JOURNAL OF CATALYSIS 155, 184–195 (1995)

Nitric Oxide Reduction by Ethylene over Cu–ZSM-5 under Lean Conditions: Study of Reaction Dynamics by Transient Experiments

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Received May 10, 1994; revised March 29, 1995

This work has investigated the dynamic behavior of a Cu–ZSM-5 catalyst for NO reduction by ethylene under highly oxidizing conditions, typical of lean-burn engine exhaust, using a fixed-bed laboratory reactor. The role of hydrocarbon and oxygen in the NO reduction process has also been investigated, employing transient experimental techniques such as cyclic operation and temperature-programmed desorption and oxidation experiments. Results have indicated that the chromatographic separation effect among the reactants due to different adsorption affinity plays an important role in determining the catalytic activity of Cu–ZSM-5. Various reaction mechanisms proposed in the literature are discussed along with the role of hydrocarbon and oxygen. Based on our observations we propose a reaction mechanism which involves NO decomposition and hydrocarbon oxidation. We also demonstrate experimentally that the activity of the Cu–ZSM-5 catalyst can be significantly improved for NO reduction by a proper cyclic operation. © 1995 Academic Press, Inc.

INTRODUCTION

Encouraging literature reports on catalytic reduction of NO by hydrocarbons in the presence of excess oxygen have generated considerable interest among catalysis researchers in this reaction system due to its practical importance in controlling exhaust emissions from lean-burn gasoline and diesel-powered engines (1–11). Cu–ZSM-5 has been widely touted as the most promising "lean NO_x catalyst," even though more recent reports indicate that Pt–ZSM-5 is more efficient than Cu–ZSM-5 for low-temperature applications such as diesel engine exhaust (12). Among hydrocarbon reductants, ethylene and propylene have been most frequently used as the reducing agent. Although both ethylene and propylene are active for selective reduction of NO over Cu–ZSM-5 under lean conditions, ethylene has been shown to be a more efficient reductant than propylene due to its superior selectivity (7). When a mixture of ethylene and propylene was used, the activity of propylene toward NO reduction was almost completely suppressed in the presence of ethylene. This antagonistic kinetic interaction between two hydrocarbons was attributed to the competitive adsorption/diffusion processes occurring in the zeolite pore structure (7). These earlier studies concentrated on steady-state activity of the catalysts, with the exception of several transient studies reported recently (13–15).

Perhaps the most important characteristic feature of lean-NO_x catalysts such as Cu–ZSM-5 is the fact that the catalyst's steady-state activity as a function of temperature exhibits a maximum NO conversion. The temperature at which the NO conversion reaches its maximum corresponds to the temperature where complete (or nearly complete) oxidation of hydrocarbon is achieved (7). Above this temperature, the NO conversion decreases monotonically. In general, the desirable level of catalytic activity of Cu–ZSM-5 is confined to a narrow temperature range, commonly known as the *temperature window* of the NO reduction activity. Both the peak conversion level and the width of the temperature window of a Cu–ZSM-5 catalyst depend on the type of hydrocarbon reductants. Also, the overall efficiency of Cu–ZSM-5 as a lean-NO_x catalyst has been shown to depend on the lightoff characteristics of the hydrocarbon used as the reductant. The closer the lightoff temperature of the hydrocarbon oxidation (by O_2) to that of the NO reduction, the more effective the catalyst becomes. This means that the ideal hydrocarbon as the lean-NO_x reductant is expected to have the same lightoff temperature for its oxidation as the lightoff temperature of NO reduction, and that a hydrocarbon with low lightoff temperature is not necessarily a better reductant than the one with high lightoff temperature (7).

To be able to improve the catalytic activity of Cu–ZSM-5 over the entire temperature range of our interest (i.e., 200–500°C), it is desirable to widen the temperature window for the NO reduction activity. To accomplish this, better understanding of the reaction mechanism is needed. The reaction mechanism of NO reduction by hydrocarbons in the presence of excess oxygen over Cu–ZSM-5 is not yet well understood, with many unsettled questions concerning the nature of reactive intermediates as well as the role of oxygen and hydrocarbons, although the active site for NO reduction has been generally identified as Cu^{1+} sites and the adsorption sites for hydrocarbons

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are known to be acidic zeolite sites (16, 17). The major role of oxygen is thought to be to stabilize this active site (Cu^{1+}) (16) or to remove harmful carbonaceous deposits or their precursors from the catalyst (8). On carbonaceous deposits, Ansell *et al.* (13) considered them as reactive intermediates which promote the NO reduction activity of the catalyst, while d'Itri and Sachtler (8) treated them as site-blocking poisons. Partially oxidized hydrocarbons were also proposed as intermediates that are reactive toward the reduction of NO (5, 18–20). However, Petunchi *et al.* (11) could not observe any partially oxidized hydrocarbons, while Ansell *et al.* (13) observed only a very small amount of partially oxidized intermediates. Nitrogen dioxide and NCO were also proposed as reaction intermediates, which can readily react with hydrocarbons and NO, respectively (16, 21). On the other hand, Cho (7) and Burch and Millington (14) proposed the direct decomposition of NO as the essential step of the lean-NO_x catalysis, while Ansell *et al.* (13) and Bennett *et al.* (18) excluded this possibility.

To the best of our knowledge, the existing literature reports on lean-NO_x catalysis have dealt exclusively with chemical aspects of the catalytic activity. That is, the reaction dynamics involving physicochemical interactions through diffusion/adsorption processes taking place in addition to the catalytic reaction appears to be overlooked in the literature. Obviously, transient experimental techniques are very useful in investigating the effect of diffusion/adsorption on the catalytic activity, and they have been used to elucidate reaction mechanism as well as to enhance catalyst's activity (e.g., 22–24). For example, forced periodic operation of catalysts has been used for CO oxidation (24–29), NO + CO reaction (30, 31), N_2O decomposition (32), and N_2O + CO reaction (33) to enhance the reactivity of catalysts and/or to elucidate the kinetic mechanisms.

In this work, we investigate the role of hydrocarbon and oxygen in the NO reduction process under lean conditions, employing transient experimental techniques such as cyclic operation and temperature-programmed desorption (TPD) and oxidation (TPO). Ethylene was chosen as the reducing hydrocarbon based on our earlier findings that it is the most appropriate single hydrocarbon for laboratory experiments of the selective reduction of NO over Cu–ZSM-5 (7). Results have demonstrated that the chromatographic separation effect among reactants due to different adsorption affinity is an important factor in determining the catalytic activity of Cu–ZSM-5 for NO reduction under lean conditions.

EXPERIMENTAL

TABLE 1

Standard Experimental Conditions

Reactor	0.32-cm-od stainless-steel tubing Catalyst = Cu–ZSM-5 powder Si/Al ratio = 32 Cu loading = 2.4 wt% Particle size = 80–120 mesh Sample weight = 0.015 g Catalyst bed length = 1 cm Gas space velocity = 86,000 h^{-1} Temperature = 200–600°C Pressure = 101.3 kPa (1 atm)
Feed concentration	C_2H_4 = 1200 ppm NO = 230 ppm O_2 = 7% He = balance

ZSM-5 zeolite powder in the size range of approximately 0.5–1 μm was obtained from PQ Corporation, which had a high Si/Al ratio of approximately 32. The Cu–ZSM-5 catalyst was prepared by Johnson Matthey from ion exchange of copper on the ZSM-5 zeolite to obtain a copper loading of 2.4 wt%. This Cu–ZSM-5 powder was made into a disk by compressing at 10-ton pressure. The resulting Cu–ZSM-5 disk was crushed, ground, and screened for 80–120 mesh sizes to be used for reactor experiments. The catalyst was calcined in flowing air (50 cm^3/min) for 4 h at 500°C.

The reactor was made of a 0.32-cm o.d. stainless-steel tube packed with the Cu–ZSM-5 powder. The reactor temperature was measured at the inlet of the catalyst bed and controlled electronically with a typical precision of ±1°C. Before each experimental run for activity measurement, the catalyst was pretreated with 7% oxygen in He for 2 h at 600°C. The gas flow rate through the reactor was measured and controlled by electronic mass flow controllers. The pressure drop across the reactor bed was approximately 4 kPa at 300°C under the standard experimental conditions. Transient responses of the gas-phase concentration in the exit stream from the reactor were monitored as a function of time by a quadrupole mass spectrometer (Balzers QMG 311) equipped with a capillary inlet system. Mass number 27 was used for a secondary mass peak of ethylene to prevent interference between the principal mass peak of ethylene (mass number = 28) and that of N_2 or CO (mass number = 28). Details of standard experimental conditions are listed in Table 1. In the cycling experiments the pulse duration was controlled by a programmable timer.

Formation of possible reaction intermediates such as N_2O and NO_2 was negligible as measured at the reactor exit under our experimental conditions, and the nitrogen balance was within 5% of complete closure. This finding is in good agreement with recent observations by Bethke *et al.* under similar reaction conditions (34).

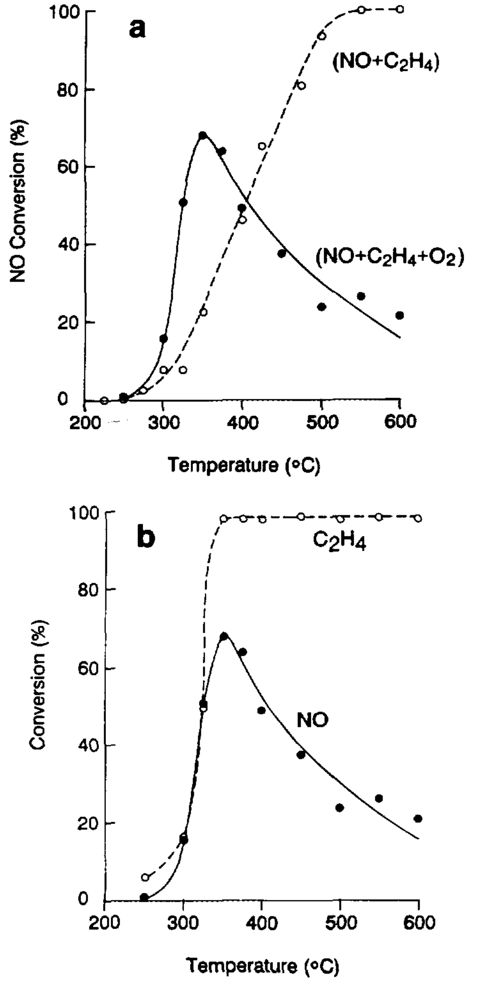

FIG. 1. (a) Effect of oxygen on steady-state activity of Cu–ZSM-5 (C_{NO} = 230 ppm, $C_{C_2H_4}$ = 1200 ppm, C_{O_2} = 7% if present). (b) Steady-state activity of Cu–ZSM-5 for ($NO + C_2H_4 + O_2$) reaction (C_{NO} = 230 ppm, $C_{C_2H_4}$ = 1200 ppm, C_{O_2} = 7%).

RESULTS

Effect of Oxygen on Steady-State Activity of Cu–ZSM-5

The effect of oxygen on the activity of the Cu–ZSM-5 catalyst for NO reduction by ethylene was examined by comparing the NO conversion efficiency in the $NO + C_2H_4$ mixture with that in the $NO + C_2H_4 + O_2$ mixture. Presented in Fig. 1a are conversions of NO to N_2 for both the $NO + C_2H_4$ and the $NO + C_2H_4 + O_2$ reaction systems at a space velocity of 86,000 h^{-1}. It indicates that both reaction systems can reduce NO to N_2. [Especially, the activity of Cu–ZSM-5 for the $NO + C_2H_4$ reaction is shown to be substantially higher than that reported by Iwamoto (35).] However, the $NO + C_2H_4 + O_2$ reaction system is more efficient for NO reduction than the $NO + C_2H_4$ reaction system in the low-temperature regime below 400°C, whereas this trend reverses in the high-temperature regime above 400°C. That is, the presence of oxygen in the $NO + C_2H_4 + O_2$ system promotes the NO conversion below 400°C, but it hurts the NO conversion above 400°C. The maximum NO conversion occurring at 350°C for the $NO + C_2H_4 + O_2$ reaction system is 68.1%, which corresponds to a turnover frequency (TOF) of 0.016 s^{-1} based on the measured Cu surface area. [The total Cu surface area in the used catalyst sample was estimated to be 148 cm^2 from the measurements of dissociative chemisorption of N_2O, assuming the ratio of O/Cu ratio to be 0.5 (36).]

Presented in Fig. 1b are the conversions of NO and C_2H_4 for the $NO + C_2H_4 + O_2$ system. In agreement with the earlier observation in the monolith reactor (7), the lightoff of the NO conversion coincides with the lightoff of the C_2H_4 conversion for the $NO + C_2H_4 + O_2$ system. (The C_2H_4 conversion for the $NO + C_2H_4$ system was negligible due to the large stoichiometric excess of C_2H_4.) Comparison of Figs. 1a and 1b suggests that the beneficial effect of oxygen for the low-temperature NO conversion in the $NO + C_2H_4 + O_2$ system may be due to the conversion of C_2H_4 via oxidation. In other words, the C_2H_4 scavenging effect of oxygen via C_2H_4 oxidation may facilitate the NO conversion in the $NO + C_2H_4 + O_2$ reaction system by clearing the NO diffusion path toward the active catalytic sites for NO adsorption. (At low temperatures, especially below the reaction lightoff temperature, the interior of the catalyst is predominantly occupied by ethylene due to its strong adsorption affinity, as will be shown later.) More detailed discussion will be presented along with the results of transient experiments.

Transient Cycling Experiments Alternating $NO + C_2H_4$ and O_2

To better understand kinetic interaction among reactant species, it is useful to examine the dynamic responses of those species under transient operating conditions. This is especially true when the adsorption/diffusion characteristics differ widely among the reactant species, as is the case for the lean NO_x catalysis over Cu–ZSM-5.

Figure 2 illustrates the cycling scheme used for transient pulse experiments with the $C_2H_4 + NO + O_2$ reaction system; a pulse of 20 s duration containing C_2H_4 + NO + Ar was introduced to the reactor packed with the Cu–ZSM-5 powder, followed by an oxygen pulse of the same duration. This cycling process was repeated until the system was stabilized. Presented in Figs. 3a through 3g are effects of catalyst temperature on transient response of the Cu–ZSM-5 catalyst as reflected by the reactor outlet concentration monitored by a mass spectrometer during symmetric cyclic operation with a cycling

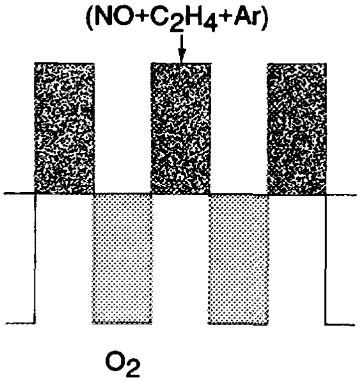

FIG. 2. Cycling scheme used for the cyclic operation of (NO + C_2H_4 + O_2) reaction (C_{NO} = 230 ppm, $C_{C_2H_4}$ = 1200 ppm, C_{O_2} = 7%).

period τ of 40 s and gas phase concentrations C_{NO} = 230 ppm, $C_{C_2H_4}$ = 1200 ppm and C_{O_2} = 7%. Argon was used as a reference gas to help identify the half-cycle that contained NO and C_2H_4 in the feed. For the purpose of our discussion here, the half-cycle containing NO + C_2H_4 + Ar will be referred to as the Ar half-cycle, while the other half-cycle containing O_2 will be referred to as the oxygen half-cycle.

The catalyst exhibited no activity for the NO + C_2H_4 + O_2 reaction below 100°C. A typical gas-phase concentration profile at the reactor outlet is shown in Fig. 3a for a reactor temperature of 70°C. The alternating solid and dotted lines at the bottom of Fig. 3a represent the oxygen and Ar half-cycles, respectively. Interestingly, the C_2H_4 concentration peak did not elute from the reactor together with the NO and Ar peaks, even though a mixture of C_2H_4, NO and Ar was fed to the reactor inlet as shown in Fig. 2. In fact, the position of the C_2H_4 pulse was shifted toward the oxygen half-cycle from the Ar half-cycle, while the NO and Ar pulses remain in the Ar half-cycle, resulting in a separation of C_2H_4 from both NO and Ar. That is, when the ethylene peak elutes there is little NO, whereas there is little ethylene when the NO peak elutes. This separation is due to large retention of ethylene compared with the retention of NO, O_2, or Ar. This is a classical example of the chromatographic effect, and appears to be a characteristic feature of zeolite-based catalysts. This phenomenon plays a significant role in determining the catalytic activity of Cu–ZSM-5 catalysts, as will be discussed later.

In Figs. 3b through 3g, the concentration profiles of the reference Ar were omitted for clarity. At 300°C (Fig. 3b), conversions of both C_2H_4 and NO become significant. The C_2H_4 concentration profile now assumes a more complex form; the main C_2H_4 peak is preceded by a small plateau, which can be attributed to the incomplete conversion of the frontal part of the C_2H_4 pulse. The small plateau in the frontal part of the C_2H_4 concentration wave appears in the Ar half-cycle, while the NO concentration wave remains in the Ar half-cycle. The latter observation is indicative of small retention of NO by the catalyst in the presence of C_2H_4. At 315°C (Fig. 3c), the positions of the concentration profiles remain the same as those at 300°C, but the conversions increase for both C_2H_4 and NO. At 350°C (Fig. 3d), nearly complete conversions of C_2H_4 was obtained, and surprisingly, the position of the NO concentration profile shifted toward the oxygen half-cycle from the original Ar half-cycle. This shift indicates that the retention of NO by the catalyst becomes significant at 350°C. This is in line with previous observations (13) that the adsorption of NO on Cu–ZSM-5 increased markedly

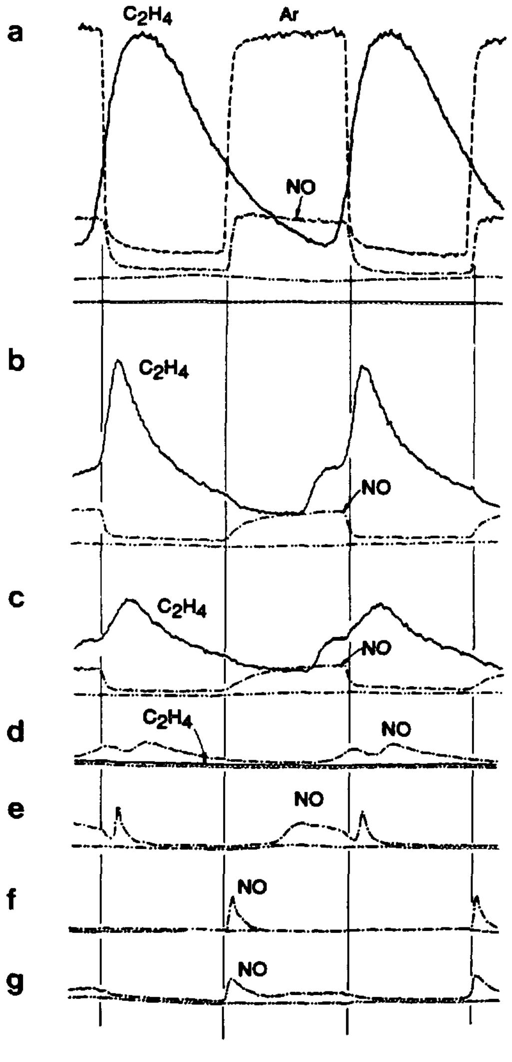

FIG. 3. Dynamic behavior of (NO + C_2H_4 + O_2) reaction over Cu–ZSM-5: Gas-phase concentrations measured at the reactor outlet as a function of time (τ = 40 s, C_{NO} = 230 ppm, $C_{C_2H_4}$ = 1200 ppm, C_{O_2} = 7%). (a) T = 70°C, (b) T = 300°C, (c) T = 315°C, (d) T = 350°C, (e) T = 400°C, (f) T = 500°C, (g) T = 600°C.

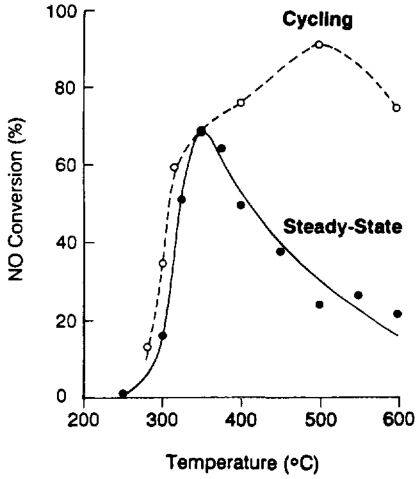

FIG. 4. Comparison of NO conversion performance of Cu–ZSM-5 for (NO + C_2H_4 + O_2) reaction: steady-state vs cyclic operation.

at temperatures between 300 and 450°C by an oxidative pretreatment. At 400°C (Fig. 3e), the conversion of C_2H_4 is complete, and the NO concentration wave moves back toward the Ar half-cycle with the tailing part still remaining in the oxygen half-cycle. This increase in the traveling speed of the NO concentration wave is an indication of increased desorption rate of NO due to the increase in catalyst temperature. The multiple peaks of NO shown in Figs. 3d and 3e suggest that NO has two or three different adsorption sites. We speculate that these sites may correspond to $NO^{\delta-}$, $(NO)_2^{\delta-}$ and $NO^{\delta+}$ sites reported recently by Iwamoto (17). The broad NO peak near the end of the Ar half-cycle in Fig. 3e disappears at 500°C (Fig. 3f), while the sharp peak shown during the oxygen half-cycle in Fig. 3e advances to the beginning of the Ar half-cycle as a result of the increased desorption rate. (Note that the NO peak should appear at the beginning of the Ar peak, when the NO adsorption is negligible.) We speculate that the broad peak shown during the Ar half-cycle in Fig. 3e consists of $NO^{\delta-}$ and $(NO)_2^{\delta-}$ which can decompose to N and O and N_2O and O, respectively (17). The remaining sharp peak must then be $NO^{\delta+}$ which strongly adsorbs on Cu^{2+} sites without decomposing (37). At 600°C (Fig. 3g), NO retention by the catalyst becomes negligible and the NO conversion decreases probably due to the increasing population of oxygen on the catalytic surface and to the decreasing availability of C_2H_4.

Figure 4 compares NO conversion performance of the Cu–ZSM-5 catalyst under steady-state operating condition of the NO + C_2H_4 + O_2 reaction with that under cyclic operating condition involving NO + C_2H_4 and O_2 pulses. (Note that the feed composition in terms of mole fraction remains the same for both operating conditions, although the time-average concentration of each reactant species under the cyclic operating condition is half of that under the steady-state operating condition due to the nature of the symmetric cyclic operation. As long as the feed composition was kept constant, reduction of the reactant concentration in half did not significantly affect the NO conversion performance of the catalyst under the steady-state condition. Thus, a direct comparison of the NO conversion performance as shown in Fig. 4 is justified.) Surprisingly, the cyclic operation exhibits a better NO conversion performance than the steady-state operation over the entire temperature regime. This is in contrast to previous observations with alumuina-supported noble metal catalysts for stoichiometric CO + O_2 and NO + CO reactions, in which cyclic operation performs better than steady-state operation only in the low temperature regime (27, 30). This behavior of Cu–ZSM-5 as a lean-NO_x catalyst bears important implications in the optimum operating strategy of lean NO_x catalysts, details of which are beyond the scope of this study.

Transient Cycling Experiments Alternating NO and C_2H_4

Another series of cycling experiments was conducted by alternating NO and C_2H_4 in the absence of oxygen, to see whether the delayed appearance of the C_2H_4 concentration wave is due to the presence of oxygen as well as to examine the effect of cycling on the NO conversion performance of the NO + C_2H_4 reaction. The cycling scheme used for the pulse experiments between NO and C_2H_4 was the same as that shown in Fig. 2 except the pulse duration and the composition of each pulse; a pulse of 30 s duration containing NO (690 ppm in He) and Ar was introduced to the reactor, followed by a C_2H_4 pulse (690 ppm in He) of the same duration. This cycling process was repeated until the system was stabilized, before kinetic data were taken. Argon was used as a reference gas for convenient identification of each half-cycle at the reactor outlet. Results are shown in Figs. 5a through 5d. For clarity, the reference Ar pulses are omitted for Figs. 5b through 5d. The NO + Ar and the C_2H_4 half-cycles are denoted by the alternating dotted and solid lines as shown at the bottom of Fig. 5d.

At 400°C under the cycling condition (Fig. 5a), the catalyst exhibited no measurable activity for the NO + C_2H_4 reaction even though its steady-state activity is substantial (see Fig. 1a). Notice that the NO and C_2H_4 pulses are in phase at the reactor outlet, despite the fact that the NO and C_2H_4 pulses are out of phase in the feedstream to the reactor. This phase lag in the C_2H_4 pulse is in line with the earlier observations in Figs. 3a through 3c, indicating that C_2H_4 retention by the catalyst is not significantly affected by the presence or absence of oxygen. At 500°C (Fig. 5b), approximately one-third of the C_2H_4 pulse

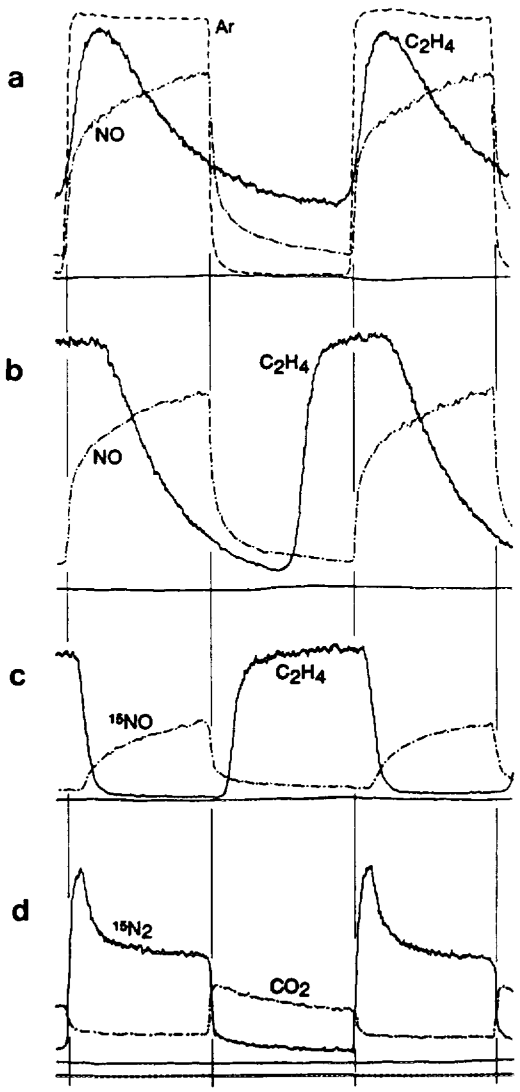

FIG. 5. Dynamic behavior of (NO + C_2H_4) reaction over Cu–ZSM-5: Gas-phase concentrations measured at the reactor outlet as a function of time (τ = 60 s, C_{NO} = 690 ppm, $C_{C_2H_4}$ = 690 ppm). (a) T = 400°C, (b) T = 500°C, (c) T = 600°C, (d) T = 600°C.

comes out of the NO half-cycle while the NO pulse remains in phase with the Ar pulse. The valley between successive C_2H_4 pulses becomes deeper than that observed at 400°C in Fig. 5a. This increase of the traveling speed of the C_2H_4 concentration wave can be attributed to the increased desorption of C_2H_4 at 500°C.

When the reactor temperature was raised to 600°C (Fig. 5c), the C_2H_4 pulse becomes almost completely out of phase with the NO pulse, similar to the cycling pattern in the feedstream. This can be attributed to a further increase in the C_2H_4 desorption rate from the catalyst. This increased desorption rate of C_2H_4 is accompanied by a large conversion of both NO and C_2H_4. This observation, together with Fig. 5a, suggests that C_2H_4 in the absence of oxygen inhibits NO reduction at low temperatures (where the rate of C_2H_4 desorption is not fast enough) by obstructing the NO molecule's access to the active sites. This in turn means that the presence of oxygen can help promote NO reduction in the low temperature regime by initiating C_2H_4 scavenging via oxidation of C_2H_4. Presented in Fig. 5d are product concentration profiles when isotopic ^{15}NO was used in place of NO in order to differentiate the principal mass peak of C_2H_4 (mass number = 28) from that of the reaction product N_2 (mass number = 28). Clearly, $^{15}N_2$ is produced during the ^{15}NO half-cycle, while CO_2 is produced during the C_2H_4 half-cycle. ($^{15}N_2O$, $^{15}NO_2$, and O_2 were not detected in the gas phase, and the nitrogen balance was within 5% of complete closure.) This clearly demonstrates that ^{15}NO decomposes to produce both $^{15}N_2$ and adsorbed oxygen, the latter of which is consumed to oxidize C_2H_4 producing CO_2 during the following C_2H_4 half-cycle. This behavior is very similar to that observed previously for NO + CO reaction system under cyclic operating conditions (30, 31). It confirms that the dissociation of NO is an essential elementary step for the sustained NO reduction with C_2H_4 in the absence of oxygen. In the presence of excess oxygen, it is possible that other reaction pathways such as the reaction between partially oxidized hydrocarbons and NO may also participate in the NO reduction process (13), enhancing the overall NO conversion efficiency. However, the comparable activity (with or without oxygen) at around 400°C shown in Fig. 1a suggests that the kinetic contribution by this additional reaction pathway is minimal, and that the reaction pathway involving NO decomposition should remain an essential contributor to the overall reduction of NO even in the presence of oxygen.

Effect of Cycling Frequency on Transient Responses of NO and C_2H_4 Pulses

Presented in Figs. 6a through 6d are transient responses of both NO and C_2H_4 concentration pulses at the catalyst temperature of 500°C for cycling periods of 60, 40, 20, and 10 s, respectively. The cycling scheme is the same as was used for Fig. 5. The alternating solid and dotted horizontal lines shown at the bottom of each figure in Fig. 6 denote the C_2H_4 and the NO + Ar half-cycles, respectively. The Ar concentration profiles were omitted for clarity in Figs. 6b through 6e. For convenience in our discussion on the retention (or storage) capacity of the catalyst for C_2H_4 during the cyclic operation, we define the retention time as the time interval in seconds between the end of the Ar half-cycle and the beginning of the C_2H_4 concentration wave measured at the reactor outlet. Physically, the retention time represents the time delay caused by adsorption of C_2H_4 in the catalyst. For the cycling period of 60 s (Fig. 6a), the retention time of the

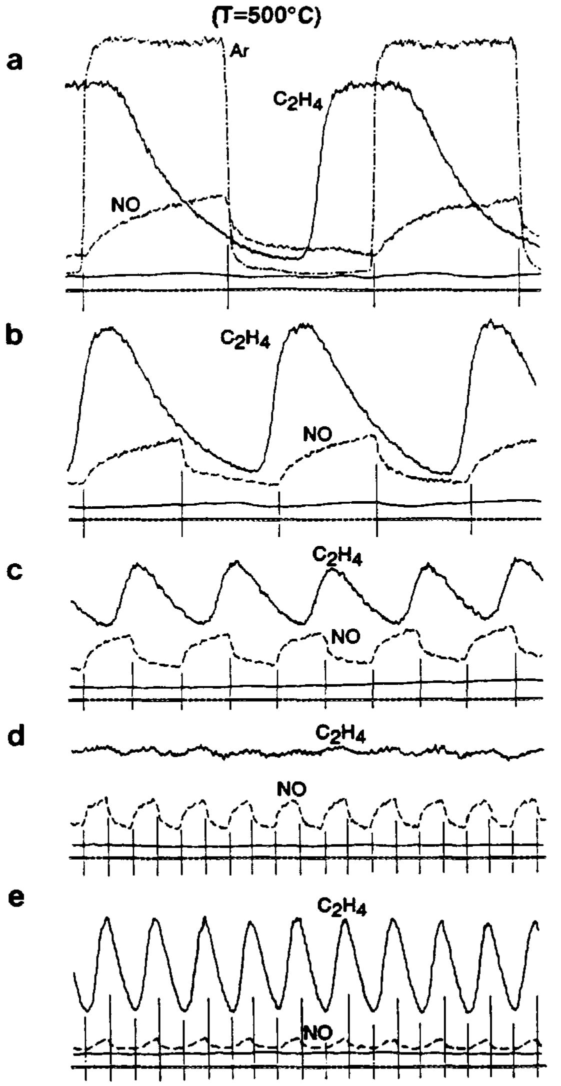

FIG. 6. Effect of cycling frequency on transient response of (NO + C_2H_4) reaction. [C_{NO} = 230 ppm, $C_{C_2H_4}$ = 1200 ppm; the time period between any two adjacent vertical lines represents a half-cycle, and any two adjacent half-cycles together constitute a complete cycling period (τ).] (a) τ = 60 s, (b) τ = 40 s, (c) τ = 20 s, (d) τ = 10 s, (e) τ = 10 s (T = 600°C).

C_2H_4 pulse is about 17.5 s; the rear 60% of the C_2H_4 pulse overlaps with the subsequent NO pulse, while the front 40% is out of the Ar half-cycle. When the cycling period is decreased to 40 s (Fig. 6b), the retention time of the C_2H_4 pulse remains the same at about 17.5 s. However, almost the entire C_2H_4 pulse now overlaps with the following NO pulse. The constant value of the phase lag, regardless of the cycling period, indicates that the adsorption characteristics of C_2H_4 is independent of the presence of NO. This is consistent with the existing literature reports; C_2H_4 adsorbs on ZSM-5, whereas NO adsorbs on Cu sites (13, 14, 16, 17). It is surprising, though, that the Cu–ZSM-5 catalyst exhibits a significant retention capacity for ethylene even at 500°C.

When the cycling period was further reduced to 20 s (Fig. 6c), the retention time of the C_2H_4 pulse still remains the same. Note, however, that the C_2H_4 pulse is almost entirely out of phase with the NO pulse. When the cycling period (10 s) becomes shorter than the constant retention time of C_2H_4 (17.5 s), the C_2H_4 pulse assumes a relaxed steady state approaching a time-invariant condition even in the face of large amplitude forcing; in contrast, the NO pulse still maintains a clear cycling pattern as shown in Fig. 6d. This relaxed steady-state behavior of the C_2H_4 pulse is due to dampening of the oscillating feedstream C_2H_4 concentration by a large C_2H_4 storage capacity of Cu–ZSM-5 catalysts; that is, C_2H_4 is stored during the half-cycle with a high gas-phase concentration, while it is released during the subsequent half-cycle with a low gas-phase concentration. In this sense, the large storage capacity of ZSM-5 support for C_2H_4 is analogous to the large oxygen storage capacity of ceria in conventional three-way catalysts (31, 38–40). When the temperature was raised from 500 to 600°C at the constant cycling period of 10 s, the relaxed steady-state behavior of the C_2H_4 pulses (Fig. 5d) disappeared and a distinct cycling pattern of C_2H_4 reappeared (Fig. 6e) due to the significantly decreased storage capacity (i.e., the increased desorption rate) of C_2H_4 at 600°C.

Effect of Catalyst Pretreatment Condition on Transient Responses of Reactant Species

The significance of C_2H_4 storage in the Cu–ZSM-5 catalyst during the lean-NO_x reduction process having been recognized so far, we examined the effect of catalyst pretreatment conditions on the transient responses of a step change in feed concentration of each individual reactant. Two pretreatment conditions were used, oxidizing and reducing conditions. In the oxidizing pretreatment, the catalyst was treated with oxygen at 500°C for 1 h; in the reducing pretreatment, the catalyst was treated with hydrogen at 500°C for 0.5 h following the oxidizing pretreatment. On completion of catalyst pretreatment, the catalyst was cooled to 350°C while He flow was maintained through the catalyst bed. When the catalyst temperature was stabilized at 350°C, a mixture of a reactant species (NO, C_2H_4, or O_2) and Ar was introduced to the reactor in a step change mode. Ar was used as the reference species for measuring the retention time of the reactant species. The transient data were collected for 60 s.

Presented in Fig. 7a are results from a step-change introduction of C_2H_4 (1200 ppm in He) at the flow rate of 30 cm^3/min. The system response time was about 1.3 s as measured by the response time of the Ar signal. The retention time of C_2H_4 was estimated by the difference in the breakthrough time between the Ar and C_2H_4 signals. (The breakthrough time was measured at half the full signal of the concentration profile.) As shown in Fig. 7a,

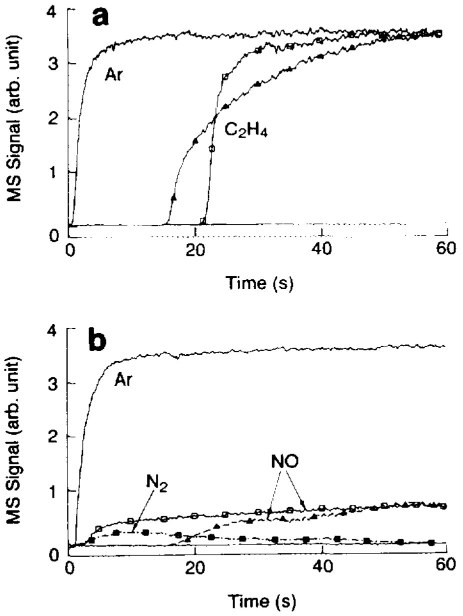

FIG. 7. (a) Effect of catalyst pretreatment condition on transient response of ethylene (T = 350°C; □, C_2H_4 over the reduced catalyst; ▲, C_2H_4 over the oxidized catalyst). (b) Effect of catalyst pretreatment condition on transient response of NO (T = 350°C; ▲, NO over the reduced catalyst; □, NO over the oxidized catalyst; ■, N_2 produced over the reduced catalyst).

the retention time of C_2H_4 is approximately 20 s for both the oxidized and reduced samples. However, the reduced sample yielded an ethylene concentration profile much sharper than that for the oxidized sample. The reason behind this interesting difference is not clearly understood at this time, but we speculate that C_2H_4 adsorption on the oxidized sample may follow an adsorption isotherm more nonlinear than that on the reduced sample. A further study is warranted in this area.

It now appears worth emphasizing an important observation in Fig. 7a: Regardless of the pretreatment condition, the Cu-ZSM-5 catalyst can adsorb a large amount of C_2H_4, resulting in a large retention time. This finding helps us to clarify our earlier observations in Fig. 3. That is, the phase shift in the C_2H_4 concentration wave observed under the reaction conditions (Figs. 3b and 3c) is due to the strong adsorption of C_2H_4 on the Cu-ZSM-5 catalyst, not due to any reaction effects.

Figure 7b shows the results from a step-change introduction of NO (230 ppm in He) at the flow rate of 30 cm^3/min. The retention time of NO in the reduced sample is very long (~22 s) compared with that in the oxidized sample. On the reduced sample, NO decomposes to produce N_2 until the catalyst is completely reoxidized by the oxygen produced. The time scale required for complete reoxidation of the catalyst due to NO decomposition appears to be on the order of 1 min, as can be seen in Fig. 7b. Figure 7b also indicates that the large retention time of NO in the reduced sample is due primarily to the decomposition of NO. The good activity of Cu-ZSM-5 for NO decomposition under the reduced condition is in line with our earlier observations in Figs. 5c and 5d. In Fig. 7b the nitrogen balance was within 5% of complete closure, and O_2, N_2O, and NO_2 were negligible in the gas phase.

The same type of experiments with O_2 (7% in He) revealed negligible retention of O_2 in Cu-ZSM-5 at 350°C; the breakthrough time of O_2 was essentially identical with that of Ar.

Ethylene Storage Capacity and Coke Formation in Cu-ZSM-5 Catalyst

In view of the transient response data indicating the importance of ethylene storage in the catalyst, we further examined the ethylene storage phenomena in the Cu-ZSM-5 catalyst in the presence of excess oxygen, using TPD and TPO techniques.

In the first TPD experiment, the catalyst was equilibrated at 160°C with a flow of C_2H_4 + O_2 mixture in He at 50 cm^3/min. The composition of the gas mixture was 1200 ppm C_2H_4 and 7% O_2 in a helium background. Following the equilibration, the catalyst was flushed out with He for 30 min while cooling down to 60°C. Then the catalyst sample was heated in He from 60 to 500°C for 7 min at a linear rate of approximately 63°C/min while monitoring the partial pressures of desorbing gases using the mass spectrometer, followed by a soaking at 500°C for 23 min. Desorption profiles presented in Fig. 8a reveal that a large amount of ethylene was stored in the catalyst at 160°C. Oxygen was not observed in the gas phase. The small amount of CO_2 formed during the TPD experiment indicates that the amount of oxygen available for ethylene oxidation in the catalyst is very small compared to the total amount of the stored ethylene. (On the equivalent carbon basis, the amount of CO_2 shown in Fig. 8a corresponds to about 2% of the stored ethylene.) This means that the interior of the catalyst is occupied predominantly by C_2H_4 with little amount of O_2, even though the gas phase surrounding the catalyst contains a large excess of oxygen. In other words, *the inside of the catalyst is in a highly rich condition, while the gas phase surrounding the catalyst is in a highly lean condition*. This interesting phenomenon should also occur under the reaction conditions, because the presence of NO (which preferentially adsorbs on copper sites) will not affect the adsorption characteristics of C_2H_4 on the zeolite sites. This is consistent with our earlier observation of a large retention time for C_2H_4 in the presence of NO during transient cycling experiments.

Quantitative analysis of Fig. 8a has indicated that the total amount of C_2H_4 desorbed from the catalyst during TPD is 4.3 μmol. This amount is much greater than the amount of exposed Cu surface which is equivalent to 0.36

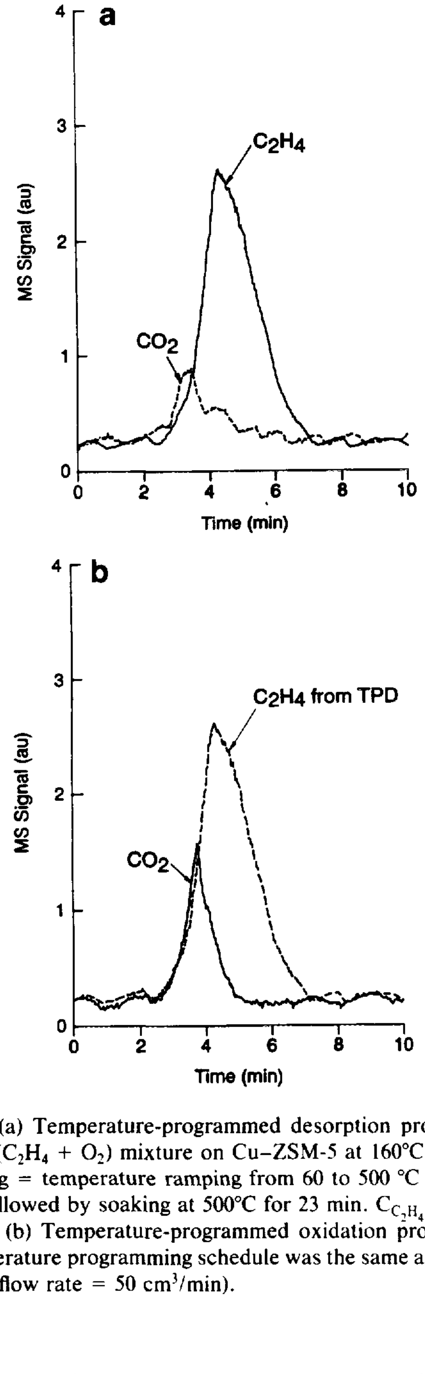

FIG. 8. (a) Temperature-programmed desorption profile after adsorption of (C_2H_4 + O_2) mixture on Cu–ZSM-5 at 160°C (temperature programming = temperature ramping from 60 to 500 °C at the rate of 63°C/min followed by soaking at 500°C for 23 min. $C_{C_2H_4}$ = 1200 ppm, C_{O_2} = 7%). (b) Temperature-programmed oxidation profile following TPD. Temperature programming schedule was the same as used in TPD (C_{O_2} = 7%, flow rate = 50 cm^3/min).

μmol of Cu. This means that the large retention of C_2H_4 in the catalyst is due primarily to the adsorption of C_2H_4 on ZSM-5, in agreement with literature reports (16, 17). It is noteworthy that the total amount of C_2H_4 desorbed during TPD corresponds to about 3% of the total micropore volume of ZSM-5 which is 0.19 cm^3/g (41).

After the TPD experiment was completed, the catalyst temperature was lowered to 60°C, and a TPO experiment was started with an introduction of 7% oxygen in He at a flow rate of 50 cm^3/min. The temperature programming schedule was the same as was used during the preceding TPD experiment. Results presented in Fig. 8b exhibit CO_2 formation, which is indicative of some carbonaceous intermediates deposited during the TPD experiments. The C_2H_4 peak obtained from the TPD experiment is also shown in Fig. 8b for comparison. From these two peaks, we can conclude that the amount of the carbonaceous deposits is relatively small in comparison with the total amount of C_2H_4 stored in the catalyst. In fact, the amount of CO_2 formed from this carbonaceous deposits corresponds to about 4% of the stored ethylene, based on the equivalent carbon content.

In the second TPD experiment, the catalyst was equilibrated at 350°C with the same (C_2H_4 + O_2) gas mixture as used in the first TPD experiment, followed by He flushing for 1 h. Subsequent TPD and TPO experiments following the same procedure as described above did not show any trace of C_2H_4, O_2, or CO_2, indicating that the carbonaceous deposit under the reaction condition at 350°C is negligible. All the stored C_2H_4 was removed during the He flushing.

DISCUSSION

On the Role of Ethylene

We have shown that the inside of the Cu–ZSM-5 catalyst is predominantly occupied by ethylene below the reaction lightoff temperature of ethylene oxidation. Above this temperature, the hydrocarbon concentration decreases with increasing temperature due mainly to its increased reaction with oxygen and, to a less extent, to its increased desorption. The amount of coke formation by the C_2H_4 + O_2 mixture was found to be very small below the reaction lightoff temperature and negligible above the reaction lightoff temperature. The negligible amount of coke deposit at 350°C under lean conditions is in line with d'Itri and Sachtler (8). These observations lead us to conclude that the major role of ethylene is to provide the catalytic sites with a reducing environment in which the catalytically active Cu^{1+} sites are more stable than in an oxidizing environment, even though the bulk gas surrounding the catalyst particles is under highly oxidizing condition.

The strong adsorption of ethylene in the catalyst pore results in the saturation of void space almost entirely by ethylene, resulting in a situation commonly called *volume-filling* (42). As a result, the diffusion and retention of other reactants, oxygen and NO, are greatly hindered. For example, we have shown for both the C_2H_4 + NO system and the C_2H_4 + NO + O_2 system that the retention of NO is negligible under the cyclic operating condition. Thus, there appears to be a dual role of ethylene; it keeps the catalytic sites in a reducing environment on the positive side, whereas it blocks the diffusion path and reduces the retention capacity for both oxygen and NO as well as deactivates the catalytic sites by coke formation on the negative side.

On the Role of Oxygen

Comparison of Fig. 3 with Fig. 5 reveals that ethylene oxidation occurs well below the temperature at which significant ethylene desorption occurs. This indicates that oxygen can play a major role in scavenging adsorbed ethylene at low temperatures where ethylene removal via desorption is slow. The scavenging of ethylene by reaction with oxygen at low temperatures may involve partially oxidized intermediates, and should facilitate both the NO and the O_2 molecules' access to the catalytic sites by clearing the pore passages, leading to the transition from the C_2H_4-dominating condition to the O_2-dominating condition inside the catalyst.

Thus, the role of oxygen can be understood through its capability to counteract the role of ethylene. As discussed above, when the catalyst's interior is occupied predominantly by ethylene (i.e., highly reducing condition) at low temperature regime, oxygen can scavenge the ethylene from the catalyst via oxidation well below the desorption temperature of ethylene, resulting in the onset of NO conversion. As a result, the rich-to-lean transition of the catalyst's interior occurs at a lower temperature in the presence of oxygen than in its absence. As complete oxidation of ethylene is approached, the inside of the catalyst is covered primarily with oxygen and the NO conversion activity starts to decrease. Thus, there are also two opposite sides in the role of oxygen; one on the positive side is to make the rich-to-lean transition occur at a low temperature, and the other on the negative side is to deactivate the catalyst after the ethylene is completely oxidized.

On the Reaction Mechanism

The catalytic reaction mechanism of NO reduction by hydrocarbons under lean conditions over Cu–ZSM-5 is not very well understood yet. There are very diverse observations reported in the literature regarding the key step of the NO reduction in lean-NO_x catalysis. The key steps or intermediates proposed so far can be categorized as follows.

a. Hydrocarbon reacts with oxygen to form partially oxidized hydrocarbon intermediates which are highly reactive toward NO reduction (13).

b. NO reacts with oxygen to form NO_2 which subsequently reacts with hydrocarbon (13, 16).

c. Hydrocarbon deposits carbonaceous intermediates on the catalytic surface which is reactive toward NO reduction (5, 13).

d. NO decomposes into nitrogen and oxygen on the vacant catalytic surface (i.e., Cu^{1+} sites) generated by the C_2H_4 + O_2 reaction (7, 14).

Our observations are not consistent with the proposal (a) above. We could not observe any partially oxidized hydrocarbon intermediate under our experimental conditions. In fact, a significant amount of this intermediate has never been observed, even though a very small amount of acrolein formation has been observed when propylene was used as the reductant (13). Furthermore, we have demonstrated that NO can be readily reduced by C_2H_4 even in the absence of oxygen under both the steady-state and the cyclic operating conditions. It follows from these observations that the contribution of the partially oxidized hydrocarbon intermediates to the reduction of NO is only of minor importance, and thus this intermediate does not seem to be essential to the kinetic description of the NO reduction process over Cu–ZSM-5 catalysts in agreement with the argument made by Birch and Millington (14).

The proposal (b) is not consistent with our observations either. We have never observed any NO_2 formation under our experimental conditions. Our calculation results based on the kinetics of NO_2 formation via both homogeneous gas-phase reaction (43, 44) and heterogeneous catalytic reaction between NO and O_2 (45) have also indicated that NO_2 formation is negligible under our experimental conditions in which a very low concentration of NO and a large space velocity were used. The nitrogen balance was within 5% of completion without including both N_2O and NO_2. This is in good agreement with recent findings by Bethke *et al.* (34) on the role of NO_2 during lean-NO_x reduction over Cu–ZSM-5 and Cu/ZrO_2 catalysts. However, there is a possibility that the adsorbed NO molecules on oxidized Cu^{2+} sites may be in the NO_2 form (37). In view of the above arguments, the formation of NO_2 via the NO + O_2 reaction does not seem to be a key elementary step for the reduction of NO by ethylene, at least under our experimental conditions. This conclusion is in agreement with the observations by Bethke *et al.* (34), and further supported by Fig. 4; the cyclic operation has little chance to form NO_2 due to its feeding scheme (i.e., NO and O_2 are fed separately in successive pulses), but still performs better than the steady-state operation in which NO and O_2 are fed together.

On the role of the carbonaceous intermediates, there are conflicting reports: they may enhance the catalyst's activity for NO reduction (13), or may suppress the catalyst's NO conversion performance (8) because they are reactive toward oxygen but not toward NO (14). We found that only a small amount of the carbonaceous intermediates is formed below the reaction lightoff temperature of C_2H_4 oxidation and that it becomes negligible above the reaction lightoff temperature. Unfortunately, this study cannot draw any conclusion on whether the carbonaceous intermediates promote or inhibit the catalytic activity for NO reduction. In any case, considering the negligible amount of the carbonaceous deposits under the reaction conditions and the controversies surrounding their kinetic contribution, we would prefer to describe the kinetics of this reaction system without explicitly invoking this intermediate. The reason is that the extremely small amount of the carbonaceous intermediates on the surface can be safely approximated by the pseudosteady-state hypothesis (PSSH), in which the overall kinetic expression can be written without explicitly including this intermediate species, as long as a lumped kinetic parameter can be determined experimentally.

The reasonably good activity of the catalyst for the C_2H_4 + NO reaction under steady-state condition (Fig. 1a) and cycled condition at high temperature (Figs. 5c and 5d) clearly demonstrates that NO decomposes to provide oxygen required for the oxidation of C_2H_4. Furthermore, the NO decomposition activity of Cu–ZSM-5 has been shown to be sufficiently high on the reduced Cu–ZSM-5 (Fig. 7b). Thus, our data in this study have confirmed our earlier hypothesis (7) that NO decomposition is an essential elementary step for NO reduction by hydrocarbons under lean conditions over Cu–ZSM-5. This conclusion is in line with literature reports (46, 47), where significant catalytic activity for NO decomposition was observed over Cu–ZSM-5. Note also that the NCO intermediate recently reported in the literature (21) requires the NO decomposition step, too.

Our observations and reasoning discussed above can be summarized in the following simplified reaction mechanism to explain our experimental observations.

—*NO decomposition on Cu surfaces:*

$$NO + S \leftrightarrow NO_a \qquad [1]$$

$$2NO_a + 2S \rightarrow 1/2\,N_2 + 2O_a \qquad [2]$$

$$O_a + O_a \rightarrow O_2 + 2S. \qquad [3]$$

—*Ethylene adsorption on ZSM-5:*

$$C_2H_4 + S' \leftrightarrow C_2H_{4a}. \qquad [4]$$

—*Ethylene oxidation on interface:*

$$C_2H_{4a} + 6O_a \rightarrow 2CO_2 + 2H_2O + 6S + S'. \qquad [5]$$

In the above chemical equations, S and S′ denote the NO adsorption sites on Cu and C_2H_4 adsorption sites on ZSM-5, respectively. The subscript "a" denotes adsorbed species. Even though any significant amount of N_2O and NO_2 formation was not observed under our experimental conditions, we do recognize the possibility of forming these species as reaction intermediates on Cu surfaces under different experimental conditions, as reported in the literature. Also it is possible that the ethylene oxidation may proceed via partially oxidized intermediates (formed by reaction with oxygen and/or NO_2) and/or hydrocarbon fragments (due to cracking), although these intermediate steps are not explicitly included in the above mechanistic model. Thus, it is hoped that the simplified mechanism proposed above may provide a groundwork for a more detailed version later.

On Improving the NO Reduction Activity of Lean–NO_x Catalysts

Probably, the most salient feature in the activity of lean-NO_x catalysts is that there is a maximum NO conversion close to the lightoff temperature of hydrocarbon oxidation (7). Above this temperature, the steady-state activity of the Cu–ZSM-5 catalyst for NO reduction decreases monotonically. One way to prevent this activity decrease at high temperature regime is to employ a cyclic operating scheme, as demonstrated in Fig. 4. This idea of the cyclic operation to improve the activity of the lean-NO_x catalysts is consistent with our earlier observation that the maximum NO conversion occurs at the transition between rich and lean conditions in the interior of the catalyst. The maximum activity of the catalyst observed during this transition may be closely related to the stabilization of the active sites (Cu^{1+}), which can either be fully reduced to Cu^0 under reducing conditions or fully oxidized to Cu^{2+} under oxidizing conditions (16) resulting in a loss of activity. Although this concept of cyclic operation stands on a sound understanding of the reaction dynamics which involves NO decomposition and hydrocarbon oxidation, the cyclic operation scheme employed for Fig. 4 is not realistic under actual exhaust conditions of the lean-burn engine. However, we believe that a more realistic cycling scheme can be devised which is applicable to the actual lean-burn engine exhaust conditions. Further studies are warrented in this area of research to improve the performance of the lean-NO_x catalysts.

SUMMARY AND CONCLUSIONS

Transient behavior of a Cu–ZSM-5 catalyst was investigated for the NO + C_2H_4 + O_2 reaction system using a packed-bed laboratory reactor under highly oxidizing conditions, typical of lean-burn engine exhaust. To elucidate the role of oxygen and ethylene, the reaction dynamics of the NO + C_2H_4 mixture was also investigated along with TPD and TPO experiments. Reaction mechanism of NO reduction was discussed in terms of NO decomposition accompanied by hydrocarbon oxidation. The important findings are listed below.

1. Catalytic decomposition of NO appears to be an essential elementary step for NO reduction with ethylene in the presence of excess oxygen.

2. Below the reaction lightoff temperature, the Cu–ZSM-5 catalyst maintains a highly rich condition due to strong adsorption of ethylene, even though the bulk gas phase external to the catalyst is highly oxidizing in nature.

3. The beneficial role of oxygen for NO reduction is to promote the onset of the reaction by removing ethylene (via oxidation) from the catalyst in the low temperature regime. The beneficial role of ethylene is to scavenge oxygen from the active catalytic sites in the high temperature regime, regenerating the active sites for NO decomposition.

4. The maximum activity of the Cu–ZSM-5 catalyst for NO reduction is obtained *during transition from a rich to a lean condition of the catalyst*, which occurs slightly above the lightoff temperature of ethylene oxidation.

5. As a result, a cyclic operation between a lean and a rich condition is more effective for the NO reduction by ethylene than a steady-state operation, where the overall time-average feed composition is lean.

ACKNOWLEDGMENT

We thank Dr. M. J. D'Aniello, Jr., of Johnson Matthey for providing the Cu–ZSM-5 catalyst sample used in this study and Dr. N. A. Potter of Analytical Chemistry Department for chemical analysis of the catalyst.

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