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Nitric Oxide Reduction by Hydrocarbons over Cu–ZSM-5 Monolith Catalyst under Lean Conditions: Steady-State Kinetics

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This work has investigated the steady-state activity of a Cu–ZSM-5 catalyst for NO reduction by hydrocarbons under highly lean conditions, typical of lean-burn engine exhaust, using a fixed-bed laboratory reactor. The efficiency of ethylene and propylene, both individually and collectively, as selective reductants for NO reduction is compared at different space velocities in order to characterize their kinetic behavior. Results have revealed that ethylene is a more efficient reductant than propylene due to its superior selectivity. Lightoff characteristics of both hydrocarbons and NO are shown to be very important in determining the catalyst's performance for the selective reduction of NO. Detailed data analysis has indicated that there exists antagonistic kinetic interaction between the two hydrocarbons, which is discussed in light of competitive adsorption/diffusion processes occurring in the zeolite pore structure. Discussions include important implications of our findings to the application of the Cu–ZSM-5 catalyst in automotive exhaust emission control. © 1993 Academic Press, Inc.

INTRODUCTION

Recently, lean-burn gasoline and diesel engines have been receiving considerable attention due to their improved fuel economy compared with the conventional gasoline engine operating under stoichiometric air/fuel ratio (i.e., $A/F = 14.6$). Diesel and lean-burn gasoline engines generally operate under net-oxidizing conditions, typically at A/F ratios greater than 17. Under these highly lean conditions, typical three-way catalysts containing primarily noble metals such as Pt, Pd, and Rh exhibit little activity toward NO_x reduction, as their reduction activity is suppressed by the presence of excess oxygen (*1–5*). Thus, a new catalyst is needed which has sufficiently high, sustained activity for NO reduction under highly lean conditions, so that lean-burn gasoline as well as diesel engines can meet the stricter future emission standards.

When the space velocity is sufficiently low, copper-exchanged zeolite catalysts, especially Cu–ZSM-5 catalysts among others, have been shown to be active for sustained NO decomposition in the absence of SO_2 (*6–9*). At high space velocities typical of lean-burn engine exhaust, nitric oxide can be selectively reduced by hydrocarbons over Cu–ZSM-5 catalysts in the presence of excess oxygen (e.g., *10, 11*). In recent vehicle tests (*12, 13*), it has been shown that Cu–ZSM-5 catalysts indeed have much better activity toward NO reduction under lean conditions than noble metal catalysts. However, this superior activity is still not high enough to bring the tailpipe NO_x emission of a lean-burn engine down to the level required by the stringent future emission standards.

In general, hydrocarbons have a certain degree of selectivity for promoting NO reduction versus its reaction with O_2 in the presence of excess oxygen. This selectivity is high for ethylene, propylene, propane and butylene (selective reductants), while the selectivity is low for methane and ethane (nonselective reductants) (*11*). Some other important reductants present in engine exhaust, such as CO and H_2, are known to be nonselective toward the NO reduction in the presence of excess oxygen (*11*).

In many emission control studies, propylene has been traditionally chosen as a

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representative hydrocarbon species for engine exhaust hydrocarbons (e.g., *3*, *14*). Although the reason behind this choice is not clear in the literature, it may have originated from the fact that the lightoff behavior of hydrocarbons in engine exhaust can be adequately simulated by propylene oxidation due to the leading role of this reaction during warmup period of automotive catalysts (*15*). In connection with the selective reduction of NO, it is important to recognize another prominent hydrocarbon in engine exhaust with good lightoff characteristics as well as good selectivity toward NO reduction—which is ethylene. In typical gasoline engine exhaust, the volume ratio of ethylene to propylene is approximately 3 to 1 (or equivalently, the mass ratio is roughly 2 to 1) (*16*). Single-cylinder engine experiments (*17*) have shown that this ratio remains roughly the same under conditions of lean combustion. For typical diesel engine exhaust, the mass ratio of ethylene to propylene has been reported to be slightly larger than that for the gasoline engine exhaust (*18*).

Most kinetic studies on the selective catalytic reduction of NO by hydrocarbon over Cu–ZSM-5 have also used propylene as a representative engine-out hydrocarbon (*11*, *13*). Thus, the selectivity of propylene toward NO reduction under lean conditions has been widely reported in the literature, whereas that of ethylene appears to have received less attention—not to mention their mutual kinetic interaction—despite its presence in actual engine exhaust in significant quantities. In this work, we systematically examine the activity of a Cu–ZSM-5 catalyst for the selective catalytic reduction of NO by both ethylene and propylene, individually and collectively, in the presence of excess oxygen.

EXPERIMENTAL

A monolith brick coated with Cu–ZSM-5 was provided by Johnson Matthey. The preparation steps are briefly described below. The ZSM-5 zeolite, which was obtained from PQ Corporation, had a high silica/alumina ratio of approximately 70. The Cu–ZSM-5 catalyst was made from ion exchange of copper on the ZSM-5 zeolite to obtain a copper loading of 3.2 wt%, which corresponds to the Cu/Al ratio of 1.15. A slurry of this Cu–ZSM-5 was then washcoated on a standard GM race track monolith brick with a cell density of 400 square-channels/in^2. After the washcoating, the overall copper loading on the monolith substrate was 90 g/ft^3. Further details of this catalyst are not available due to its proprietary nature.

Steady-state experiments were performed using a fixed-bed reactor containing a small (four square-channels of 2.5 cm in length) monolithic Cu–ZSM-5 catalyst sample cut from the Cu–ZSM-5 monolith brick provided by Johnson Matthey. The fixed-bed reactor was made by inserting the monolithic catalyst sample inside a $\frac{1}{4}$-inch-O.D. stainless steel tube and packing quartz wool between the monolith and the tube.

The reactor temperature was measured at the reactor inlet and controlled electronically with a typical precision of ±1°C. The preheating of the feed gas was achieved in a blank alumina section located upstream of the reactor. The gas flow rate through the reactor was measured and controlled by electronic mass flow controllers. The gas-phase concentrations of reactants and products were measured by a mass spectrometer. Mass number 41 was used for the principal mass peak of propylene, while mass number 26 was used for a secondary mass peak of ethylene to avoid mass interference between the principal mass peak of ethylene (mass number = 28) and that of N_2 or CO (mass number = 28). The effect of space velocity on selective reduction of NO by hydrocarbons was examined by varyng the flow rate of the feed-gas mixture. Ethylene and propylene were chosen as two representative hydrocarbons for selective catalytic reduction of NO over Cu–ZSM-5, based on the reasons discussed earlier. De-

TABLE 1

Standard Experimental Conditions

Reactor:	0.635 cm (¼ in) o.d. stainless-steel tubing Catalyst = Cu–ZSM-5 monolith Catalyst bed length = 2.5 cm Gas space velocity = 12,000 and 35,000 h^{-1} Temperature = 200–600°C Pressure = 101.3 kPa (1 atm)
Feed Concentration:	HC: 800 ppm C_3H_6 for (C_3H_6 + O_2 + NO) reaction 1200 ppm C_2H_4 for (C_2H_4 + O_2 + NO) reaction NO: 230 ppm O_2: 7% He: balance

tails of standard experimental conditions are listed in Table 1.

Effect of Space Velocity on Selective Reduction of NO by Hydrocarbons

The conversions of hydrocarbon and NO in the (HC + O_2 + NO) reaction system over the Cu–ZSM-5 catalyst were examined at two different space velocities: a low space velocity of 12,000 h^{-1} and a high space velocity of 35,000 h^{-1}. The desired space velocity was obtained by varying the flow rate of the reactant mixture through the reactor while keeping the catalyst volume constant. Results for the (C_3H_6 + O_2 + NO) reaction system are shown in Figs. 1a (C_3H_6 conversion) and 1b (NO conversion). As expected, the lightoff temperatures for both C_3H_6 and NO conversion are shown to increase with an increase in space velocity. Interestingly, however, this shift of the conversion curve is much smaller for the decreasing portion of the NO conversion curve above the temperature of the maximum NO conversion than for the increasing portion below it (see Fig. 1b).

In Fig. 1b the temperature for a maximum NO conversion (hereafter referred to as the maximum NO-conversion temperature) is shown to depend on the space velocity; at the space velocity of 12,000 h^{-1} the maximum selectivity for the NO conversion is achieved at 350°C, whereas it is 375°C at the space velocity of 35,000 h^{-1}. It

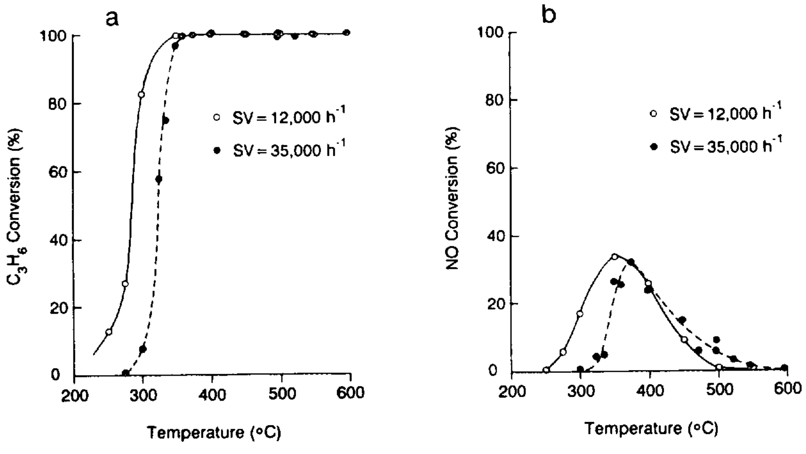

FIG. 1. Effect of space velocity on the conversion of (a) C_3H_6 and (b) NO in the (C_3H_6 + O_2 + NO) reaction system.

is important to note that the selective reduction of NO below the maximum NO-conversion temperature can be dramatically improved by reducing the space velocity, while the space velocity exerts little effect on the selectivity above this temperature. As a result, the overall efficiency of NO conversion over the entire temperature range is much greater for the low space velocity than that for the high space velocity.

Presented in Figs. 2a and 2b are results for the (C_2H_4 + O_2 + NO) reaction system. The experimental conditions were the same as those used for the (C_3H_6 + O_2 + NO) system except that 800 ppm of C_3H_6 was replaced by 1200 ppm of C_2H_4. (The carbon and hydrogen content in 1200 ppm of C_2H_4 is the same as that in 800 ppm of C_3H_6.) As was also the case for the (C_3H_6 + O_2 + NO) reaction system shown in Figs. 1a and 1b, an increase in space velocity shifted the lightoff temperatures for both C_2H_4 and NO conversions to higher temperatures. The data of Fig. 2b show that a low space velocity is preferred for the NO conversion below 400°C, whereas a high space velocity is preferable above 400°C. This indicates that the optimum space velocity depends on the temperature regime of the converter operation. Interestingly, the decreasing portion of the NO conversion curve is more sensitive to the space velocity for the (C_2H_4 + O_2 + NO) system (Fig. 2b) than that for the (C_3H_6 + O_2 + NO) system (Fig. 1b). Figure 2b also indicates that the overall efficiency of NO conversion over the entire temperature range remains essentially the same for both space velocities, in contrast to the earlier observation in Fig. 1b for the (C_3H_6 + O_2 + NO) system.

Efficiency of Hydrocarbon Species as Selective Reductants for NO

The conversion efficiency of C_3H_6 is compared with that of C_2H_4 for the selective reduction of NO at the space velocities of 12,000 and 35,000 h^{-1} in Figs. 3a and 3b, respectively. The number of both carbon and hydrogen atoms was kept constant in all cases by adjusting the hydrocarbon concentrations. Figures 3a and 3b show that the lightoff temperature of C_3H_6 conversion is substantially lower than that of C_2H_4 conversion. Interestingly, however, the initial phase of NO conversion follows essentially the same conversion-vs-temperature profile for both hydrocarbon species. For the (C_2H_4 + O_2 + NO) system, the lightoff temperature for the NO conversion nearly coincides with that for the C_2H_4 conversion for both space velocities, while for the

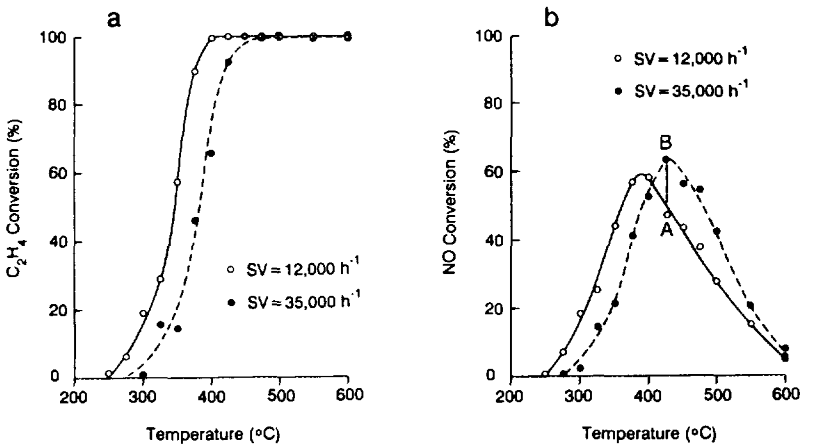

FIG. 2. Effect of space velocity on the conversion of (a) C_2H_4 and (b) NO in the (C_2H_4 + O_2 + NO) reaction system.

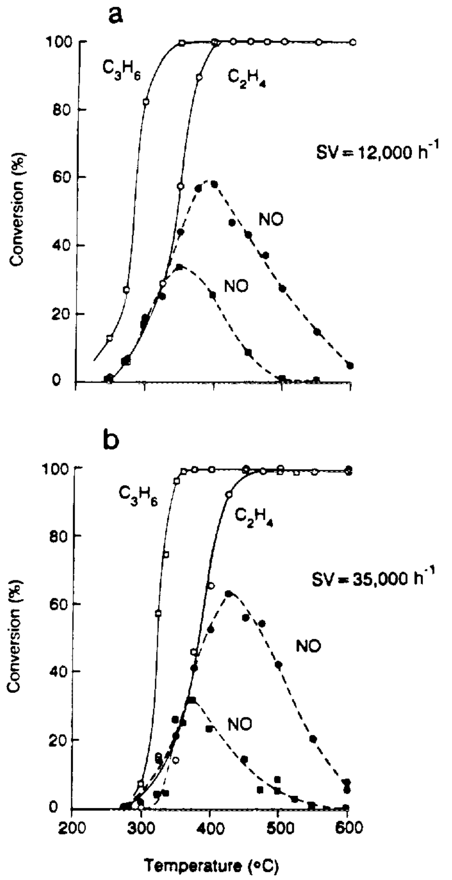

FIG. 3. Individual efficiency of C_2H_4 and C_3H_6 as a selective reductant for NO [○ = C_2H_4, □ = C_3H_6, ● = NO in the (C_2H_4 + O_2 + NO) system, and ■ = NO in the (C_3H_6 + O_2 + NO) system]. (a) SV = 12,000 h^{-1} and (b) SV = 35,000 h^{-1}.

(C_3H_6 + O_2 + NO) system the lightoff temperature for the NO conversion is higher than that for the C_3H_6 conversion by approximately 40°C for both space velocities. This means that the NO conversion proceeds almost simultaneously with the C_2H_4 conversion in the (C_2H_4 + O_2 + NO) system regardless of the space velocity, whereas the C_3H_6 conversion via (C_3H_6 + O_2) reaction proceeds well below the temperature where the NO conversion starts in the (C_3H_6 + O_2 + NO) system. This further implies that a hydrocarbon reductant with lower lightoff temperature is not necessarily a better selective reductant for NO reduction than the one with higher lightoff temperature. These observations indicate that C_2H_4 is a more efficient reductant than C_3H_6 for the selective reduction of NO. In fact, the low-temperature lightoff of the C_3H_6 conversion may adversely affect its effectiveness as a selective reductant for NO. In accordance with this conclusion, Figs. 3a and 3b also show that the total amount of NO conversion by C_2H_4 over the entire temperature range is approximately 2 to 3 times greater than that by C_3H_6. At high space velocity (Fig. 3b), the superiority of C_2H_4 to C_3H_6 as a selective reductant is even more pronounced than that observed at the low space velocity shown in Fig. 3a. Clearly, increasing the space velocity deteriorates somewhat the overall selectivity of C_3H_6 for NO reduction, while it hardly affects the overall selectivity of C_2H_4 over the entire temperature range. The maximum conversion of NO always coincides with nearly complete conversion of either reductant. Hence the decrease of the NO conversion with increasing temperature above the maximum NO-conversion temperature can be attributed to the shortage of either reductant. This suggests that the maximum NO conversion level can be improved by increasing the hydrocarbon concentration.

Effect of Multicomponent Hydrocarbon Species on NO Reduction Efficiency

In view of the multicomponent nature of hydrocarbon species present in actual engine exhaust, it is important to investigate the NO reduction activity of the Cu–ZSM-5 in a mixture of hydrocarbon species. We were able to compare the individual efficiency of C_2H_4 and C_3H_6 as separate reductants with the overall efficiency of a mixture of C_2H_4 and C_3H_6. The volume ratio of C_2H_4 to C_3H_6 in this mixture was chosen to be 3 : 1 to simulate typical engine exhaust conditions (*16–18*). The feed gas compositions employed to study the effect of multicomponent hydrocarbon species are listed in Table 2. The total number of both carbon

TABLE 2

Feed Gas Composition Used to Study the Effect of Multicomponent Hydrocarbon Species

	($C_2H_4 + O_2 + NO$) System	($C_3H_6 + O_2 + NO$) System	($C_2H_4 + C_3H_6 + O_2 + NO$) System
C_2H_4	1200 ppm	0	800 ppm
C_3H_6	0	800 ppm	267 ppm
O_2	7%	7%	7%
NO	230 ppm	230 ppm	230 ppm
He	Balance	Balance	Balance

and hydrogen atoms for the (C_2H_4 + C_3H_6 + O_2 + NO) system was the same as that for the single-hydrocarbon cases. All other experimental conditions were the same as those listed in Table 1 for the standard experiments.

Presented in Fig. 4 are the results for the (C_2H_4 + C_3H_6 + O_2 + NO) reaction system at the space velocity of 35,000 h^{-1}, where the feed concentrations of C_2H_4 and C_3H_6 were 800 and 267 ppm, respectively. Note that this mixture contains the same number of carbon and hydrogen atoms as either 1200 ppm of C_2H_4 or 800 ppm of C_3H_6. As was observed in the single component hydrocarbon experiments shown in Fig. 3b, Fig. 4 shows that the lightoff of C_3H_6 conversion occurs at a lower temperature than that of C_2H_4 conversion and that the C_2H_4 conversion is closely followed by NO conversion. Interestingly, there is a clear difference between the lightoff temperature of C_2H_4 and that of NO, in contrast to Fig. 3a and 3b, where the two lightoff temperatures were essentially the same. The reason behind this difference can be found by overlaying Fig. 3b with Fig. 4; the presence of C_3H_6 lowers the lightoff temperature of C_2H_4, while it does not significantly affect the lightoff temperature of NO. As will be shown later, the decreased level of the C_2H_4 concentration does not affect its lightoff temperature or that of NO significantly.

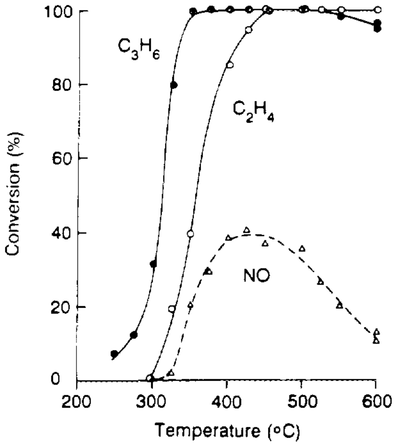

FIG. 4. Collective efficiency of a 3 : 1 volume-ratio mixture of C_2H_4 and C_3H_6 for NO reduction in the (C_2H_4 + C_3H_6 + O_2 + NO) reaction system (SV = 35,000 h^{-1}).

Figure 5 compares the NO conversion efficiency in the C_2H_4–C_3H_6 mixture (taken from Fig. 4) with that of C_2H_4 or C_3H_6 alone (taken from Fig. 3b), when the total number of carbon atoms contained in the hydrocarbon reductants is the same. Among the three reductant compositions, viz., C_2H_4, C_2H_4–C_3H_6 mixture, and C_3H_6, apparently C_2H_4 is the most efficient selective reductant while C_3H_6 is the least. The NO conversion data for the 3 : 1 volume-ratio mixture of C_2H_4 and C_3H_6 falls in between those for C_2H_4 or C_3H_6 alone, which might have been expected. The onset of the NO conversion requires practically the same temperture for all three cases, irrespective of the type of the reducing hydrocarbon species.

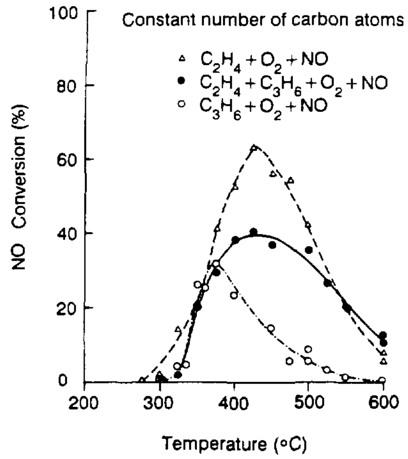

FIG. 5. Comparison of NO conversion for different reductant compositions. The total amount of carbon was kept constant [○ = (C_3H_6 + O_2 + NO) system, △ = (C_2H_4 + O_2 + NO) system, and ● = (C_2H_4 + C_3H_6 + O_2 + NO) system].

Kinetic Antagonism between Multicomponent Hydrocarbon Species in Selective Reduction of NO

When there are more than one hydrocarbon species, each of which is reactive toward NO reduction, it is useful to understand how the individual hydrocarbons interact with each other during the selective NO reduction over the Cu–ZSM-5 catalyst. More specifically, an important question is whether two hydrocarbons, C_2H_4 and C_3H_6, interact additively, or synergistically, or antagonistically, in determining the overall efficiency of the selective reduction of NO over Cu–ZSM-5 in the presence of excess oxygen.

With this in mind, we chose as our reference system the (C_2H_4 + C_3H_6 + O_2 + NO) feedstream at the space velocity of 35,000 h^{-1}. From this reference system containing two hydrocarbons (i.e., C_2H_4 and C_3H_6), we first eliminated C_3H_6 so that the reaction system would be reduced to the (C_2H_4 + O_2 + NO) system with the C_2H_4 concentration being kept at the same level as the reference system (i.e., 800 ppm of C_2H_4 for both systems). Thus, the only difference between this reduced reaction system and the reference multicomponent hydrocarbon system was the absence of C_3H_6, while everything else remained the same. Details of feed composition changes involved in this experiment are listed in Table 3. Results are shown in Fig. 6, which presents the conversions of C_2H_4 and NO. When the NO conversion for this reduced (C_2H_4 + O_2 + NO) system (Fig. 6) was directly compared with that for the reference (C_2H_4 + C_3H_6 + O_2 + NO) system, Fig. 7 resulted. Surprisingly, the NO conversion remains essentially the same for both systems, indicating that the contribution by C_3H_6 for the NO reduction is negligible in the presence of C_2H_4! Comparison of Fig. 4 with Fig. 6 shows that the C_2H_4 conversion is en-

TABLE 3

Feed Gas Composition Used to Study Kinetic Antagonism between Hydrocarbon Species

	Reference system	(C_2H_4 + O_2 + NO) System	(C_3H_6 + O_2 + NO) System
C_2H_4	800 ppm	800 ppm	0
C_3H_6	267 ppm	0	267 ppm
O_2	7%	7%	7%
NO	230 ppm	230 ppm	230 ppm
He	Balance	Balance	Balance

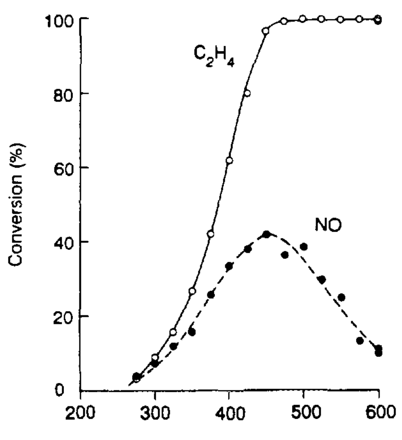

FIG. 6. Conversions of C_2H_4 and NO when C_3H_6 was taken out of the reference (C_2H_4 + C_3H_6 + O_2 + NO) system (SV = 35,000 h^{-1}).

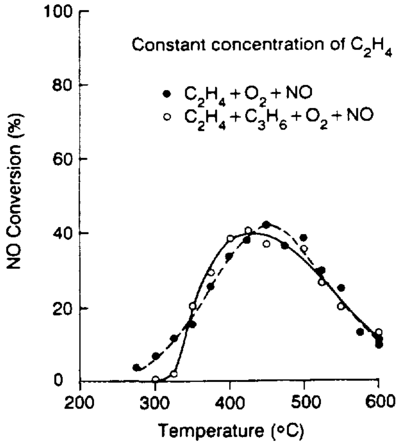

FIG. 7. Comparison of NO conversion for the reference system with that for the reduced (C_2H_4 + O_2 + NO) system (SV = 35,000 h^{-1}).

hanced in the presence of C_3H_6. Overlaying Fig. 3b with Fig. 6, we also note that the lightoff temperatures for both C_2H_4 and NO conversion remain essentially the same when the C_2H_4 concentration decreased from 1200 ppm to 800 ppm.

In the next experiment, we eliminated C_2H_4 from the reference system so that the reaction system be reduced now to the (C_3H_6 + O_2 + NO) system with the C_3H_6 concentration being kept constant at 267 ppm. The results are shown in Fig. 8. They indicate that the kinetic contribution by C_3H_6 to the selective reduction of NO is substantial, when C_3H_6 is the only hydrocarbon reductant present in the system. This observation is in striking contrast with the earlier observation that the same amount of C_3H_6 contributed little to the NO reduction when it coexisted with C_2H_4 in a mixture. This *antagonistic kinetic interaction* (as opposed to synergistic interaction in the sense that the total effect is smaller than the sum of the two effects taken independently) between C_2H_4 and C_3H_6 in their mixture during the selective NO reduction is a very interesting kinetic phenomenon which has not been previously reported. It appears to be important in understanding the catalytic activity of Cu–ZSM-5 catalysts. We speculate that this kinetic antagonism may be closely related to competitive adsorption/diffusion processes occurring in the zeolite structure, the details of which are beyond the scope of this work and await further study.

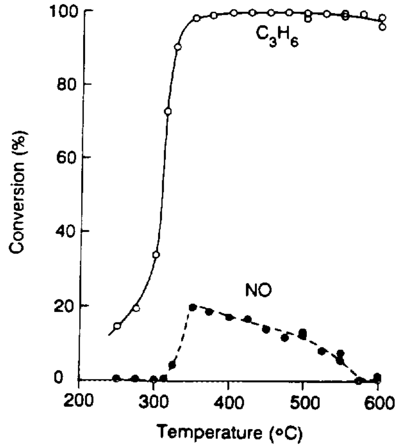

FIG. 8. Conversions of C_3H_6 and NO when C_2H_4 was taken out of the reference (C_2H_4 + C_3H_6 + O_2 + NO) system (SV = 35,000 h^{-1}).

DISCUSSION

We have investigated the activity of a Cu–ZSM-5 catalyst for NO reduction with hydrocarbons under lean conditions using a fixed-bed laboratory reactor. The results have revealed some interesting and potentially important new phenomena. In agreement with existing literature data, the NO conversion as a function of catalyst temperature exhibits a maximum. Our data have indicated that this maximum conversion of NO is closely related to the complete conversion of hydrocarbon reductants. Below the maximum NO-conversion temperature the selectivity of hydrocarbons toward the reduction of NO increases with temperature, whereas the selectivity decreases with temperature above the maximum NO-conversion temperature. Comparing Figs. 1b and 2b with Figs. 8 and 6, respectively, we confirm that increasing the hydrocarbon concentration improves the maximum NO conversion level. In this connection, it is important to recognize that a higher level of hydrocarbon concentration at temperatures above the maximum NO-conversion temperature can also be achieved by increasing the space velocity without actually increasing the feed concentration of the hydrocarbon. (See Figs. 1 and 2.) This observation bears an important implication in the operation of catalytic converters containing Cu–ZSM-5 catalysts to optimize the NO conversion efficiency, since the NO conversion above the maximum NO-conversion temperature can be improved by increasing the space velocity rather than by decreasing it. (Note that this statement is applicable only when the temperature regime for actual vehicle operation corresponds to the decreasing portion of the NO conversion curve.) Obviously, this is contrary to the conventional physical intuition. However, it can be explained by the increase in the lightoff temperature of hydrocarbons with an increase of the space velocity. For example, the increase in C_2H_4 concentration due to an increase of the space velocity resulted in an increase of the NO conversion from A to B in Fig. 2b. This is in accordance with our earlier postulate that the decrease of the NO conversion with increasing temperature above its maximum is due to the shortage of available hydrocarbon reductants.

We have observed that the lightoff of hydrocarbon conversion is dependent on the type of the hydrocarbon species, but the lightoff of NO conversion is essentially independent of the hydrocarbon species. (See Figs. 3a and 3b.) This suggests that the conversion of hydrocarbon may not be responsible for the initial conversion of NO; it rather implies either that the initial conversion of NO may be controlled by its own decomposition or that the NO conversion may be indirectly related to the hydrocarbon conversion through some form of intermediates. There are two possible sources of intermediates which can indirectly connect the hydrocarbon conversion to the NO conversion, because the intermediates may come from both hydrocarbon and NO. The C_xH_yO-type intermediates proposed by Iwamoto and Mizuno (*19*) belong to one category, while N_2O and oxygen produced by NO decomposition similar to those in the (NO + CO) reaction system (*20, 21*) belong to the other. In fact, there are evidences in the literature that the intermediate N_2O indeed forms during NO decomposition over Cu–ZSM-5 catalysts (*7, 22, 23*), whereas the C_xH_yO-type intermediate has not yet been observed, even though it has been speculated for some time. Unfortunately, this study cannot unambiguously determine which intermediates are involved in the rate-limiting step for the selective reduction of NO. However, it seems reasonable to speculate that the intermediates from the NO decomposition must be involved in the rate-limiting step of the selective reduction of NO by hydrocarbons. The reason behind this speculation is the fact that the lightoff of the NO conversion occurs independently of the type of the hydrocarbon species, suggesting that the rate limiting step of the NO conversion may be the decomposition of NO itself, which in turn may be controlled under certain conditions by the desorption rate of adsorbed oxygen. A further study employing transient responses is warranted to elucidate the importance of these intermediate steps and species.

Regarding the NO reduction mechanism, it seems appropriate to point out that Bennett *et al.* (*24*) ruled out the NO decomposition as a possible mechanism for the NO reduction in the (NO + O_2 + C_3H_6) reaction system over Cu–ZSM-5 catalyst. However, their conclusion is not consistent with the data due to the following reason. The first-order kinetics for the NO conversion in the low-concentration regime coupled with the zero-order kinetics in the high-concentration regime shown in their data (Fig. 2a of Ref. (*24*)) is a classical example of a unimolecular decomposition reaction on the catalytic surface, the rate (R) of which can be written as

$$R = k\,\theta, \qquad (1)$$

where k and θ are the decomposition rate constant and surface coverage of NO, respectively. When adsorption equilibrium of the Langmuir type is established on the surface, Eq. (1) reduces to

$$R = \frac{k\,KC}{1 + KC}, \tag{2}$$

where K and C are adsorption equilibrium constant and gas-phase concentration of NO, respectively. Obviously, the rate expression shown in Eq. (2) can describe the NO conversion characteristics observed by Bennett *et al.* (*24*), suggesting that the NO decomposition is an important part of the NO reduction mechanism during the (NO + O_2 + HC) reaction over Cu–ZSM-5 catalysts.

Comparing the (C_2H_4 + O_2 + NO) reaction system with the (C_3H_6 + O_2 + NO) reaction system has revealed that C_2H_4 is a more efficient reductant for NO reduction than C_3H_6, when the number of carbon atoms are kept constant in both reaction systems. Furthermore, when the gas-phase molar concentrations of C_2H_4 and C_3H_6 are kept the same, C_2H_4 exhibits greater selectivity toward NO reduction than C_3H_6. Thus, it appears reasonable to conclude that C_2H_4 is a more efficient selective reductant than C_3H_6 for NO reduction in the presence of excess oxygen. We speculate that at least the following two characteristics of C_2H_4 are responsible for this superior selectivity of C_2H_4. First, C_2H_4 has higher diffusivity than C_3H_6 owing to its smaller size. Second, the lightoff temperature of C_2H_4 conversion is much closer to the lightoff temperature of NO conversion than that of C_3H_6 conversion. The lightoff characteristics of HC and NO are very important in determining catalyst's performance for the selective reduction of NO, because the selectivity of a hydrocarbon for NO reduction will deteriorate if the lightoff of the hydrocarbon conversion via oxidation with oxygen occurs far below the temperature at which significant NO conversion begins to occur possibly via its own decomposition. This explains why a hydrocarbon with superior lightoff characteristics (i.e., low lightoff temperature) is not a better reductant for the selective NO reduction than the one with inferior lightoff characteristics (i.e., high lightoff temperature). The important point is that the lightoff temperatures for HC conversion and NO conversion being close to each other is beneficial to the selective NO reduction, and thus the most effective reactant is the one that has the same lightoff temperature for its own conversion as that for the NO conversion. Based on the above observations and arguments, we conclude that C_2H_4 is the most important selective reductant among other hydrocarbons in engine exhaust due to its superior selectivity as well as to its abundant presence in the exhaust.

Both C_2H_4 and C_3H_6, individually, can selectively reduce NO under highly lean conditions. However, the activity of C_3H_6 for the NO reduction is greatly reduced in the presence of C_2H_4. This interesting phenomenon, which we may call *kinetic antagonism*, may be explained by the competitive adsorption–diffusion processes occurring in the zeolite structure between C_2H_4 and C_3H_6. That is, C_2H_4 readily diffuses into the zeolite structure, thereby inhibiting the diffusive influx of C_3H_6 whose diffusion rate is much slower than C_2H_4. Note that this kind of antagonistic interaction between two species with differing diffusivities is expected to occur only in micropore structures such as that existing in zeolites, where the pore diameter is about the same as the molecular diameter of the diffusing species. More detailed discussion of these competitive processes will be treated in a subsequent paper. Due to this kinetic antagonism, the intrinsic selectivity of C_3H_6 is nearly lost when it coexists with C_2H_4 in the engine exhaust. The C_3H_6 conversion apparently results from its oxidation with O_2 near the external surface of the zeolite, while the selective reduction of NO is achieved mainly by C_2H_4 in the internal pore volume over the entire temperature range of our interest.

Our discovery of this kinetic antagonism between C_2H_4 and C_3H_6 during the selective reduction of NO bears another important implication in the application of Cu-ZSM-5 catalysts in automotive exhaust emission control. It implies that C_2H_4 is a more appropriate *single reductant* for laboratory reactor studies of the selective NO reduction than C_3H_6, even though the latter has been widely used as a representative reductant in the literature. A general implication is that only one or two hydrocarbon species among many others may play the predominant role in the selective reduction of NO over Cu-ZSM-5. Obviously, this kinetic antagonism may have a different impact for different zeolitic materials due to their different geometric and energetic characteristics relative to the constituent HC species in automobile exhaust.

SUMMARY AND CONCLUSIONS

Steady-state activity of a Cu-ZSM-5 catalyst for the (NO + HC + O_2) reaction system was measured using a laboratory monolith reactor under highly oxidizing conditions, typical of lean-burn engine exhaust. Of particular interest were the effects of both gas space velocity (12,000 and 35,000 h^{-1}) and the type of hydrocarbon reductant (ethylene and propylene) on the NO conversion efficiency of the Cu-ZSM-5 catalyst. Important findings are listed below.

1. Both C_2H_4 and C_3H_6, individually, are active for selective reduction of NO over Cu-ZSM-5 under lean conditions. However, C_2H_4 is a more efficient reductant than C_3H_6 due to its superior selectivity.
2. The activity of C_3H_6 toward NO reduction is almost completely suppressed in the presence of C_2H_4. In a 3:1 volume-ratio mixture of C_2H_4 and C_3H_6 which is typical of gasoline engine exhaust, the major contribution for the selective NO reduction comes from C_2H_4, while the contribution by C_3H_6 is negligible. This antagonistic interaction between two hydrocarbons may be explained by the competitive adsorption/diffusion processes occurring in the zeolite pore structure.
3. C_2H_4 appears to be the most appropriate single hydrocarbon reductant for laboratory experiments of the selective reduction of NO over Cu-ZSM-5.
4. The NO conversion as a function of temperature exhibits a maximum. The temperature at which the NO conversion reaches its maximum corresponds to the temperature where complete HC conversion is achieved.
5. The lightoff temperatures for the HC and NO conversions being close to each other appear to be beneficial to the selective reduction of NO. This means that a hydrocarbon with low lightoff temperature is not necessarily a better reductant than the one with high lightoff temperature.

It is hoped that the information obtained in this study provides useful guidance in developing better catalysts as well as in devising optimal operating conditions to reduce NO_x emission from lean-burn engine exhaust. Particularly, the discovery of the *kinetic antagonism* operating between two different hydrocarbons in their competition for NO reduction promises to provide a sound basis for proper design of laboratory experiments to simulate lean-burn engine exhaust conditions. Specifically, we recommend that C_2H_4 (rather than C_3H_6, which has been widely used in the recent literature) be used as the representative hydrocarbon species for selective reduction of NO over Cu-ZSM-5 in laboratory feedstreams aimed at simulating engine exhaust.

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