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Comparison of Catalyzed and Homogeneous Reactions of Hydrocarbons for Selective Catalytic Reduction (SCR) of NO_x

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When NO_2 (0.21% in He) was passed over CoZSM-5 or HZSM-5 at SVH = 45,000 h^{-1}, equlibrium with NO + O_2 was approached at temperatures above 673 K. The reactions of NO_2 + CH_4, NO_2 + CH_4 + O_2, and NO + CH_4 + O_2 were compared over these catalysts and in the empty reactor. The latter two reactions yielded essentially identical results when catalyzed, as did NO_2 + CH_4 up to about 22% conversion of CH_4, i.e., to the point where the oxygen supply became exhausted. Without added O_2, NO appeared as a reduction product of NO_2 along with N_2. In the empty reactor, no N_2 was formed although NO_2 could be quantitatively reduced to NO; combustion of CH_4 with O_2 (or with NO) alone was not observed at temperatures less than 873 K, but light-off with NO_2 or NO_x + O_2 occurred at about 723 K. In the absence of O_2, the homogeneous CH_4 conversion was limited to about 22% at 873 K where the conversion of NO_2 to NO reached 100%. With added O_2, conversion of CH_4 reached 62% at 873 K and approached 100% under more severe conditions. These data illustrate the key role played by NO_2 in the selective catalytic reduction reaction. They also show that a catalyst is necessary for the formation of N_2 and emphasize the importance of O_2 in maintaining an adequate supply of NO_2, particularly at temperatures above 800 K where equilibrium favors NO. When C_3H_8 or i-C_4H_{10} was substituted for CH_4, the order of reactivity was i-C_4H_{10} > C_3H_8 > CH_4 in both the catalyzed and the homogeneous reactions. Moreover, in the empty reactor dehydrogenation to the corresponding olefins was found to be important with the former two; the mass balance did not close with CH_4, possibly due to the formation of formaldehyde.

INTRODUCTION

In many ways selective catalytic reduction (SCR) of NO resembles a free radical combustion process. At room temperature the gas mixture is stable; no reaction can be detected on a laboratory time scale. As the temperature is raised to a critical "light-off" temperature, however, the catalytic oxidation of hydrocarbons and the conversion of NO_x to N are initiated. These processes increase rapidly with temperature until the hydrocarbon (in the presence of excess O_2) is completely converted to CO_2 + H_2O. The NO_x is converted to N_2 more rapidly than the hydrocarbon to CO_2 at low conversions, but slows as the NO_x concentration falls. Complete conversion of NO to N_2 may be attained at reasonable space velocities over a range of temperatures, but above 773 K the conversion falls (1). This fall-off in N_2 yield may be related to the shift in the equilibrium of the $NO + \frac{1}{2} O_2 = NO_2$ reaction from the regime where NO_2 is heavily favored to the regime where NO becomes dominant. NO_2 was found to be more reactive and slightly more effective than NO itself (1) even in the presence of a large excess of O_2.

Evidence that free radical processes are occurring stems from the observations of Cowan *et al.* (2a). They observed a first-order isotope effect in the rate of SCR when CD_4 was substituted for CH_4, indicating that breaking a C–H bond is rate limiting in the formation of N_2. An analogous isotope effect occurred in the methane coupling reaction (2b), a well-documented free radical process. Further support stems from the work of Vannice and coworkers (3), who found that a typical methane coupling catalyst was effective for SCR with CH_4. Finally, recently published papers from this laboratory (4a, 4b) have established a correlation between the rates of N_2 and CO_2 formation which is independent of the hydrocarbon employed. The data suggested that NO_x participates selectively in the combustion process and that the two reactions are coupled. It is shown herein, confirming earlier work (1, 5), that in the absence of a reducing agent equilibrium NO_2/NO ratios are obtained over CoZSM-5 and HZSM-5 at temperatures above about 673 K, whereas they were not in the absence of a catalyst or during SCR (5). In the steady state, NO_2 is continually being formed, but it is also being consumed in reactions with the hydrocarbon. Hence, the net NO_2 concentration may be far from equilibrium (5), emphasizing its importance as a reactant. We suggest, therefore, that the first step in the SCR reaction may be the facile conversion of NO to NO_2

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which then preferentially reacts with the hydrocarbon. In this process, it may be supposed that a carbonaceous nitrogen-containing radical is deposited on the catalyst in small amounts and that this in turn reacts with NO_x to form the N–N bond.

Our recent work (4a) led us to think that the SCR might be, at least partly, a homogeneous process. When various hydrocarbons of increasing complexity were studied, all of the data for a given space velocity and set of reactant concentrations could be correlated on a single curve with the single constraint that a constant flux of carbon over the catalyst be maintained. Small molecules like CH_4, NO, NO_2, and O_2 can easily penetrate the 5.5 Å pore systems of ZSM-5 and ferrierite, but other molecules such as isobutane or neopentane should be restricted by diffusion. Still others like 3,3-dimethylpentane and 3,3-diethylpentane should be excluded from these molecular sieves. Yet ferrierite catalysts, which are even more restrictive than ZSM-5, were actually more active than similar ZSM-5 catalysts (4a, 4b). These results were perplexing. The expected molecular sieving effects were not observed. Further, if diffusion was a problem, the rates of N_2 formation and of combustion should have decreased as the molecular size increased because the concentration of hydrocarbon would be decreased in proportion to the carbon number. In fact, the reactions of the large molecules were faster than those of the smaller ones. It was concluded, therefore, that either the reactions were occurring outside the zeolite pore system (on the external surface of the zeolite particles or homogeneously), or else the hydrocarbons must be being broken externally into parts small enough to enter the pores.

The present work was undertaken to better define the homogeneous reactions which may occur under the conditions of the SCR reactions of NO_x. To reach this goal, the homogeneous oxidation of hydrocarbons with NO_2, NO, and their mixtures with O_2 has been studied and these results are compared with those obtained using Co- and HZSM-5 catalysts.

EXPERIMENTAL

Catalysts and Materials. The CoZSM-5-11-98 and HZSM-5-11-100 were prepared by conventional ion-exchange procedures from a parent NaZSM-5 template free preparation supplied by Air Products and Chemicals Co. Identification is provided by giving the cation form first, followed by the type of zeolite (ZSM-5), the Si/Al ratio, and finally the percent of the base exchange capacity occupied. Further details are supplied elsewhere (4a). The HZSM-5 was prepared by heating NH_4ZSM-5-11-100 in flowing 10% O_2 in He at 673 K for 12 h.

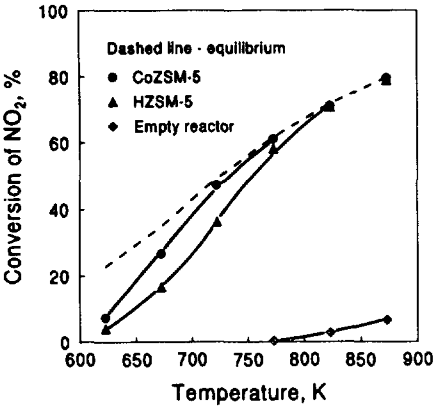

FIG. 1. Catalytic decomposition of NO_2 at various temperatures vs the uncatalyzed reaction. 0.21% NO_2 in He flow of 75 ml/min. Catalyst weights were 50 mg each.

The gases were all of high purity and except for He were used as received. He was passed through an oxyabsorbent Alltrap to insure removal of any traces of H_2O. Instrument grade CH_4, C_3H_8, and i-C_4H_{10} in helium were provided by Matheson. The NO and NO_2 (1% in He) and O_2 (10% in He) were instrument grade and obtained from the same source. These gases were all of >99.9% purity and blended with He (Linde, >99.995% purity) to provide the desired gas mixtures.

Standard pretreatment. Aliquots of the catalyst were dehydrated in flowing O_2 as the temperature was slowly increased (4 K/min) from 298 to 773 K and held there for 12 h before cooling to the preselected temperature. Finally the reactor was flushed with He for 15–30 min or until no trace of O_2 could be detected by gas chromatography.

Reaction studies. These were carried out in a flow reactor with an empty volume in the hot zone of approximately 7 cm^3. The catalyst was packed into a small fraction of this volume (<0.2 cm^3) near the center of the hot zone. The experimental equipment, the analytical procedure by gas chromatography, and treatment of the data are described in detail elsewhere (6a, 6b). Briefly, conversion of NO_2 was determined by quantifying the yield of nitrogen-containing products (NO, N_2). However, in the presence of O_2, it was not possible to quantify either NO or NO_2. All other components were determined directly by gas chromatography.

RESULTS

Catalyzed reactions. The decomposition of NO_2 into NO and $\frac{1}{2}$ O_2 was studied and the results are presented in Fig. 1. Under our flow conditions (SVH = 45,000 h^{-1}) chemical equilibrium was achieved over CoZSM-5-11-98 near 723 K and over HZSM-5-11-100 near 773 K. The uncatalyzed reaction in the empty reactor was very far from equilibrium at the highest temperature tested (873

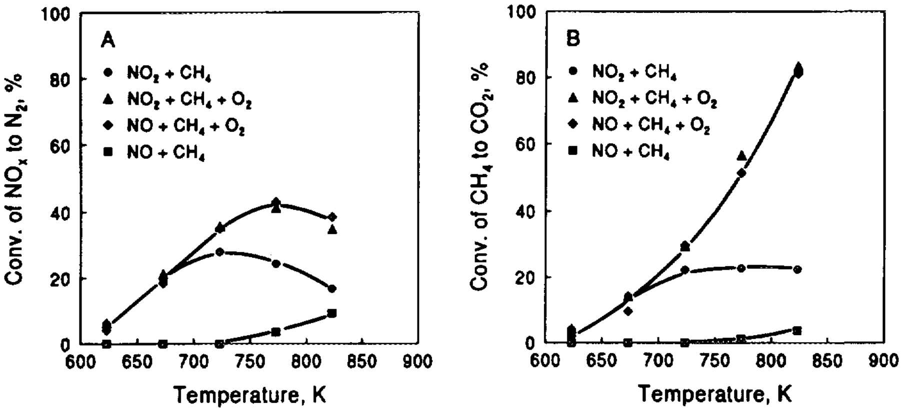

FIG. 2. Reduction of NO_x (A), and oxidation of CH_4 (B), at various temperatures over 50 mg of catalyst CoZSM-5-11-98. The feed gas contained 0.21% NO_2 or NO, 0.28% CH_4, and 2.6% O_2 (when used) in He at a flow rate of 75 ml/min. The percent conversion may be converted to TON (molecules sec^{-1} Co^{-1}) by multiplying by 3.6×10^{-5} (based on total Co).

K). Hence, when NO_2 is used as a feed in reactions with CH_4 over these catalysts, both NO and NO_2 will be present in the temperature range of interest for SCR. Probably the same may be said for SCR compositions of NO, CH_4, and excess O_2. These findings confirm and extend earlier work (1, 5) reported for CuZSM-5 catalysts. Therefore, NO_2 as a feed is equivalent to the NO + O_2 mixture of the same overall composition when used over Cu-, Co-, and HZSM-5. These results demonstrate that HZSM-5 has a redox function. It is therefore unnecessary to assume that acid catalysis plays a role in the SCR reaction as has sometimes been suggested. Perhaps this is not surprising since it has been known for many years that aluminum silicates readily form cation radicals from polynuclear aromatic hydrocarbons after exposure to O_2 (6b).

As shown in Fig. 2A, NO_2 and NO were about equally effective for the formation of N_2 and for the combustion of CH_4 in the presence of excess O_2 as found previously (1) for isobutane over CuZSM-5. Over CoZSM-5, calculation of the conversion from the CH_4 which disappeared and from the CO_2 produced yielded essentially identical results (Fig. 2B). Without O_2 the same conversion levels were maintained with NO_2 at reaction temperatures up to about 723 K where further combustion ceased. These results can be readily understood since most of the NO_2 had been converted to the N_2 and NO at this temperature (Fig. 3). Thus a function of O_2 is to establish a steady state NO_2 concentration. Significantly, NO and NO_2 produced essentially identical results over CoZSM-5 when O_2 was added (Fig. 2), suggesting that NO_2 is essential in the initiation process.

In Fig. 4A, the conversions of NO_2 to N_2 when reacted with CH_4 over CoZSM-5 and HZSM-5 are compared with the reaction in the empty tube. The same comparisons are made for the conversion of NO_2 into NO in Fig. 4B. Interestingly, without added O_2 conversions to NO ultimately greatly exceeded those to N_2. Moreover, in the absence of a catalyst, N_2 formation was not observed, i.e., the NO_2 molecule can supply only one atom of O for reaction with a hydrocarbon. The formation of N_2 requires the presence of a catalyst. Because of the limited amount of oxygen available, the conversion of CH_4 leveled out at about 22% (Fig. 5A). When O_2 was added to the NO_2, the data shown in Fig. 5B resulted. Comparison of Figs. 5A and 5B shows the pronounced effect of addition of O_2 on methane conversion. The sharp increase on adding O_2 occurs at the point where conversion of NO_2 to N_2 plus NO approached 100% (Figs. 3 and 4). Hence, this suggests that the main role of O_2 is not to participate directly in the oxidation of methane, but to oxidize NO into NO_2.

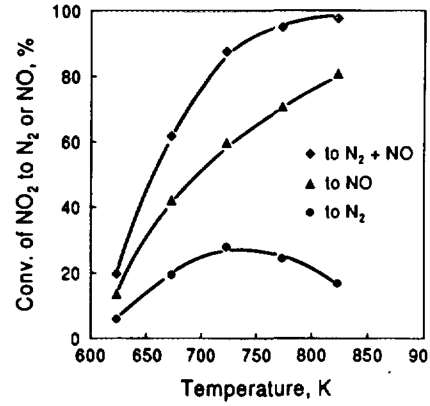

FIG. 3. Partition of products (Fig. 2) from NO_2 (0.21% in He) into N_2 and NO over CoZSM-5-11-98 at various temperatures. The flow rate was 75 ml/min and 50 mg of catalyst was used. The upper curve shows the sum of conversions to N_2 and NO, and the difference to 100% shows the NO_2 remaining in the gas exiting the reactor.

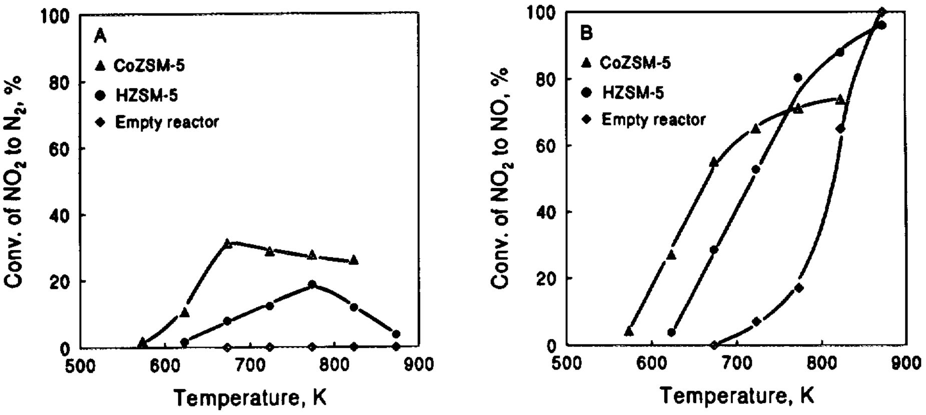

FIG. 4. Comparison of catalyzed and uncatalyzed reactions of NO_2 with CH_4 at various temperatures. (A) Conversion to N_2 and (B) conversion to NO. The feed gas contained 0.21% NO_2 and 0.28% CH_4 in He at a total flow rate of 75 ml/min; 100 mg of each catalyst was employed.

Note that while no N_2 was produced in the homogeneous reaction, the remainder of the data behaved very similarly. They differed mainly in the temperature required for the CoZSM-5, HZSM-5, and the empty reactor. This suggests that a common chemistry is occurring in the combustion reaction. Preliminary blank experiments for several hydrocarbons are reported elsewhere (4a, 4b).

Data obtained at high space velocity (112,500 h^{-1}) for the reaction of NO_2 with CH_4 with varying O_2 concentration are listed in Table 1. A striking feature of these results is the relatively small effect on the conversions of NO_2 and CH_4 to N_2 and CO_2, respectively, with the added O_2. The ratio of the amount of O supplied by the NO_2 to the moles of CH_4 converted was virtually unity, *vide infra* (Row C). This emphasizes once again the key role of NO_2 in the reaction mechanism at low conversions. Note that the conversion to N_2 and to CO_2 increased only slightly (~5%) on adding O_2 to the reaction stream. Hence, NO_2 must be supplying virtually all of the oxygen required under these reaction conditions, i.e., it both activates the CH_4 and carries the combustion. N_2 is formed concomitantly.

The data obtained for 0% O_2 (Table 1) were extended by varying the temperature. These data are shown in Fig. 6 where the points at 673 K correspond to those in the table. Below this temperature, the conversion to nitrogen was nearly identical for the NO_2 and the NO + O_2 systems, as were the data for combustion of CH_4. As shown in Table 1, nearly equivalent amounts of NO_2 and CH_4 were converted to N_2 and CO_2 + H_2O, respectively. The overall reaction

$$2NO_2 + CH_4 \rightarrow N_2 + CO_2 + 2H_2O \qquad [1]$$

shows that $2NO_2$ must be reacted to completely oxidize one CH_4 molecule. Why then is the observed ratio close

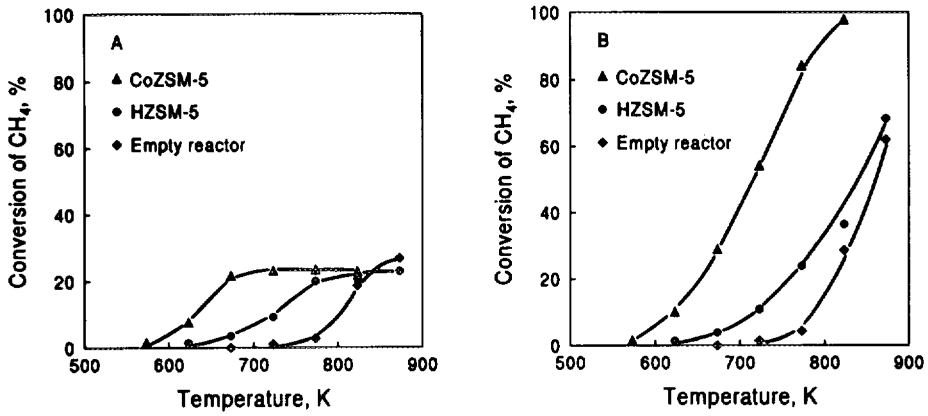

FIG. 5. Comparison of (A) the oxidation of CH_4 by NO_2 in the empty reactor with reactions catalyzed by 100 mg of CoZSM-5-11-98 and HZSM-5-11-100, and (B) the effect of adding O_2 on these same reactions. The feed gas contained in (A) 0.21% NO_2 and 0.28% CH_4, and in (B) 2.6% O_2 was added.

TABLE 1

Mass Balances for Reaction of CH_4 with $NO_2 + O_2$ over CoZSM-5-11-98 at 673K[a]

		Concentration of O_2 (%)				
Step		0	0.4	1.0	2.6	5.2
A	Conversion of NO_2 used to form N_2 (μmol/min)	0.759	0.787	0.766	0.807	0.794
B	Conversion of CH_4 to $CO_2 + H_2O$ (μmol/min)[b]	0.703	0.731	0.684	0.759	0.731
C	$\frac{A}{B} = \frac{\text{NO}_2\text{ converted to N}_2}{\text{CH}_4\text{ converted}}$	1.08	1.08	1.12	1.05	1.09
D	Conversion of NO_2 to NO (μmol/min)[c]	1.265	—	—	—	—

[a] The reactant gas contained 0.21% NO_2 + 0.28% CH_4 + x% O_2 in He flowing at 75 ml/min over 20 mg of catalyst (corresponding to SVH = 112,500 h^{-1}).

[b] This conversion was equal to the overall conversion of CH_4.

[c] This conversion could be determined only in the absence of O_2.

to unity (Table 1) instead of 2.0 as predicted? This may be understood by recalling that a major fraction of the reacted NO_2 produced NO, not N_2. These data are tabulated in Row D. To strike a carbon balance, the consumption of Row A must be divided by two (Eq. [1]) and that of Row D by four (Eq. [2]),

$$4NO_2 + CH_4 \rightarrow 4NO + CO_2 + 2H_2O. \quad [2]$$

When this was done, the corresponding values for CH_4 converted to CO_2 by Eqs. [1] and [2] are 0.380 and 0.316 μmol/min, respectively. These sum to 0.696 vs the value of 0.703 μmol/min listed in Row B. These give a ratio of 1.01 vs the 1.08 shown in Row C. Therefore, the experimental ratios near unity (instead of 2) result from the nearly equivalent amounts of CH_4 converted by Eqs. [1] and [2]. Interestingly, the addition of up to 5.2% O_2 had no significant effect at conversions of <10% obtained at 673 K although this may not be true at higher temperatures where selectivity is known to fall (4a, 4b). This suggests (but does not prove) that the SCR reaction, which is initiated by the oxidation of CH_4 to $CH_3 \cdot$ (2a), is effected by NO_2, not O_2, as is usually thought to be the case for homogeneous oxidations. This could happen if NO_2 deposited a very reactive O atom on a surface site as it reacted to form NO.

As the temperature was raised (Fig. 6), selectivity was lost as more NO_2 was converted into NO at the expense of the N_2 formed. Concomitantly the NO_2 concentration dropped (to zero at 873 K). Of course this could have been avoided had O_2 been added to the system as was done with the NO. Petunchi *et al.* (1) showed complete

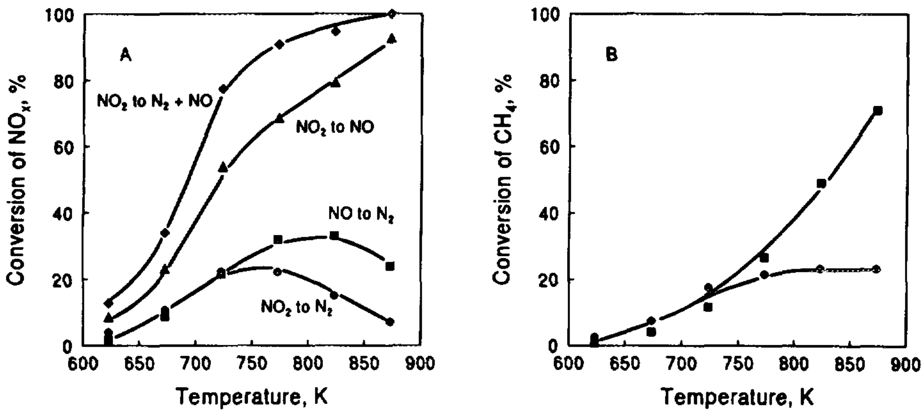

FIG. 6. Comparison of NO_2 (●, ▲, ◆) vs NO + O_2 (■) in (A) SCR over 20 mg of CoZSM-5-11-98 and in (B) combustion of CH_4. The gas compositions were NO_2 (0.21%), or NO (0.21%) + O_2 (2.6%), and CH_4 (0.28%) in He. The flow rate was 75 ml/min equivalent to SVH ~ 112,000 h^{-1}. At 673 K the TON for N_2 formation (based on total Co) was 1×10^{-3} for NO_2 and 0.8×10^{-3} molecules sec^{-1} for NO + O_2.

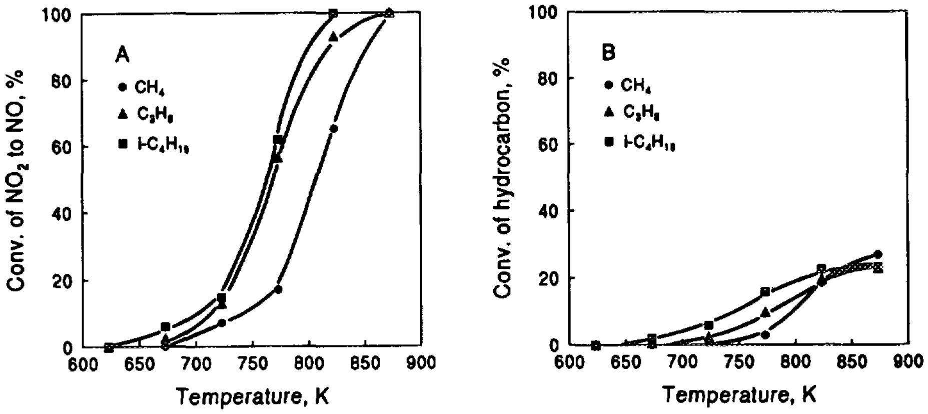

FIG. 7. Comparison of the uncatalyzed reactivities of CH_4, C_3H_8, and i-C_4H_{10} with NO_2 in He. The gas compositions were NO_2 (0.21%) and hydrocarbons (0.28%) in He. Flow rate was 75 ml/min and volume of the hot zone in the empty reactor was ~7 ml. (A) Conversion of NO_2 to NO; (B) conversion of the three hydrocarbons to all products.

conversion of NO_2 into N_2 over CuZSM-5 when O_2 was present and isobutane was used as the hydrocarbon. The combustion (Fig. 6B) leveled with the NO_2 system as the supply of this oxidizing agent approached zero. In the presence of NO + O_2, however, it swung sharply upward as was shown previously (1). The addition of O_2 would prevent the depletion of NO_2, but the equilibrium level would decrease as the temperature is raised. At high space velocity the conversion of NO to N_2 in the presence of 2.6% O_2 passed through a maximum near 823 K (Fig. 6A). The combustion of CH_4 reached 70% at 873 K whereas the conversion of NO_2 to N_2 remained roughly constant at 24%. Moreover, when the space velocity was lowered by increasing the catalyst weight to 100 mg, the data obtained were quite similar except that higher conversions of NO and CH_4 were obtained. These data clearly illustrate the key role played by NO_2 in the combustion of the hydrocarbon.

Homogeneous reactions of CH_4, C_3H_8, and i-C_4H_{10} with NO, NO_2, and O_2. These were studied in the empty reactor between 623 and 873 K. No N_2 was formed in any of this work, although NO_2 reacted with these hydrocarbons to form NO and oxidation products. Moreover, combustion did not occur with O_2 (or with NO) alone below 873 K, although it did with NO_2 and on addition of NO_2 or NO to the O_2. In Fig. 7 the data obtained for methane, propane, and isobutane are compared. The hydrocarbon concentrations were kept constant at 0.28% while 0.21% NO_2 was used and only one O/NO_2 was available for reaction (Fig. 7A). Thus, the amount of oxidation products produced was limited by the supply of oxygen (Fig. 7B). Moreover, since i-C_4H_{10} and C_3H_8 hydrocarbons contain four and three times as much carbon, respectively, as CH_4, and since the NO_2 was constant, it appears strange that the conversions of all three hydrocarbons converge at about 25% in the 823–873 K range. This result was possible because olefins were produced from the C_3 and C_4 hydrocarbons, as shown in Fig. 8.

Light-off occurred with CH_4 and NO_2 in the empty reactor (Fig. 7B) between 723 and 773 K; the CoZSM-5 catalyzed reaction (Fig. 6B) was initiated between 623 and 673 K, i.e., $\Delta T \sim 100$ K. Aside from this translation, the curves look the same; they level out at about 24 to 26% conversion of CH_4 as the NO_2 supply becomes exhausted. These data support the idea that the rate-determining step for the catalytic and noncatalytic process is the same, i.e., the initiation step is the formation of $CH_3\cdot$ from CH_4 by NO_2. This process may be catalyzed by a redox center; the radical produced may remain on the surface or evaporate into the gas phase. Thus, so far as combustion is concerned, some of the reaction may be partly homogeneous even in the presence of a catalyst. Interestingly in this connection, the order of reactivities is iso-C_4H_{10} > C_3H_8 > CH_4, i.e., the same for the uncatalyzed as for the catalyzed reaction; it is typical of free radical chemistry (4).

The total combustion shown in Fig. 7B is limited by the availability of oxygen. All of the data shown in Fig 8A were obtained with a surplus of oxygen over that required for total oxidation to $CO_2 + H_2O$. Nevertheless, the same order of reactivities was obtained. A steep rise in total conversion of CH_4 occurred above 773 K; a similar rise was found for the catalyzed reaction (Fig. 2B) above 673 K. Complementary data obtained in the presence of excess O_2 when NO was substituted for NO_2 are shown in Fig. 9. Comparison with Fig. 8A shows a surprisingly small decrease in conversion when NO is used. Presumably this is because NO must react with O_2 homogeneously, forming NO_2 above 773 K. Thus, a remarkable similarity exists for the combustion processes, whether catalyzed or not.

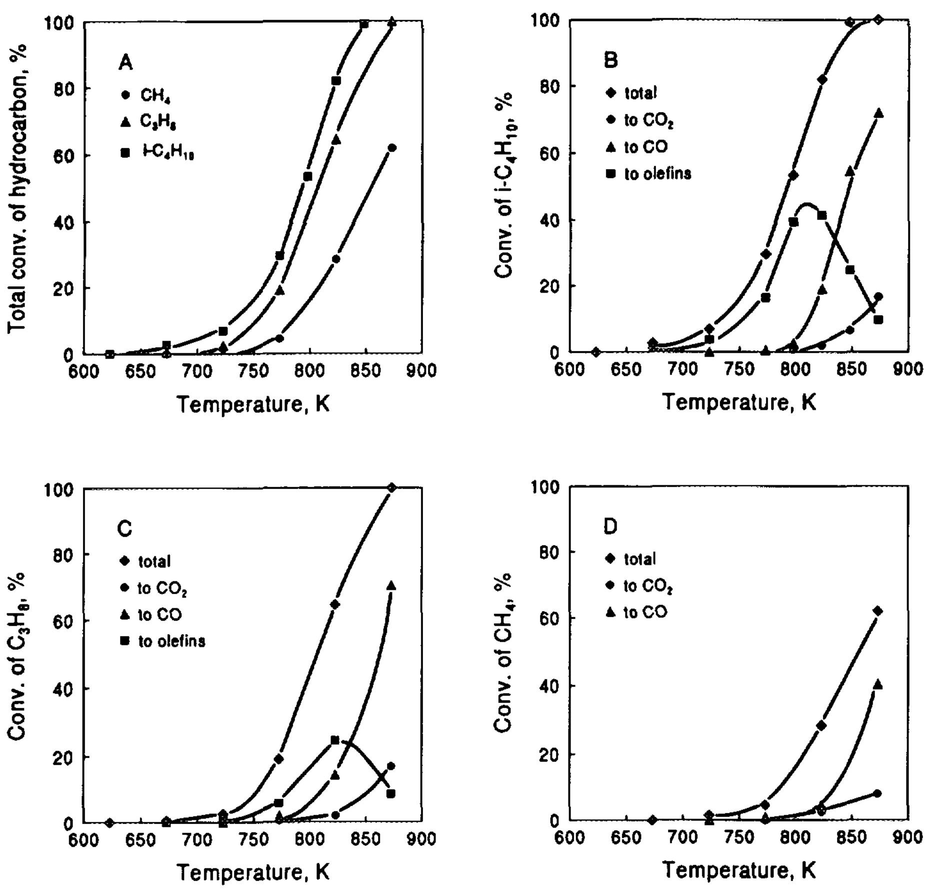

FIG. 8. (A) Relative reactivities of CH_4, C_3H_8 and *i*-C_4H_{10} with a feed stream comprised of 0.21% NO_2, 0.28% hydrocarbon and 2.6% O_2 in He. The flow rate was 75 ml/min (hot volume ≈ 7 ml); (B) distribution of oxidation products from i-butane in the experiments shown in (A); (C) same as (B), but for C_3H_8; (D) same as (B), but for CH_4.

The distribution of combustion products from *i*-C_4H_{10}, C_3H_8, and CH_4 are shown in Figs. 8B, 8C, and 8D, respectively. Below 798 K very little CO or CO_2 was produced from *i*-butane (Fig. 8B). The chief products were hydrocarbons, mainly butenes and propene. Even so, an important difference exists between the overall consumption of *i*-butane and the sum of the measured products. At higher temperatures the hydrocarbon formation decreased, presumably due to secondary oxidation to CO, CO_2, and H_2O. At 873 K, 99^+% of the carbon could be accounted for by these three products. Much the same thing can be said about the combustion of propane (Fig. 8C). Interestingly, in both cases the formation of CO was much higher than that of CO_2 at all temperatures, suggesting that the latter may be formed by secondary oxidation of the former. The carbon missing from the mass balances at the lower temperatures is presumably partial oxidation or amoxidation products. These would be lost by strong adsorption on the chromatographic column.

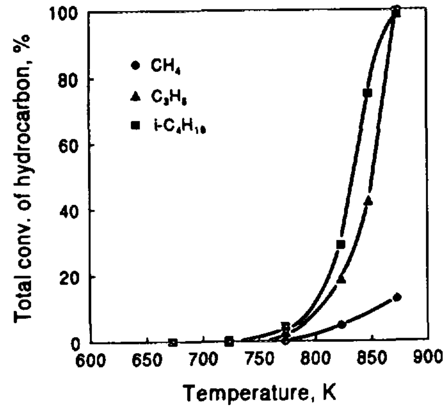

FIG. 9. Relative reactivities as in Fig. 8, but with NO replacing NO_2.

As is typical of homogeneous combustion processes, CH_4 was the most difficult to burn. Not only were higher temperatures required to achieve a given level of total conversion (Fig. 8A), but the conversion of NO_2 to NO

TABLE 2

Mass Balances for the Uncatalyzed Homogeneous Reaction of CH_4 with NO_2 in the Empty Reactor[a]

Step		Temperature (K)	
		823	873
A	Overall conversion of CH_4 (μmol/min)	1.74	2.51
B	Overall conversion of NO_2 into NO (μmol/min)	4.57	7.03
C	Conversion of CH_4 into CO and CO_2 (μmol/min)	0.46	1.24
D	Corresponding conversion of NO_2 into NO (μmol/min)	1.74	4.25
E	Conversion of CH_4 into unknown compounds, μmol/min (A–C)	1.28	1.27
F	Conversion of NO_2 into NO (μmmol/min) (B–D) = O atoms unaccounted for.	2.83	2.78
G	Ratio, F/E	2.21	2.19

[a] The reactant gas contained 0.21% NO_2 and 0.28% CH_4 in the following at a rate of 75 ml/min. The corresponding rates were CH_4 = 9.375 μmol/min and NO_2 = 7.03 μmol/min.

was lowered correspondingly (Fig. 7A) when it was the only oxidizing agent present. CH_4, unlike the other two hydrocarbons, cannot form olefins by oxidative dehydrogenation. The data of Fig. 8D also show a deficit in the carbon balance of 20 to 15% between 823 and 873 K. The formation of formaldehyde may have been partly responsible. An attempt to strike mass balances on carbon and NO_2 converted to NO, releasing O atoms, is made in Table 2. After deducting from the total CH_4 reacted (Step A) the amounts converted to CO and CO_2 (C), a substantial fraction was unaccounted for (E). Similarly, after deducting from the total conversion of NO_2 (B), the amount required to furnish the oxygen needed to produce the CO and CO_2 formed (D), an amount that could not be accounted for could be deduced (F). The ratio of F/E = 2.2 should be 4 for oxidation to CO_2, 3 for oxidation to CO (Eqs. [1] and [2]), and 2 for $H_2C{=}O$. Consequently, we infer that the missing CH_4 and NO_2 is probably mainly formaldehyde. This has been reported previously (8) when *n*-butane was oxidized in air in the presence of NO.

DISCUSSION

Many years ago Wojciechowski and Laidler (9) studied the homogeneous decomposition of CH_4 and of C_2H_6 in the presence of NO. They reported that NO acted as a catalyst for methane coupling and for the dehydrogenation of ethane to ethylene and H_2. They pointed out that NO is a stable free radical that can abstract an H from C_2H_6 forming $C_2H_5\cdot$ + HNO. $C_2H_5\cdot$ then discharged an H· to become C_2H_4 while the H· reacted with another C_2H_6 to form H_2 and $C_2H_5\cdot$, establishing a chain process. The termination steps were suggested to be the reaction of HNO with $C_2H_5\cdot$ to re-form C_2H_6 and release the NO. In a word, the stable free radical NO acted as a chain initiator forming $C_2H_5\cdot$ and the rather stable HNO, whereas the reverse reaction functioned as the chain termination step. With CH_4, initiation was by

$$CH_4 \rightarrow CH_3\cdot + HNO, \qquad [3]$$

but since olefin formation is not possible, coupling occurred forming C_2H_6. Secondary reaction of the C_2H_6 (as above) occurred forming $C_2H_4 + H_2$. In the present work, oxygen was always available, either from NO_2 or from O_2 + NO. No $CH_3\cdot$ coupling was observed, although dehydrogenation of C_3 and C_4 paraffins to olefins was. Coupling of 2 $CH_3\cdot$ could not be expected in the presence of the much higher concentrations of NO or NO_2; both are radical traps, but NO_2 is also a strong oxidizing agent. Thus $CH_3\cdot$ may be produced at lower temperatures either catalytically or by

$$CH_4 + NO_2 \rightarrow CH_3\cdot + \cdot OH + NO. \qquad [4]$$

Recently, Bromly *et al.* (8) reported on the homogeneous reactions of *n*-butane in air modulated by NO over a temperature range 600 to 720 K. Low concentrations of NO in the *n*-butane/air system promoted oxidation of *n*-butane; conversely, low concentrations of *n*-butane in air promoted the oxidation of NO to NO_2. The latter process was accompanied by the consumption of *n*-butane and the formation of C_3H_7CHO, CO, HCHO, $(CH_3)_2CO$, various butenes, and propene. These workers assumed that the free radical processes were initiated by reaction of O_2 (0.2 atm) directly with *n*-butane, i.e.,

$$n\text{-}C_4H_{10} + O_2 \rightarrow C_4H_9\cdot + HO_2 \qquad [5]$$

rather than by reaction with NO as postulated previously (9). Then NO_2 was formed by

$$NO + HO_2 \rightarrow NO_2 + \cdot OH \qquad [6]$$

and the $C_4H_9\cdot$ was regenerated by reaction of ·OH with *n*-C_4H_{10} forming H_2O. Alkyl radicals readily add O_2 forming peroxy radicals and thus leading to subsequent chemistry. Trace quantities (as little as 0.02 ppm) of NO had a profound promoting effect on these reactions by virtue of the ability of NO to convert relatively unreactive HO_2 into reactive HO· radicals that regenerated the $C_4H_9\cdot$ as described above. Other important reactions of NO included $RO_2\cdot + NO \rightarrow RO\cdot + NO_2$ and $NO + HO\cdot + M = HONO + M$. The above-mentioned products accounted for more than 80% of the measured consumption of the *n*-butane. Interestingly, N_2 was not found among the reaction products. In these studies when 90 ppm of NO was introduced into a stream of air containing excess (600 ppm) *n*-butane, the NO was quantitatively converted to NO_2. The residence time in the reactor was about 5 sec, a value similar to that used in the present work. In the temperature range investigated (603 to 723 K), the chemical equilibrium in mixtures of NO, NO_2, and O_2 strongly favors NO_2. The possible role of this compound as a chain initiator or an oxygen transfer agent was not considered by these workers. In the present work (Fig. 7A), NO_2 was quantitatively converted to NO (in the absence of O_2) by reaction with hydrocarbons. Unfortunately, our facilities did not permit the determination of NO_2/NO in the presence of O_2. Hence, we were unable to obtain the distribution in the tail gas from the system NO_2, O_2, CH_4. Further work is needed to clarify the apparent contradictions. Undoubtedly some of this same chemistry is occurring in the homogeneous reactions of i-C_4H_{10} and C_3H_8 reported herein. Alkyl radicals react with O_2 forming ROO· and these peroxy radicals react with NO forming $NO_2 + RO\cdot$. Evidently NO and NO_2 are interconvertable during combustion. As shown in Fig. 8, olefins, as well as CO and CO_2, were formed and a portion of these paraffins was unaccounted for over part of the conversion range. We may suppose, therefore, that aldehydes and ketones were included in the missing reacted hydrocarbon. Probably these compounds were intermediates in the combustion process when catalysts were employed, but were further burned to CO_2 and H_2O. N_2 was formed only in the presence of a catalyst. We suppose, as did Yokoyama and Misono (10), that organic nitro compounds are deposited on the catalyst in small amounts and that these react with NO_x forming an N–N bond leading to release of N_2. These workers also showed that CH_3NO_2 reacted with O_2 over CuZSM-5 to release N_2 together with a small amount of N_2O. If $CH_3\cdot$ is present, reaction with NO_2 to form CH_3NO_2 might also be expected.

A referee has called our attention to an apparent contradiction on the effects of O_2 in heterogeneous vs homogeneous systems. With the former, O_2 greatly enhances the reduction of NO to N_2 whereas with the homogeneous systems near equilibrium conversion of NO to NO_2 results from the reaction of $HO_2\cdot$ with NO. Here it is generally assumed that the reaction is initiated by reaction of the hydrocarbon with the much larger concentration of O_2 forming HO_2 and the corresponding hydrocarbon radical; formation of NO_2 results. We have assumed that since NO_2 is a stronger oxidizing agent than O_2, it can preferentially initiate radical formation in the presence of much lower concentrations of O_2 than that in air. Our data (Figs. 5 and 6) show that CH_4 can be burned with NO_2 alone or with O_2 and with or without a catalyst. It also shows that N_2 is not formed in the absence of a catalyst. With a catalyst, the evidence suggests that NO_2 is readily formed from NO and O_2 (explaining the great rate enhancement on O_2 oxidation) and that it is NO_2 that then initiates formation of the first hydrocarbon radicals. Either NO or NO_2, or both, may be required for N_2 formation and the catalyst is required to form and hold the organic nitro compound needed for coupling of the N–N bond.

The route to form CO_x has been investigated for the CH_4 coupling reaction. Lin *et al.* (11) proposed that an important source of carbon oxides is the homogeneous oxidation of methyl radicals through the formation and reaction of the methylperoxy radical, $CH_3O_2\cdot$. On rearrangement, this may form formaldehyde and HO· radical. The HO· may then react with CH_4 to form H_2O and regenerate the methyl radical. The formaldehyde is readily burned to CO_2 and H_2O. As shown in the work described above (8, 9), the introduction of stable free radicals NO or NO_2 will modify this chemistry, but free radical reactions will remain dominant. Over the zeolite catalysts, Tong and Lunsford (12) suggested that $CH_3\cdot$ reacts mainly by a reductive addition process to form surface methoxide ions. On transition metal ion sites, these are readily oxidized to carboxylates and ultimately to CO_2. The analogous combustion chemistry found in the present work does not support the idea that a completely different mechanism is operative in the catalyzed and uncatalyzed reactions. Instead our results suggest that the catalyst simply decreases the temperature required to produce a given rate by ~100 K (probably more for CuZSM-5). Blank experiments carried out earlier (4), using the same blends of CH_4, i-C_4H_{10} or neo-C_9H_{20} with NO and O_2 as in the catalytic experiments, showed similar chemistry. No N_2 formation occurred, but combustion was observed at a light-off temperature of about 850 K for CH_4 and 773 K for the other two gases. Complete combustion to CO_2 and H_2O was observed above 873 K, i.e., at temperatures ~100 K higher than with CoZSM-5 (35% exchanged). Interestingly, neononane, the largest molecule, was among the fastest burning. In the present work these measurements were extended to include homogeneous reactions of hydrocarbons with NO_2 and $NO_2 + O_2$ mixtures.

The foregoing paragraphs have dealt mainly with the chemistry of combustion processes. The key question of how dinitrogen is formed remains unanswered. The data of Fig. 1 show that NO_2 is a ready source of oxygen which may appear as O_2 or be used to attack hydrocarbons directly. It also seems evident that NO_2 is a better oxidizing agent than O_2, although whether this is sufficient to offset the large concentration difference usually present in SCR is uncertain. Alternative explanations have been advanced concerning many aspects of the underlying chemistry. Most of this earlier work has focused on the *reduction* of NO to N_2 with the questions concerning the *oxidation* of the hydrocarbon relegated to secondary status. It has been our intention to refocus thought to view this interesting chemistry as a competitive oxidation where three oxidizing agents are available to react with the hydrocarbon, viz., NO_2, O_2, and NO. It is already known (4a, 4b) that the selectivity for N_2 formation decreases very dramatically as NO_x is consumed so that at high conversions, combustion with O_2 becomes dominant. The present paper will not settle the questions of mechanism. It has been our intention to point out that homogeneous combustion is a free radical process, that the character of these results is altered materially by the presence of small amounts of NO_x and that the NO/NO_2 couple can act as an oxygen carrier, as can a catalyst. Our previous work (4a, 4b) with large hydrocarbons has suggested that the reactions over ZSM-5 and Ferrierite catalysts may not be entirely heterogeneous. The present work shows analogous behavior over these catalysts and in the empty reactor with the significant difference that N_2 does not form in the absence of the solid catalysts. We attribute this to the necessity of retaining some organic nitro intermediates on the surface that function to form the N–N bond. How much the picture developed herein will need to be modified remains to be seen. We can only hope that looking at SCR from this different perspective will prove helpful.

CONCLUSIONS

(i) The results of this work suggest that the SCR reaction involves free radical chemistry and may be partly homogeneous.

(ii) These reactions are initiated on the catalyst surface (probably on the exterior of the particles or at the pore mouths). Combustion may be initiated in the homogeneous gas phase at somewhat higher temperatures.

(iii) NO_2 appears to be involved in initiating radical formation; an important function of O_2 may be to convert NO into NO_2.

(iv) N_2 formation requires a catalyst; combustion does not, suggesting that an intermediate is formed on the catalyst surface which can couple with NO or NO_2 to form the N–N bond.

(v) In the absence of a catalyst, combustion is not initiated by either NO or O_2 alone up to 873 K, but light-off occurs below 773 K when both are present, and at still lower temperatures with NO_2. This homogeneous combustion imposes an upper limit on the temperature for the SCR of NO_x by hydrocarbons in the presence of excess O_2.

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REFERENCES

1. Petunchi, J. O., and Hall, W. K., *Appl. Catal. B* **2,** L17 (1993).
2. (a) Cowan, A. D., Dumpelmann, R., and Cant, N. W., *J. Catal.* **151,** 356 (1995); (b) Cant, N. W., Kennedy, E. M., and Nelson, P. F., *J. Phys. Chem.* **97,** 1445 (1993).
3. Zhang, X., Walters, A. B., and Vannice, M. A., *J. Catal.*, **146,** 568 (1994).
4. (a) Witzel, F. O., Sill, G. A., and Hall, W. K., *J. Catal.*, **149,** 229 (1994); (b) *in* "Zeolites and Related Microporous Materials, State of the Art" (J. Weitkamp, H. J. G. Karge, H. Pfeiffer, and W. Holderich, Eds.), Studies in Surface Science and Catalysis, Vol. 84, Part C, No. 84, p. 153. Elsevier, Amsterdam, 1994.
5. (a) Shelef, M., Montreuil, C. N., and Jen, H. W. *Catal. Lett.* **26,** 277 (1994); (b) Chajar, Z., Primet, M., Praliand, H., Chevier, M., Gautier, C., Mathis, F., *Catal. Lett.* **28,** 33 (1994).
6. (a) Petunchi, J. O., Sill, G. A., and Hall, W. K., *Appl. Catal. B* **2,** 303 (1993); (b) Hall, W. K., *J. Catal.* **1,** 53 (1962); *J. Phys. Chem.* **71,** 1005 (1967).
7. Li, Y., and Armor, J. N., *Appl. Catal. B* **3,** L1 (1993).
8. Bromly, J. H., Barnes, F. J., Mandyczewski, R., Edwards, T. J., and Haynes, B. S., *in* "Proceedings, 24th International Symposium on Combustion." p. 899. The Combustion Institute, Pittsburgh, PA, 1992.
9. Wojciechowski, B. W., and Laidler, K. J., *Can. J. Chem.* **38,** 1027 (1968).
10. Yokoyama, C., and Misono, M., *J. Catal.* **150,** 9 (1994).
11. Lin, C. H., Ito, T., Wang, J. X., and Lunsford, J. H., *J. Catal.* **111,** 302 (1988).
12. Tong, Y., and Lunsford, J. H., *J. Am. Chem. Soc.* **113,** 4741 (1991).