reaction. At 300 and 400°C, the combustion of propane is slow compared to the oxidation of NO by O_2 (Figs. 1, 3, and 7). Therefore, the oxidation of NO to NO_2 may initiate the SCR reaction at these low temperatures. The reaction rates of propane burning approximate the rates of the oxidation of NO at 500°C and substantially exceed them at 600°C (Fig. 7). Consequently, the $C_3H_8 + O_2$ reaction may be the initial reaction step for the SCR process near 600°C.

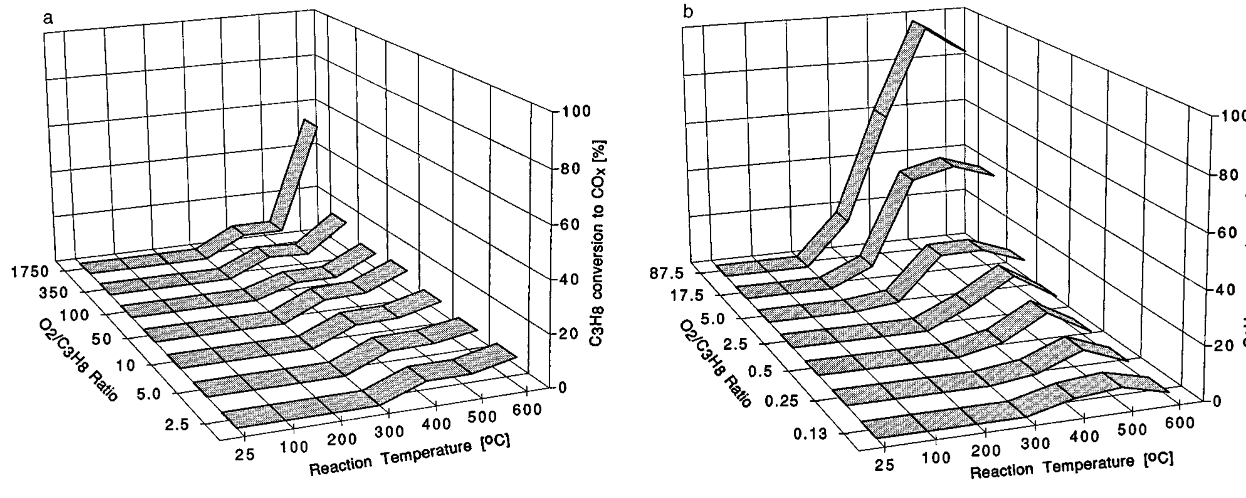

FIG. 16. Total conversion of C_3H_8 to CO_x at various reaction temperatures and O_2/C_3H_8 molar ratios with feeds containing 50 ppm (a) and 1000 ppm (b) C_3H_8, 1000 ppm NO, and variable O_2; total $P = 1 \times 10^5$ Pa; SV = 9600 h^{-1}.

These observations coincide with the recently suggested possibility that the SCR reaction can proceed via two different reaction pathways below and above 500°C even over a single H-ZSM5 catalyst (34). It was proposed that the low temperature reactions are possibly homogeneous–heterogeneous processes involving NO_2 as the key reactant to form radical surface intermediates. At high temperatures, homogeneous radical reactions involving both NO and NO_2 were suggested to be rate determining. The present results suggest that different reaction pathways below and above 500°C may also exist when the SCR feedstock contains as little as 0.1% NO and 0.1% C_3H_8, which are close to their concentrations in automotive exhausts (62). It also appears that the initial reaction step is different in the low and high temperature SCR reactions.

At low temperatures, the formation of NO_2 is a likely initial reaction. As mentioned before, NO_2 is widely considered to be an important intermediate in the SCR of NO over H-ZSM5 because it can react directly with C_3H_8 both in the presence or in the absence of oxygen (1–4, 7–9, 23–26, 41–48). The remarkable similarity of Figs. 1 and 8 also suggests that the oxidation of NO to NO_2 may have an important role in the SCR process. Only recently has it been noted that the formation of NO_2 may be a necessary but not sufficient requirement for the SCR of NO to N_2 (1, 24). Results in Figs. 10–14 demonstrate that the presence of NO_2 alone is not sufficient to initiate the SCR process. In contrast to common belief, the reaction temperature and the concentration of oxygen have only little effect on the interaction of the NO_2 with propane. Figures 11, 12, and 13 show that both NO_2 and N_2 can be selectively formed in the reaction of NO, O_2, and C_3H_8 over H-ZSM5 at very different reaction conditions and mainly the NO/C_3H_8 ratio controls whether NO_2 or N_2 is formed.

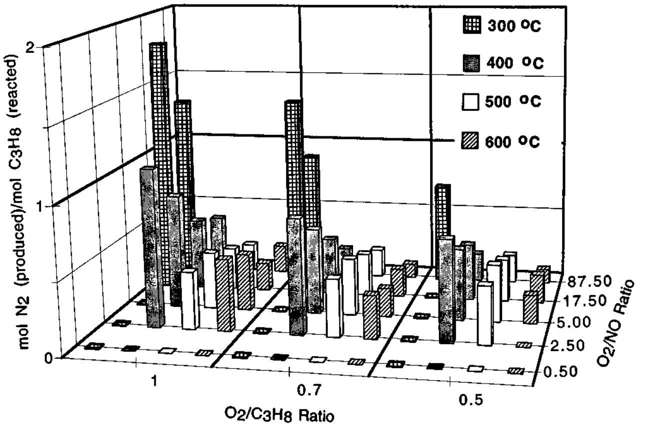

FIG. 17. Efficiency of C_3H_8 to produce N_2 (N_2/C_3H_8) over H-ZSM5 catalyst at various reaction conditions.

The disappearance of the initially formed NO_2 to selectively yield N_2 largely depends on the NO/C_3H_8 ratio in the SCR feedstock. Figures 10–13 show that this change occurs when the partial pressure of C_3H_8 approximates or exceeds the partial pressure of NO, i.e., when $NO/C_3H_8 \leq 1$. Figures 15 and 16 indicate that, simultaneous with the appearance of N_2, a significant propane combustion begins at $NO/C_3H_8 \leq 1$. Several papers have emphasized that the NO/C_xH_y ratio can affect the conversion of NO to N_2 over different catalysts (8, 62). However, this effect has never been associated with a switch from the selective formation of NO_2 to the selective production of N_2 near $NO/C_3H_8 = 1$. The relation between the NO/C_3H_8 ratio and the conversion of propane has also not been previously noted.

Since NO or O_2 alone do not react with C_3H_8 at 300 or 400°C, it is unlikely that C_3H_8 totally suppresses the formation of NO_2 at $NO/C_3H_8 \leq 1$. In agreement with the prior opinions (1–4, 7–9, 23–26), it is likely that NO_2 or its adsorbed precursors initiate the reaction of propane at these low temperatures. Once the propane is activated, NO_2 is totally used up to produce N_2. Figures 1 and 7–9 support the idea that NO_2 can be a reactant in the SCR process because they suggest that the reaction temperature and the concentration of oxygen can control the amount of NO_2 produced in the initial step, and therefore they also affect the production of N_2.

The comparison of Figs. 3b and 16b also suggests that NO_2 can be an intermediate in the SCR process because the accelerated combustion of C_3H_8 in Fig. 16b is probably promoted by NO_2. It has been reported that small amounts of NO can promote the homogeneous combustion of hydrocarbons by converting unreactive HO_2 radicals into chain propagating OH radicals by the reaction $NO + HO_2 \Rightarrow NO_2 + OH$ (67). However, this possibility seems unlikely for the increased propane conversion in Fig. 16b for several reasons: (i) NO does not react with C_3H_8 at the studied reaction conditions; (ii) there is no promotion when NO is in excess compared to C_3H_8 (Fig. 16a); (iii) the promotion of the homogeneous combustion of C_3H_8 by NO does not result in N_2 formation (67), whereas Fig. 9 shows that significant N_2 formation can occur at the reaction conditions of Fig. 16b; (iv) the promotion effect is negligible at 600°C (Fig. 16b), where only minimum NO_2 can form (Figs. 1, 12) (23).

Figure 11 indicates that the hydrocarbon can promote the oxidation of NO, and the conversion of NO to NO_2 approaches equilibrium in the presence of propane (at $NO/C_3H_8 > 1$) but not in its absence (line "Cat.") It is well known that low levels of hydrocarbons can promote the homogeneous oxidation of NO to NO_2 (67, 68). Although data in Fig. 11 unambiguously indicate that the oxidation of NO is mainly a heterogeneously catalyzed process over H-ZSM5 (there is no significant $NO + O_2$ reaction in an empty reactor, designated as "Ho."), the promoting effect of C_3H_8 suggests that the mechanisms of the homogeneous and heterogeneous oxidations may include similar reaction steps. Fast interaction of NO with alkylperoxy radicals ($RO_2 + NO \Rightarrow RO + NO_2$) is a conceivable key reaction for the hydrocarbon promoted homogeneous oxidation of NO by O_2 (67). Thus, the catalytic process may also involve radicals.

As proposed before (34), the interaction of C_3H_8 and NO_2 (a free radical) is probably a homogeneous–heterogeneous process over the H-ZSM5 catalyst involving the formation of radical surface intermediates. Figures 11 to 16 demonstrate that this reaction requires a catalyst at our reaction conditions because even excess NO_2 did not initiate significant homogeneous reaction with C_3H_8. By comparing Figs. 13 and 14, one can conclude that the selective N_2 production is mainly a catalytic process even at high concentrations of reactants when the reaction temperature is below 500°C. In contrast, the SCR of NO by C_3H_8 was found to be a homogeneous process at these high reactant concentrations near 600°C (34).

NO_2 can activate the C_3H_8 either by nitration (1, 3, 63) or by oxidation (2, 24, 48). Over H-ZSM5, both reactions are heterogeneous–homogeneous processes involving BA-OH active sites to form HNO_2, NO_2^+, $C_3H_9^+$, $OH^\bullet$, and other radical intermediates (59, 63). The NH_4^+ exchange capacity of our H-ZSM5 sample indicates that about one-half of the lattice aluminum atoms are associated with BA-OH sites. This result suggests that roughly 25% of the total aluminum content is in extra lattice position and blocks the exchange positions on another 25% of the aluminum ions. It is known that similar neutralization can occur even when the zeolite is only physically mixed and calcined with a binder oxide, e.g., with boehmite at 350°C (50).

In agreement with prior observations (2, 23, 24, 48), the low activity of Li-ZSM5 for the oxidations of NO and C_3H_8 by O_2 compared to that of H-ZSM5 (Figs. 2 and 6) suggests that the BA-OH sites of H-ZSM5 are involved in the active sites for both reactions because the only difference between the two zeolites was that the exchangeable protons of H-ZSM5 were substituted with Li^+ ions in Li-ZSM5. Hence, it is possible that the competition of NO and C_3H_8 for these sites can explain the crucial role of the NO/C_3H_8 ratio in the SCR process: until the partial pressure of C_3H_8 is low compared to that of NO ($NO/C_3H_8 > 1$), the activated adsorption of C_3H_8 (probably in the form of $C_3H_9^+$ (34, 64–66)) can be inhibited by adsorbed NO_x species that preferably adsorb on the BA-OH sites of zeolites (63, 65, 86). Hence, C_3H_8 cannot react with NO_2 at these conditions if the activated adsorption of C_3H_8 is a prerequisite for this reaction. Consistent with this description, the total conversion of NO in Fig. 11 probably decreases at $NO/C_3H_8 \leq 1$ because adsorbed intermediates from the $C_3H_8 + NO_2$ reaction (organic nitro deposits are likely participants in forming N–N bonds (1–3, 34, 48)) partly cover the active sites for the oxidation of NO to NO_2. The reported periodic rate oscillations near 400°C (34) may also be associated with the alternative accessibility of the active sites for the reactions of $NO + O_2$ and $C_3H_8 + NO_2$. Olefins may not require BA-OH sites to react with NO_2. For instance, N_2 production was observed in the direct reaction of NO_2 and C_3H_6 (but not C_3H_8) over a Na-ZSM5 catalyst which is probably free of BA-OH (3, 71). Although some BA-OH site may be present on the surface of Na-ZSM5 (72, 73), it is likely that the easy adsorption of olefins on Lewis sites is more important here. It is known that olefins readily adsorb on the Lewis acidic sites of oxides and are able to create Brønsted acidic sites from their own hydrogens for further reactions (74, 75). It is also possible that base catalysis occurs which is typical for the alkaline exchanged zeolites (76, 77).

Near 600°C, the oxidation of C_3H_8 by O_2 is probably an initial reaction step in the SCR process over H-ZSM5. As shown in Fig. 12, NO_2 is an unlikely initial catalytic product at this temperature, although homogeneously formed NO_2 can participate in the SCR reaction. After correcting for the homogeneous (or wall-induced) formation of NO_2 at high O_2/NO ratios (line "Ho."), it is seen that significant catalytic oxidation of NO to NO_2 does not occur in the absence of propane (line "Cat."). Thus, the conversion of NO to N_2 probably does not require the preliminary formation of NO_2 at the reaction conditions of Fig. 12 (however, the homogeneously formed NO_2 is also used up at $NO/C_3H_8 \leq 1$). This observation agrees with the earlier suggestion that both NO and NO_2 may directly participate in the SCR process at 600°C (34). Although significant CO production was observed even at this high reaction temperature (average CO_2/CO ratio is 1/2), it is well documented that CO is not a good reductant for NO at net oxidizing conditions (1, 21, 44, 51–53, 59, 78). Large CO production is typical when the oxidation of hydrocarbons involves the decomposition of alkoxy of alkyl peroxy intermediates ($C_xH_yO_z$) to CO because the oxidation of CO is a relatively slow catalytic process (57, 58). $C_xH_yO_z$ derivatives have been suggested to be possible intermediates in the SCR process over many catalysts (1, 6, 21, 40, 60, 61). Although this possibility has rarely been considered for the H-ZSM5 zeolite (1, 40), present results suggest that formation of $C_xH_yO_z$ can be a viable initial step in the SCR reaction over this catalyst above 400°C.

The combustion of hydrocarbons by O_2 is a typical radical process which can proceed homogeneously at temperatures much lower than 600°C (57). However, this process requires a catalyst at our reaction conditions. Figure 6 demonstrates that the BA-OH sites of H-ZSM5 are probably involved in the active sites for this reaction. Since some catalytic activity remained after replacing the protons of H-ZSM5 by Li^+ ions, it is likely that the oxidation of propane can proceed on the Lewis acidic and basic sites of the zeolite. This is reasonable, because such sites are capable of generating oxygen and hydrocarbon radicals and an exchange between gas phase and lattice oxygen can also occur (13–16, 48, 59, 79–81). Lewis sites and lattice oxygens may also participate in the oxidation of NO(1, 12, 14, 79, 80, 82–85). The comparison of Figs. 3a and 16a indicates that the combustion of propane is inhibited in the presence of NO when $NO/C_3H_8 > 1$ (excess NO). Consistent with the previous description, the strong adsorption of NO (probably mainly on the BA-OH sites (65, 86)) may prevent the adsorption of propane at these conditions and, hence, its ignition by O_2. A similar inhibition effect of NO in the aromatization of propane has been recently reported (65).

The different trends in the N_2 production when $NO/C_3H_8 \leq 1$ shown in Figs. 11 and 12 coincide with the proposed different reaction routes at temperatures below and above 500°C. At 300°C (Fig. 11), excess C_3H_8 (decreasing NO/C_3H_8 ratio) has no significant effect on the conversion of NO to N_2 because the formation of NO_2 controls the SCR process. At 600°C (Fig. 12), excess C_3H_8 enhances the production of N_2 because more C_3H_8 can produce more $C_xH_yO_z$ to initiate reaction with NO_x.

Since both the low and the high temperature SCR processes likely involve radicals, it is understandable that a variety of intermediates could be detected at different reaction conditions as mentioned in the Introduction. Radical type mechanisms have been recently proposed for several metal exchanged ZSM5 zeolites (1–3, 48). Some of the metal exchanged ZSM5 samples may be more active for the SCR of NO than H-ZSM5. By replacing the protons of H-ZSM5 with suitable multivalent metal cations, enhanced N_2 production can be observed when the metal cation can accelerate the oxidative dehydrogenation of hydrocarbons (10, 19, 26, 27, 31, 34) or the oxidation of NO to NO_2 (24) (both reactions have been suggested to be rate determining (1–3, 23, 38, 39, 48) or can increase the capacity of zeolites to adsorb hydrocarbons (69). Accelerated hydrocarbon burning is probably not helpful because it will reduce the concentration of $C_xH_yO_z$ intermediates that may be required for the subsequent interaction with NO_x (87).

According to Fig. 17, the best efficiency for the SCR of NO by C_3H_8 to N_2 is about 1.5 N_2/C_3H_8. Since the direct oxidation of C_3H_8 by O_2 to CO_x is not significant when $N_2/C_3H_8 \sim 1.5$, this value can be used to calculate the stoichiometry of the SCR reaction. Hence, the third equation in Table 1 is the closest to describe this stoichiometry at 300°C. Recalling that CO is virtually the only product from C_3H_8 at this temperature, the equation is

$$2C_3H_8 + 6NO + 4O_2 \Rightarrow 6CO + 8H_2O + 3N_2.$$

At higher temperatures, where CO_2 formation was also observed, the direct combustion of C_3H_8 by O_2 (without N_2 production) is probably significant.

Although the H-ZSM5 catalyst itself can be more active for certain SCR reactions than many other ZSM5 catalysts (2, 42–46), its hydrothermal stability above 600°C (an important practical consideration) is lower than that of the metal exchanged ZSM5 zeolites (70, 88, 89). Our H-ZSM5 sample was used for more than 1.5 years. Despite large amounts of H_2O produced during the experiments at different reaction conditions, the activity of the catalyst for the SCR of NO to N_2 proved to be quite stable. Repeated measurements at the beginning and at the end of the 1.5-year period showed less than 5% difference in the N_2 production when the SCR experiments were carried out at identical reaction conditions. However, the conversion of propane in the oxidation of C_3H_8 by O_2 decreased by about 30% during this time. The XRD pattern of the sample did not change.

CONCLUSIONS

(1) The reaction of $NO + C_3H_8 + O_2$ over H-ZSM5 catalyst can result in the selective production of either NO_2 or

N_2. The selectivity for N_2 largely depends on the ratio of NO/C_3H_8 in the feedstock. The concentration of oxygen and the reaction temperature have only minor impact on the selectivity for N_2.

(2) In agreement with prior findings, the SCR of NO by C_3H_8 to N_2 probably proceeds via two different mechanisms at temperatures below and above 500°C over H-ZSM5. It is also likely that the initial reactions are different in these temperature regimes. Homogeneous (or wall catalyzed) and heterogeneous reactions of radicals can be involved in both the initial and the subsequent reaction steps.

(3) Oxidation of C_3H_8 by O_2 is a likely initial step in the SCR process near 600°C. Both NO and NO_2 may directly participate in the SCR process at these high temperatures and the interaction of NO_x and $C_xH_yO_z$ is a possible reaction step.

(4) The SCR process may begin with the oxidation of NO to NO_2 below 500°C. There is no significant homogeneous interaction between NO_2 and C_3H_8 at these temperatures. When the partial pressure of NO exceeds the partial pressure of C_3H_8 in the SCR feed, the catalytic interaction of NO_2 and C_3H_8 is also inhibited.

(5) The oxidation of NO by O_2 and the oxidation of C_3H_8 by O_2 are both catalytic processes and the active sites of H-ZSM5 probably involve BA-OH groups. These groups may also be involved in the active sites for the reaction of NO_2 with C_3H_8.

(6) The concentration of oxygen and the reaction temperature affect the rates of the reactions $C_3H_8 + O_2$ and $NO + O_2$, therefore these parameters also affect the production of N_2 in the SCR process.

(7) Since significant coke formation was not observed in the absence of oxygen, it is an unlikely intermediate in the SCR process. The direct interaction of NO and C_3H_8 is also an unlikely reaction step.

(8) The efficiency of propane to produce N_2 varies from about 0.1 to 1.8 N_2/C_3H_8. The efficiency decreases with increasing temperatures as well as with increasing O_2 and C_3H_8 concentrations in the feedstock. The likely overall stoichiometry of the SCR process at 300°C is $2C_3H_8 + 6NO + 4O_2 \Rightarrow 6CO + 8H_2O + 3N_2$. At higher temperatures, formation of CO_2 also occurs.

ACKNOWLEDGMENTS

The authors thank the Ford Motor Company and the Institute for Manufacturing Research at Wayne State University for support of this research. We also thank Mr. Michael Lukitsch for determining the NH_4^+ exchange capacity of the H-ZSM5 sample.

REFERENCES

1. Shelef, M., *Chem. Rev.* **95**, 209 (1995).
2. Witzel, F., Sill, G. A., and Hall, W. K., *J. Catal.* **149**, 229 (1994).
3. Yokoyama, C., and Misono, M., *J. Catal.* **150**, 9 (1994).
4. Li, Y., Slager, T. L., and Armor, J. N., *J. Catal.* **150**, 388 (1994).
5. Burch, R., and Scire, S., *Appl. Catal. B* **3**, 295 (1994).
6. Cho, B. K., *J. Catal.* **142**, 418 (1993).
7. Iwamoto, M., and Mizuno, N., *J. Automotive Eng.* **207**, 23 (1993).
8. Petunchi, J. O., Sill, G., and Hall, W. K., *Appl. Catal. B* **2**, 303 (1993).
9. Ansell, G. P., Diwell, A. F., Golunski, S. E., Hayes, J. W., Rajaram, R. R., Truex, T. J., and Walker, P., *Appl. Catal. B: Environmental* **2**, 81 (1993).
10. Larsen, S. C., Aylor, A., Bell, A. T., and Reimer, J. A., *J. Phys. Chem.* **98**, 11533 (1994).
11. Moretti, G., *Catal. Lett.* **23**, 135 (1994).
12. Lei, G. D., Adelman, B. J., Sarkany, J., and Sachtler, W. M. H., *Appl. Catal. B* **5**, 245 (1995).
13. Loktev, M. I., and Slinkin, A. A., *Russ. Chem. Rev.* **45**, 807 (1976).
14. Rabo, J. A., and Gajda, G. J., *Catal. Rev.* **31**, 385 (1989–1990).
15. Volodin, A. M., Bolshov, V. A., and Panov, G. I., *J. Phys. Chem.* **98**, 7548 (1994).
16. Valyon, J., Millman, W. S., and Hall, W. K., *Catal. Lett.* **24**, 215 (1994).
17. Li, Y., and Armor, J. N., *J. Catal.* **145**, 1 (1994).
18. Petunchi, J. O., and Hall, W. K., *Appl. Catal. B* **3**, 239 (1994).
19. Nishizaka, Y., and Misono, M., *Chem. Lett.* 2237 (1994).
20. Li, Y., and Armor, J. N., *Appl. Catal. B* **2**, 239 (1993).
21. Hamada, H., Kintaichi, Y., Yoshinari, T., Tabata, M., Sasaki, M., and Ito, T., *Catal. Today* **17**, 111 (1993).
22. Centi, G., Perathoner, S., and Dall'Olio, L., *Appl. Catal. B* **4**, L275 (1994).
23. Halasz, I., Brenner, A., and Ng, S. K., *Catal. Lett.* **34**, 151 (1995).
24. Shelef, M., Montreuil, C. N., and Jen, H. W., *Catal. Lett.* **26**, 277 (1994).
25. Shimokawabe, M., Ohi, A., and Takezawa, N., *React. Kinet. Catal. Lett.* **52**, 393 (1994).
26. Bethke, K. A., Li, C., Kung, M. C., Yang, B., and Kung, H. H., *Catal. Lett.* **31**, 287 (1995).
27. Chajar, Z., Primet, M., Praliaud, H., Chevrier, M., Gauthier, C., and Mathis, F., *Catal. Lett.* **28**, 33 (1994).
28. Bell, V. A., Feeley, J. S., Deeba, M., and Farrauto, R. J., *Catal. Lett.* **29**, 15 (1994).
29. Obuchi, A., Ogata, A., Mizuno, K., Ohi, A., Nakamura, M., and Ohuchi, H., *J. Chem. Soc. Chem. Commun.* 247 (1992).
30. Obuchi, A., Nakamura, M., Ogata, A., Mizuno, K., Ohi, A., and Ohuchi, H., *J. Chem. Soc. Chem. Commun.* 1150 (1992).
31. Poignant, F., Saussey, J., Lavalley, J.-C., and Mabilon, G., *J. Chem. Soc. Chem. Commun.* 89 (1995).
32. Adelman, B. J., Lei, G.-D., and Sachtler, W. M. H., *Catal. Lett.* **28**, 119 (1994).
33. Sasaki, M., Hamada, H., Kintaichi, Y., and Ito, T., *Catal. Lett.* **15**, 297 (1992).
34. Halasz, I., Brenner, A., Shelef, M., and Ng, S. K., *J. Phys. Chem.* **99**, 17186 (1995).
35. Radtke, F., Koeppel, R. A., and Baiker, R. A., *Catal. Lett.* **28**, 131 (1994).
36. Hayes, N. W., Grünert, W., Hutchings, G. J., Joyner, R. W., and Shpiro, E. S., *J. Chem. Soc. Chem. Commun.* 531 (1994).
37. Radtke, F., Koeppel, R. A., and Baiker, A., *J. Chem. Soc. Chem. Commun.* 427 (1995).
38. Bennett, C. J., Bennett, P. S., Golunski, S. E., Hayes, J. W., and Walker, A. P., *Appl. Catal. A* **86**, L1 (1992).
39. Cowan, A. D., Dümpelmann, R., and Cant, N. W., *J. Catal.* **151**, 356 (1995).
40. Hamada, H., Kintaichi, Y., Sasaki, M., Ito, T., and Tabata, M., *Appl. Catal.* **64**, L1 (1990).
41. Hamada, H., Kintaichi, Y., Sasaki, M., Ito, T., and Tabata, M., *Appl. Catal.* **70**, L15 (1991).
42. Hamada, H., Kintaichi, Y., Tabata, M., Sasaki, M., and Ito, T., "67th CATSJ Meeting Abstracts," No. A1, Vol. 33, p. 59. 1991.

43. Yogo, K., Tanaka, S., Ihara, M., Hishiki, T., and Kikuchi, E., *Chem. Lett.* 1025 (1992).
44. Hamada, H., Kintaichi, Y., Tabata, M., Sasaki, M., and Ito, T., *Sekiyu Gakkaishi* **36**, 149 (1993).
45. Yogo, K., Umeno, M., Watanabe, H., and Kikuchi, E., *Catal. Lett.* **19**, 131 (1993).
46. Yogo, K., Ihara, M., Terasaki, I., and Kikuchi, E., *Appl. Catal. B* **2**, L1 (1993).
47. Satsuma, A., Yamada, K., Mori, T., Niwa, M., Hattori, T., and Murakami, Y., *Catal. Lett.* **31**, 367 (1995).
48. Lukianov, D. B., Sill, G., d'Itri, J. L., and Hall, W. K., *J. Catal.* **153**, 265 (1995).
49. Li, Y., and Armor, J. N., *Appl. Catal. B* **1**, L31 (1992).
50. Martin, A., and Berndt, H., *React. Kinet. Catal. Lett.* **52**, 405 (1994).
51. Halasz, I., Brenner, A., Shelef, M., *Appl. Catal. B: Environmental,* **2**, 131 (1993).
52. Halasz, I., Brenner, A., and Shelef, M., *Catal. Lett.* **22**, 147 (1993).
53. Halasz, I., Brenner, A., and Shelef, M., *Catal. Lett.* **16**, 311 (1992).
54. Halasz, I., Brenner, A., Shelef, M., and Ng, K. Y. S., *J. Catal.* **126**, 109 (1990).
55. Halasz, I., Brenner, A., Shelef, M., and Ng, K. Y. S., *Catal. Lett.* **6**, 349 (1990).
56. Brandin, J. G. M., Andersson, L. A. H., and Obenbrand, C. U. I., *Acta Chem. Scand.* **44**, 784 (1990).
57. Benson, S. W., *Prog. Energy Combust. Sci.* **7**, 125 (1981).
58. Krylov, O. V., and Shub, B. R., "Nonequilibrium Processes in Catalysis." CRC Press, Boca Raton, Ann Arbor, London, Tokyo, 1994.
59. Yu. Sinev, M., Ya. Margolis, L., and Korchak, V. N., *Russ. Chem. Rev.* **64**, 349 (1995).
60. Iwamoto, M., and Hamada, H., *Catal. Today* **10**, 57 (1991).
61. Montreuil, C. N., and Shelef, M., *Appl. Catal. B.* **1**, L1 (1992).
62. Taylor, K. C., *Catal. Rev. Sci. Eng.* **35**, 457 (1992).
63. Malysheva, L. V., Paukshtis, E. A., and Ione, K. G., *Catal. Rev. Sci. Eng.* **37**, 179 (1995).
64. Giannetto, G., Monque, R., and Galiasso, R., *Catal. Rev. Sci. Eng.* **36**, 271 (1994).
65. Buckles, G., and Hutchings, G. J., *J. Catal.* **151**, 33 (1995).
66. Meusinger, J., and Corma, A., *J. Catal.* **152**, 189 (1995).
67. Bromly, J. H., Barnes, F. J., Mandyczewsky, R., Edwars, T. J., and Haynes, B. S., "Proceedings of the Twenty-Fourth International Symposium on Combustion Sydney, Australia," p. 899. Organized by the Combustion Institute, Pittsburgh, Pennsylvania, 1992.
68. Hori, M., Matsunaga, N., Malte, P. C., and Marinov, N. M., "Proceedings of the Twenty-Fourth International Symposium on Combustion Sydney, Australia," p. 899. Organized by The Combustion Institute, Pittsburgh, Pennsylvania, 1992.
69. Jen, H. W., and Otto, K., *Catal. Lett.* **26**, 217 (1994).
70. Grinsted, R. A., Jen, H. W., Montreuil, C. N., Rokosz, M. J., and Shelef, M., *Zeolites* **13**, 602 (1993).
71. Yokoyama, Ch., Yasuda, H., and Misono, M., *71th CATSJ Meeting Abstracts: No. 1B6* **35**, 125 (1993).
72. d'Itri, J. L., and Sachtler, M. H., *Appl. Catal. B* **2**, L7 (1993).
73. Parrillo, D. J., Dolonec, D., Gorte, R. J., and McCabe, R. W., *J. Catal.* **142**, 708 (1993).
74. Irvine, E. A., John, C. S., Kemball, C., Pearman, A. J., Day, M. A., and Sampson, R. J., *J. Catal.* **61**, 326 (1980).
75. Gati, Gy., and Halasz, I., *J. Catal.* **82**, 223 (1983).
76. Garces, J. M., Vrieland, G. E., Bates, S. I., and Scheidt, F. M., *Stud. Surf. Sci. Catal.* **20**, 67 (1985).
77. Martens, L. R. M., Grobet, P. J., and Jacobs, P. A., *Nature* **315**, 568 (1985).
78. d'Itri, J. L., and Sachtler, W. M. H., *Catal. Lett.* **15**, 289 (1992).
79. Kasai, P. H., and Bishop, R. J., Jr., *ACS Monogr.* **171**, 350 (1976).
80. Poutsma, M. L., *ACS Monogr.* **171**, 529 (1976).
81. Chang, Y.-F., Somorjai, G. A., and Heinemann, H., *J. Catal.* **154**, 24 (1995).
82. Védrine, J. C., Auroux, A., Bolis, V., Dejaifve, P., Naccache, C., Wierzchowski, P., Derouane, E. G., Nagy, J. B., Gilson, J. P., van Hooff, J. H. C., van den Berg, J. P., and Wolthuizen, J., *J. Catal.* **59**, 248 (1979).
83. Witzel, F., Karge, H. G., Gutsze, A., and Hartel, U., *Chem. Ing. Tech.* **63**, 744 (1991).
84. Anderson, L. A. H., Brandin, J. G. M., and Odenbrand, C. U. I., *Catal. Today* **4**, 173 (1989).
85. Brandin, J. G. M., Anderson, L. A. H., and Odenbrand, C. U. I, *Catal. Today* **4**, 187 (1989).
86. Hoost, T. E., Laframboise, K. A., and Otto, K., *Catal. Lett.* **33**, 105 (1995).
87. Nishizaka, Y., and Misono, M., *Chem. Lett.* 1295 (1993).
88. Suzuki, K., Sano, T., Shoji, H., Murakami, T., Ikai, S., Shin, S., Hagiwara, H., and Takaya, H., *Chem. lett.* 1507 (1987).
89. Iwamoto, M., Yahiro, H., Shin, H. K., Watanabe, M., Guo, J., Konno, M., Chikahisa, T., and Murayama, T., *Appl. Catal. B* **5**, L1 (1994).
90. Ciambelli, P., Corbo, P., Gambino, M., Minelli, G., Moretti, G., and Porta, P., *Catal. Today* **26**, 33 (1995).