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Reaction Studies of the Selective Reduction of NO by Various Hydrocarbons

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A number of factors affecting the behavior of ZSM-5 and Ferrierite zeolites have been studied and implications concerning mechanism have been deduced. Increasing the loading of the ZSM-5 with Co^{2+} is shown to increase both the selective catalytic reduction (SCR) of NO and hydrocarbon combustion activities, but not to alter the selectivity under a given set of reaction conditions. The latter was nearly constant at all temperatures and valued at unity up to 673 K, where it precipitously fell at higher temperature. Selectivity was also a function of space velocity and of the NO/C_4H_{10} ratio. Both SCR and combustion followed similar patterns with different charge balancing cations (including H) with a few notable exceptions. The shifts in temperature required to obtain a given conversion of NO to N_2 were relatively minor compared with those required for constant combustion. NO and NO_2 were equivalent in SCR in the presence of excess O_2. In the absence of O_2, NO_2 was the better oxidant at low temperature although NO became quite effective above 800 K. The tabulated data at various temperatures showed a strong molecular sieve effect in the SCR reaction when neononane was employed, but not for the combustion reaction. None of the other molecules employed showed this behavior. Plots of conversion of NO to N_2 vs conversion of hydrocarbon to CO_2 correlated the data for all hydrocarbons, regardless of size, on single curves, *except* for neononane over Co- and CH_4 over CuZSM-5. Even HZSM-5 behaved in this way. A further interesting molecular sieve effect was found when reactions over CoFer (Ferrierite) were compared with those over CuZSM-5.

INTRODUCTION

The selective catalytic reduction of NO to N_2 by hydrocarbons in the presence of excess O_2 (SCR) is an interesting and important reaction. This chemistry provides a needed solution for the problem of removal of NO_x from the exhausts of diesel and lean burn engines. Moreover, it may become a desirable substitute for the reduction of NO with NH_3 for fixed site operations such as electric utilities. In the latter, the substitution of CH_4 for NH_3 has obvious practical benefits. Many of the chief characteristics of SCR are by now well established but many key points remain debatable or are simply not understood. The present work was undertaken in hopes of shedding additional light on these matters.

During the past several years, some issues seem to have been settled. First, it is now generally agreed that this reaction is independent of the NO decomposition reaction. Hence, this is a new ball game; requirements for NO decomposition may not apply and the possibility of the development of new and better catalysts exists. Needed to guide this effort is a basic understanding of the mechanism and of the factors which control catalyst effectiveness. It does not now appear that altervalent base-exchange cations are essential to act as oxygen carriers (1, 2). Second, an important role for NO_2 has been outlined (3, 4). The NO_2 can either be fed directly or manufactured by the catalyst through reaction of NO and O_2. Further evidence has been obtained suggesting that some intermediate formed during the oxidation of the hydrocarbon acts to couple two N atoms to form N_2. In particular it has been suggested (5, 6) that this intermediate may be ·NCO which can then couple with ·NO to form ON–NCO. This radical, when generated photolytically from BrNCO, has been shown to undergo this reaction and to decompose into N_2 and CO_2 (6). A plausible explanation is lacking, however, for how ·NCO may be formed during SCR. Nevertheless, it reportedly (7) has been observed by IR spectroscopy on the surfaces of catalysts active for the reaction.

In the present experiment, a series of catalysts containing a variety of base-exchange cations has been examined using eight different molecules, viz., CH_4, C_3H_8, i-C_4H_{10}, n-C_5H_{12}, neopentane, 3,3-dimethylpentane, 2,2,4-trimethylpentane, and 3,3-diethylpentane (neononane). The sizes of the pore openings of ZSM-5 vary between 5.1 and 5.6 Å (8). Among the aforementioned molecules, CH_4, C_3H_8, n-C_5H_{12}, and i-C_4H_{10} may be expected to enter the pore system. However, other more highly branched molecules should not. According to Breck (9),

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neopentane has a kinetic diameter of 6.2 Å and therefore should be excluded, whereas isobutane (kd = 5.0) should just fit into the pores of ZSM-5, but not permit passage of other smaller molecules such as NO_x or O_2. However, this zeolite has an interconnecting pore system so that small molecules may detour around the larger ones and reaction is possible. Ferrierite, on the other hand, has a unidimensional 10-ring system and should further constrain the reactions of larger molecules. These 10-ring channels are connected by smaller 8-ring passages through which CH_4, NO_x, and O_2 may diffuse. In any case, diffusional constraints should become more severe the larger the hydrocarbon molecules and should be more obvious with Ferrierite than with ZSM-5.

According to Haag (10) neononane has been shown experimentally to be excluded from ZSM-5. Moreover, it seemed probable that 3,3-dimethylpentane would be also. In any case these larger molecules would be expected to be constrained by diffusion under our experimental conditions, the more so the higher the molecular weight. These ideas have been tested and the results are of some interest in connection with the reaction mechanism. A preliminary report of the molecular sieving effects has been made previously (11).

EXPERIMENTAL

Base exchange procedure. The parent NaZSM-5 sample with Si/Al = 11 and Na/Al = 1.26 was provided by Air Products; it was a template-free preparation. The ^{27}Al–MAS–NMR spectrum showed no detectable octahedral aluminum in this material. For the low exchange levels of about 30% of the BEC, 15 g of the zeolite was added to 1500 ml of distilled water containing 3.5×10^{-3} mol metal acetate. The mixture was stirred for 24 h at 353 K. The pH of these solutions was near 7 before and after the ion exchange. The solid was removed by filtration, washed three times with 500 ml of distilled water at room temperature, and dried overnight at 350 K. The metal contents of the zeolites were determined by XRF as well as by AAS. The base-exhanged zeolites are identified here as CoZSM-5-11-35, NiZSM-5-11-28, CuZSM-5-11-30, GaZSM-5-11-35, and LaZSM-5-11-27, where the cationic form is defined first, then followed by the type of zeolite (ZSM-5), the Si/Al ratio, and finally the percentage of the base-exchange capacity occupied (calculated as the ion in the valence state in the acetate). The amounts of Na, Si, and Al were also measured and the idealized unit cell was calculated, e.g., for the CoZSM-5-11-35 zeolite, $Na_{5.4}Co_{1.35}(AlO_2)_{7.7}(SiO_2)_{88.3}$.

For the excessively exchanged CoZSM-5 zeolite, 15 g of the parent NaZSM-5 was added to 1500 ml water containing 2×10^{-2} mol Co–acetate. The mixture was stirred for 24 h at 353 K. The pH of the starting solution was 7.3; this was adjusted with acetic acid to pH 7. The solid was removed by filtration and washed three times with 500 ml of distilled water and the exchange procedure was repeated three times. Then the zeolite was dried overnight at 353 K. This preparation was identified as CoZSM-5-11-151. Its unit cell composition was $Na_{0.2}Co_{5.8}(AlO_2)_{7.7}(SiO_2)_{88.3}$. Clearly the Co^{2+} was partially hydrolyzed.

The parent NaZSM-5 zeolite was exchanged at Air Products into the NH_4^+ form and NH_4ZSM-5-11-100 was obtained. Calcining this at 773 K for 8 h converted it into the H form.

A CoZSM-5 zeolite with a Si/Al ratio of 11 and an exchange level of 98% and a Co–ferrierite with a Si/Al ratio of 8.5 and an exchange level of 78% were provided by Air Products; these preparations are designated CoZSM-5-11-98 and CoFer-8.5-78, respectively.

Reaction studies. The catalysis tests were carried out in the steady state flow mode in the same apparatus described previously (2). The catalysts were given the standard pretreatment: samples were dehydrated in flowing 10% O_2 in He as the temperature was increased (5 K/min) from room temperature up to 773 K with a 2-h isothermal step at 423 K. They were held at 773 K for 8 h. We know that this treatment effects the formation of a Co_3O_4 phase which is about equivalent to the extent of overexchange (12). The catalysts were flushed with dried He for about 15 min at 473 K before the reaction was initiated. The effluent gas was sampled and analyzed by an on-line GC as described elsewhere (2).

Eight different hydrocarbons were tested as reducing agents: methane, propane, isobutane, *n*-pentane, neopentane, 3,3-dimethylpentane, 2,2,4-trimethylpentane, and 3,3-diethylpentane. In all experiments, the concentrations of NO and O_2 were kept constant at 0.2 and 10% in He, respectively. The hydrocarbon percentages were varied to maintain a constant flux of carbon, i.e., at 0.8% CH_4, 0.27% C_3H_8, 0.2% i-C_4H_8, 0.16% *n*-C_5H_{12}, 0.16% neo-C_5H_{12}, 0.11% C_7H_{16}, 0.1% i-C_8H_{18}, or 0.09% C_9H_{20}. The total flow rate was maintained constant at 75 cm^3 (NTP)/min and 250 mg of catalyst was used; contact time of an average molecule was $t = 0.2$ s.

The reactant gases (methane, 10% in He; propane, 1% in He; isobutane, 10% in He; NO or NO_2, 1% in He; O_2, 10% in He) were instrument grade obtained from Matheson; they were used as received. Neopentane was provided by Columbia Organic Company, nominal purity 98%. Ultrapure grade helium obtained from Linde was used as a diluent; it was passed through an oxy-absorbent Alltech trap before mixing. Pentane (purity 99+%), 3,3-dimethylpentane (purity 99%), and 2,2,4-trimethylpentane (purity 99+%) were obtained from Aldrich. The 3,3-diethylpentane was an API Standard

TABLE 1

Effect of Extent of Exchange on Activity and Selectivity over CoZSM-5-11-35 at Various Temperatures

Temp. (K)	Loading Co-ZSM-5[a] (%)	Conv. of NO into N_2 (%)	Conv. of CH_4 into CO_x and H_2O (%)	Selectivity[b]
573	35	4	2	1.0
	151	10	5	1.0
623	35	24	11	1.1
	151	38	20	0.95
673	35	45	25	0.9
	151	80	42	0.95
725	35	62	60	0.51
	151	85	88	0.48
775	35	55	90	0.31
	151	64	100	0.32

[a] Percent of base exchange capacity calculated as CO^{2+}.

[b] Selectivity here is defined as $\alpha = r_1/r_2 = \{[NO]_0 \times X_{NO}\}/\{[CH_4]_0 \times X_{CH4}\}$, where $[CH_4]_0$ and $[NO]_0$ are inlet concentrations of 4000 and 2000 ppm, respectively, and the X_i are the percent conversions of these compounds. Also 10% O_2 was present and the balance to 1 atm was He. The flow rate was 75 cc(NTP)/min over 0.25 g of catalyst.

Reference Material provided by Carnegie Mellon University, with a purity of 99.98%. The flows of these separate gases were fixed and held constant with Brooks flow regulators and pure He was used to maintain the total pressure at 1 atm.

RESULTS

(*1*) *Effect of metal loading on activity and selectivity.* The effect of Co^{2+}-ion loading on the selective catalytic reduction of NO into N_2 with methane as a reducing agent is shown in Table 1. With higher loadings, higher conversions of methane into CO_x and higher conversions of NO into N_2 were achieved under the same reaction conditions (similar behavior was found with isooctane as a reducing agent over CoZSM-5 zeolites (11)). The temperature of the maximum conversion rate was around 723 K and was identical for both CoZSM-5-11-35 and CoZSM-5-11-151.

The selectivity in the SCR of NO can be expressed as the ratio of the rates of conversion of NO to N_2 to the rates of conversion of CH_4 to CO_2 and H_2O. The selectivity at a given temperature was the same for the two different metal loadings (Table 1). In the temperature region between 573 and 673 K, the selectivities were nearly constant ($S \approx 1$), but they decreased sharply at higher temperatures to a value of $S = 0.32$ at 775 K. This behavior suggests that, especially in the low temperature region between 573 and 673 K, NO participates in the combustion of methane.

(*2*) *Comparison of various charge balancing cations in combustion and SCR.* The reactivities of CH_4 and i-C_4H_{10} in total combustion to CO_2 and H_2O and in SCR are compared in Fig. 1 for zeolites made from the same parent NaZSM-5-11-100 by introducing other cations to the extent of about 27 to 35% of the BEC. The sole exception was HZSM-5 where the Na was essentially completely replaced by H. Inspection reveals that generally i-C_4H_{10} was more reactive than CH_4 in both reactions. Light-off occurred below ~523 K with the former and above ~573 K with the latter. The curves for conversion of NO to N_2 also ranged about 100 K lower with i-C_4H_{10} than with CH_4. In all these experiments the inlet concentrations of the hydrocarbon were adjusted so that the same number of C atoms passed over the catalyst per unit time, i.e., as single-carbon molecules (CH_4) or as bundles of C atoms in molecules, e.g., i-C_4H_{10}. The most remarkable feature of these data is the great similarity in behavior of all catalysts including HZSM-5, with a few notable exceptions: (a) the CuZSM-5 was among the most active for combustion, but was completely inactive for SCR when CH_4 was the reducing agent, (b) LaZSM-5 was inactive for both reactions with CH_4, but active for both with i-C_4H_{10}; and (c) HZSM-5 was among the least active for combustion, but was among the most active for SCR when CH_4 was employed. Reliable data could not be obtained for SCR with i-butane over HZSM-5 because of rapid coking. This collection of data illustrates once again that the altervalent base-exchange cations are not essential for SCR and that the chemistry occurring is common for all of these catalysts. The reasons for these exceptions are not understood at present.

(*3*) *Conversion of NO using various reactants.* CoZSM-5-11-35 was used in this work. Figure 2A shows that *decomposition* of NO was not observed for reaction temperatures up to 973 K. This is in contrast to results from CuZSM-5 zeolites which are active for this reaction.

CH_4 did not effect the reduction of NO into N_2 up to a temperature of 773 K, where combustion first became observable (Fig. 2B). For temperatures higher than 773 K, however, methane reduced NO very efficiently, even in the absence of O_2. At 973 K almost 70% of NO was converted.

When O_2 was introduced into the system of methane and NO, the catalyst became active at temperatures above 573 K for SCR (Fig. 2A) and for converting methane into CO_2 (Fig. 2B). So the questions arise, "Why was conversion of NO not observed below 773 K in the absence of O_2, while significant conversions were observed in the presence of O_2?" and "What is the task of O_2 in the SCR of NO?" The results suggest that the conversion of NO into N_2, and the combustion of CH_4 are coupled (not parallel) reactions and that O_2 is needed not only to

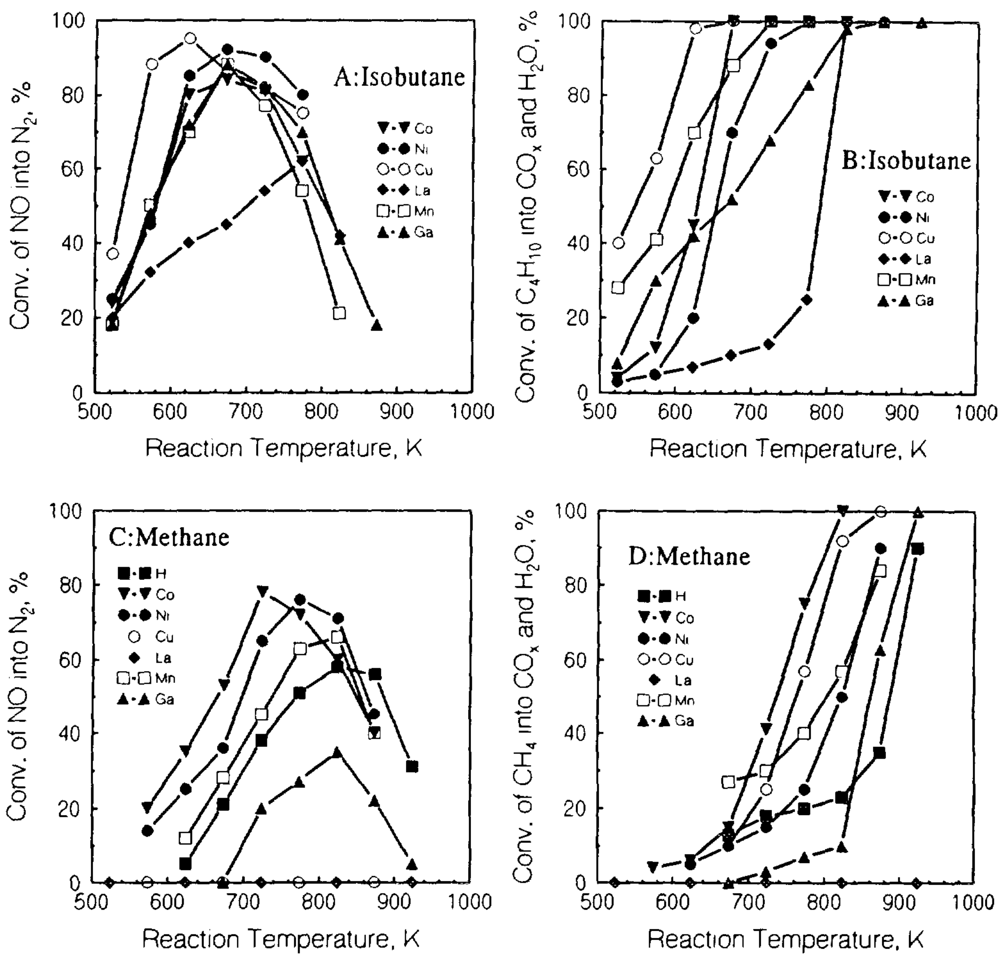

FIG. 1. Comparison of isobutane (A and B) and methane (C and D) as reducing agents in the SCR of NO in the presence of excess O_2 and in combustion to CO_2 and H_2O over various NaZSM-5 preparations partially exchanged (~30%) with various cations. The reactants were NO (0.2%), CH_4 (0.8%), or i-C_4H_{10} (0.2%) and O_2 (10%). The flow rate was 75 cm^3 (NTP)/min and 0.25 g of catalyst were used in each experiment. Thus, $F/W = 80.6 \times 10^{20}$ total molecules/gs, and for 0.2% NO, $F/W = 1.6 \times 10^{19}$ NO/gs. Rate = (F/W) (% conversion). Hence at 50% conversion to N_2 over CoZSM-5-11-35 (1.3 wt% Co), the TOF was 0.06 sec^{-1}.

keep the catalyst clean and stabilize altervalent cations in their highest valence states, but also to participate in the reaction mechanism.

In the presence of O_2, NO and NO_2 were about equally effective in their reactions with CH_4 (Fig. 2). In the absence of O_2, NO_2 burned CH_4 to CO_2 and H_2O, and at low conversions converted NO to N_2 with nearly the same efficiency as with O_2, but then leveled off near 20% (both to N_2 and to CO_x). Much higher conversions were not achieved to the highest temperatures tested (873 K). With NO_2, O_2 is not needed to convert NO to NO_2, an essential step in the mechanism (2, 3, 12). Perhaps reduction of NO_2 to NO occurred above 20% causing this leveling. Our facilities did not permit determination of the NO/NO_2 ratio in the exit stream.

When the NO concentration in the NO/i-C_4H_{10}/O_2 stream was varied holding the other components constant, complete conversion of NO into N_2 was obtained for NO/i-C_4H_{10} ratios < 2. This conversion decreased sharply as this ratio was increased further. A very similar result was obtained earlier (2) using an excessively exchanged CuZSM-5 preparation. The behavior was very similar when equivalent CH_4 was substituted for i-C_4H_{10}.

One further effect, contact time, is of interest in making comparisons of equivalent concentrations of CH_4 and i-C_4H_{10} in the reaction stream. When CH_4 was used as a reducing agent, almost complete conversion to N_2 was maintained at 723 K as the GHSV was varied from 4,600 to 20,000 h^{-1}. In the same experiment, combustion of CH_4 into CO_2 and H_2O dropped by more than 50%. Thus, the selectivity increased by over 100% in this range. At SVH = 96,000 h^{-1} both conversions decreased, again effecting an increase in selectivity. These experiments suggest that NO_x reacts faster than O_2, although the latter is

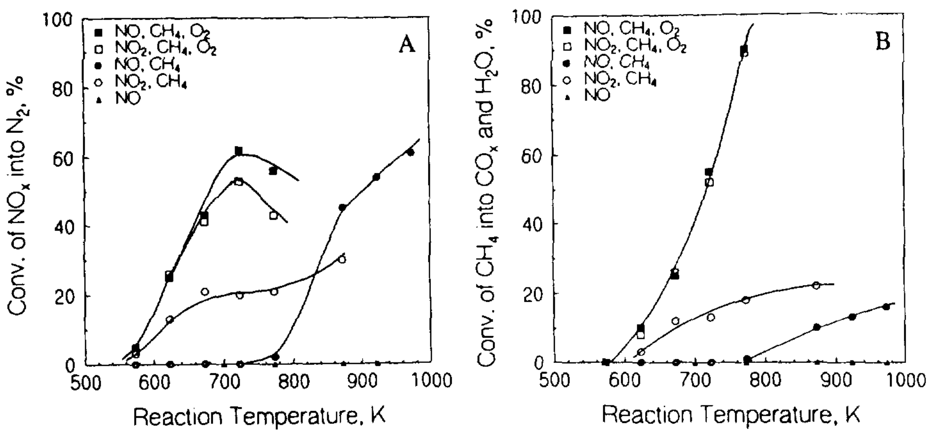

FIG. 2. (A) Reaction characteristics in the SCR and (B) in the combustion of CH_4, using different reaction mixtures over CoZSM-5-11-35. The reaction conditions were flow rate = 75 cm^3 (NTP)/min over 0.25 g catalyst. The feed stream concentrations were NO (0.2%), NO_2 (0.2%), CH_4 (0.4%), and O_2 (10%) when used. For calculation of rates, see legend for Fig. 1.

essential for high activity. With i-C_4H_{10}, complete conversion of NO into N_2 and CH_4 into CO_2 and H_2O could be achieved at GHSV = 92,000 h^{-1}.

(4) *Activity comparisons of various hydrocarbons over catalysts CoZSM-5-11-35 and HZSM-5 at various temperatures.* Comparisons are made in Table 2 and Fig. 3, respectively. Although the relative effectiveness of various hydrocarbons is readily apparent, it is also true that activity differences are small relative to many other kinetic data. Data for HZSM-5 shown in Fig. 3 are plotted as the rate of conversion to N_2 vs the rate of combustion. As found previously for CoZSM-5 and NiZSM-5, the data for all of the hydrocarbons tested could be correlated by a single curve, the slope of which at any point is a measure of the selectivity for N_2 formation. It is high at low conversions (low temperatures) and decreases as the conversion (temperature) is raised.

(5) *Molecular sieve effects.* Figure 4 was taken from our previous paper (11) with new data for neononane added. The first evidence of the effects of exclusion of hydrocarbon from the internal pore system appeared. Neononane (3,3-diethylpentane) has been shown experimentally (10) to be excluded from the zeolite in the temperature range of interest here. It is now evident that most of the N_2 formation must occur in the intrazeolitic channels: any external homogeneous component must be small.

A comparison of the reactions of CH_4, i-C_4H_{10}, and neo-C_9H_{20} over CoZSM-5-11-98 and CoFer-8.5-78 is found in Fig. 5. The general behavior for each reactant hydrocarbon was about as expected: the conversion of NO to N_2 passed through maxima as the combustion increased and approached completion. However, note that over CoZSM-5 (Figs. 5A and 5B), isobutane as usual was the most reactive for both reactions, followed by CH_4 and neo-C_9H_{20}. Interestingly, the latter was slightly easier to burn than CH_4, but was not very efficient for NO_x reduction. Over CoFer the order was different. Here CH_4 reacted fastest in SCR, in agreement with Li and Armor (13), whereas i-C_4H_{10} was invariably superior with CoZSM-5. Note also that for combustion, i-C_4H_{10} was no longer the most facile hydrocarbon. CH_4 burned faster. These differences may be attributed to molecular sieving effects. Both ZSM-5 and Ferrierite have channels limited by 10-membered rings. With the former these channels are interconnected by 10-membered rings, whereas in the latter the cross connections are made with 8-membered rings. A molecule the size of isobutane completely fills the 10-ring channels; another molecule cannot pass these larger hydrocarbon molecules (or fragments) directly. With the ZSM-5, the other reactant molecules may detour via an adjacent channel in the three-dimensional pore system. This is less easy with the unidimensional Ferrierite, where such molecules must diffuse through the 8-membered rings.

Results of blank experiments made in the same system without any zeolite present are given in Table 3. Interestingly, light-off for the *homogeneous* combustion was observed with i-C_4H_{10} and neononane at about 773 K, i.e., at the temperature at which the catalyzed reaction became 100%. No SCR was observed in these experiments at any temperature tested (up to 973 K).

DISCUSSION

At the start of this work molecular sieve effects were expected. The literature (8, 9) suggested that molecules as large as or larger than neopentane should be excluded from the pore systems of the MFI zeolites. In fact, no evidence of such constraints on the rates of either combustion or SCR of NO were observed until neononane was

TABLE 2A

Reactivity of Various Hydrocarbons in SCR over CoZSM-5-11-35[a]

Feed Gas[a]		% of Entering NO Converted to N_2 at Various Temp.						
Hydrocarbon	Conc. %	573 K	623 K	673 K	723 K	773 K	823 K	873 K
CH_4	0.8	19	35	42	78	60	N/A	N/A
C_3H_8	0.27	12	55	62	58	56	N/A	N/A
i-C_4H_{10}	0.20	45	80	84	81	62	N/A	N/A
n-C_5H_{12}	0.16	38	60	68	73	65	N/A	N/A
neo-C_5H_{12}	0.16	23	44	60	68	74	73	23
3,3-DMP[b]	0.11	22	33	50	58	55	N/A	N/A
2,2,4-TMP[b]	0.10	30	43	56	66	70	71	23
3,3-DEP[b]	0.09	2	5	10	12	14	18	5

[a] Reaction conditions: HC (x%), NO (0.2%), O_2 (10%), 75 cc/min, 0.25 g cat.

[b] 3,3-DMP = 3,3-dimethylpentane; 2,2,4-TMP = 2,2,4-trimethylpentane; 3,3-DEP = 3,3-diethylpentane (neononane).

TABLE 2B

Reactivity of Various Hydrocarbons in Combustion over CoZSM-5-11-35[a]

Feed Gas[a]		% of Entering Hydrocarbon Converted to CO_2 + H_2O at Various Temperatures						
Hydrocarbon	Conc. %	573 K	623 K	673 K	723 K	773 K	823 K	873 K
CH_4	0.8	4	6	15	41	75	N/A	N/A
C_3H_8	0.27	3	12	34	100	100	N/A	N/A
i-C_4H_{10}	0.20	12	45	100	100	100	N/A	N/A
n-C_5H_{12}	0.16	8	28	40	60	100	N/A	N/A
neo-C_5H_{12}	0.16	3	14	27	50	81	100	100
3,3-DMP[b]	0.11	5	7	22	30	78	N/A	N/A
2,2,4-TMP[b]	0.10	3	7	20	49	78	100	100
3,3-DEP[b]	0.09	10	12	25	48	100	100	100

[a] Reaction conditions: HC (x%), NO (0.2%), O_2 (10%), 75 cc/min, 0.25 g cat.

[b] 3,3-DMP = 3,3-dimethylpentane; 2,2,4-TMP = 2,2,4-trimethylpentane; 3,3-DEP = 3,3-diethylpentane (neononane).

studied, and here a peculiar result was obtained. As shown in Table 2A, this hydrocarbon was relatively inactive for SCR compared with the remainder of the data, but as Table 2B reveals, it was among the most active for combustion to CO_2 and H_2O. Take at face value these data suggest that the internal surface of the zeolite is required for SCR, but is not of critical importance for combustion of these hydrocarbons to CO_2 and H_2O. A possible explanation for these observations might be that the *larger* hydrocarbons react only on the external surfaces of the crystals or near the pore mouths. Smaller molecules such as NO and O_2, on the other hand, may enter the zeolite crystals and react on the cation sites to form NO_2, which then diffuses out of the crystal and reacts with hydrocarbons, initiating the combustion process. Of course, the n-paraffins, CH_4, and even isobutane can pass through the 10-membered rings and enter the zeolite channels, but the reaction rates should decrease markedly with chain branching. Neononane would be expected to be particularly effective as a pore blocker thus slowing, but not eliminating, the SCR reaction (see Figs. 4 and 5, where three different catalysts were employed).

It is of interest in this connection to consider the "Constraint Index" used by Haag and co-workers (14) to describe the effect of chain branching on cracking rates. The CI may be described as the ratio of rate constants for cracking of n-hexane and 3-methylpentane. For 12-, 10-, and 8-ring systems, the CI was found to range between 0.4 and 0.6, 3.4 and 8.3, and 40 and 100, respectively. From these results one can see diffusional constraints already appearing with these simple molecules with 10-ring systems; i.e., the faster reacting branched chain molecules having the readily attacked tertiary hydrogens now crack more slowly than the straight chain

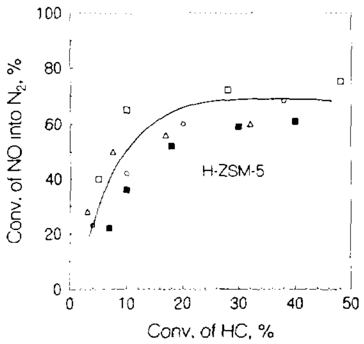

FIG. 3. Selectivity plot of conversions of NO to N_2 vs hydrocarbon into CO_2 and H_2O over HZSM-5 for 0.8% CH_4 (■), 0.27% propane (□), 0.16% *n*-pentane (△), and 0.11% 3,3-dimethylpentane (○); 0.2% NO and 10% O_2 were the oxidizing agents. The flow rate was 75 cm^3 (NTP)/min and 0.25 g of catalyst were used.

hexane (which has only secondary and primary hydrogens). The reverse is true in our case, where we found that isobutane reacted faster than any of the other molecules tested, including *n*-C_5H_{12}. This demonstrates once again that the combustion of these molecules is occurring external to the zeolite pore system.

Combustion reactions of hydrocarbons have been studied intensively (15). Catalyzed or not, these are free radical processes. As such they may be initiated or terminated at the surface of a solid, but many times enter into chain processes which occur in the gas phase above the surface. Typical of this are the methane coupling reactions (16). Here $CH_3\cdot$ are formed on the surface of various oxides; these radicals desorb and couple in the gas phase, forming C_2H_6 and other products. Cant *et al.* (17) have confirmed these ideas by their observation of a first order isotope effect on substitution of CD_4 for CH_4 as a reactant in CH_4 coupling, indicating that rupture of a C–H bond is critical in the rate determining step. Interestingly they find a similar value of $k_H/k_D = 2.4$ for the SCR over CoZSM-5, using these two methanes as the reductant (18). This may be taken as prima facie evidence that this reaction proceeds by a free radical mechanism and that breaking of a C–H vs a C–D bond is involved in the rate-determining step. This may help to explain why we see so little difference in the behavior of the various hydrocarbons studied, i.e., the lack of evidence for the expected molecular sieve effect.

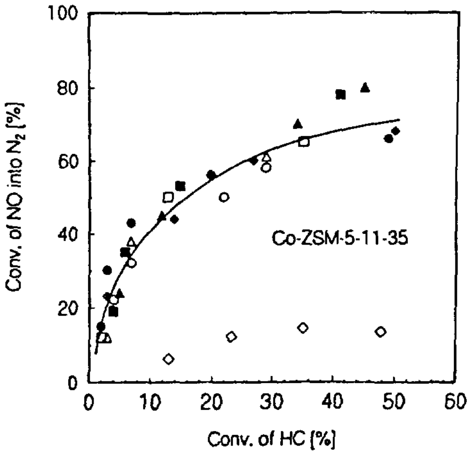

FIG. 4. Selectivity plot taken from Ref. (11) with new data for 0.09% of 3,3-diethylpentane (neononane) added (◇). The remaining hydrocarbons correlated on the single curve, above, i.e., 0.8% CH_4 (■), 0.27% propane (□), 0.2% isobutane (▲), 0.16% *n*-pentane (△), 0.16% neopentane (◆), 0.11% 3,3-dimethylpentane (○), and 0.10% 2,2,4-trimethylpentane (●). The oxidants were 0.2% NO and 10% O_2. The flow rate was 75 cm^3 (NTP)/min and 0.25 g of CoZSM-5-11-35 was used.

The results of the blank experiments in Table 3 show that homogeneous combustion lights off at temperatures only a little higher than 773 K. Interestingly, however, no conversion to N_2 occurred without a catalyst at temperatures as high as 973 K. This indicates that an essential intermediate must be formed on the catalyst, but not in the gas phase. Wojciechowski and Laidler (19) showed many years ago that NO (a stable free radical, as is NO_2) can both initiate and inhibit the homogeneous combustion and partial oxidation by reactions such as

$$CH_4 + \cdot NO \rightleftarrows CH_3\cdot + HNO,$$
$$CH_3\cdot + CH_4 \rightarrow C_2H_6 + \cdot H$$
$$H\cdot + CH_4 \rightarrow CH_3\cdot + H_2, \quad \text{and}$$
$$H\cdot + \cdot NO \rightarrow HNO.$$

It is curious, therefore, that we see no evidence of methane coupling in our products. Perhaps NO_2 functions to drive these reactions to total oxidation.

Our experiments were carried out with a constant flux of carbon passing over the catalyst, i.e., the concentration of CH_4 was four times higher than that of the *i*-butane and eight times higher than *i*-octane. Thus, a single-carbon molecule, CH_4, could be compared on an equivalent basis with bundles of carbon atoms in the larger molecules. Under these conditions, as illustrated in Figs. 3 and 4, all of the data except for neononane (and CH_4 over CuZSM-5) could be fitted onto a single curve. We had anticipated that small molecules like CH_4 would freely enter the pore system and utilize the whole of the zeolite channels, whereas the larger molecules would either be excluded or at least their mobilities very much slowed by diffusion at the lower concentrations used to keep the carbon flux constant. The results suggested to us that an important part of the process was occurring at the external surfaces of the crystals or at the pore mouths. Possibly the larger molecules may be being broken up so that smaller

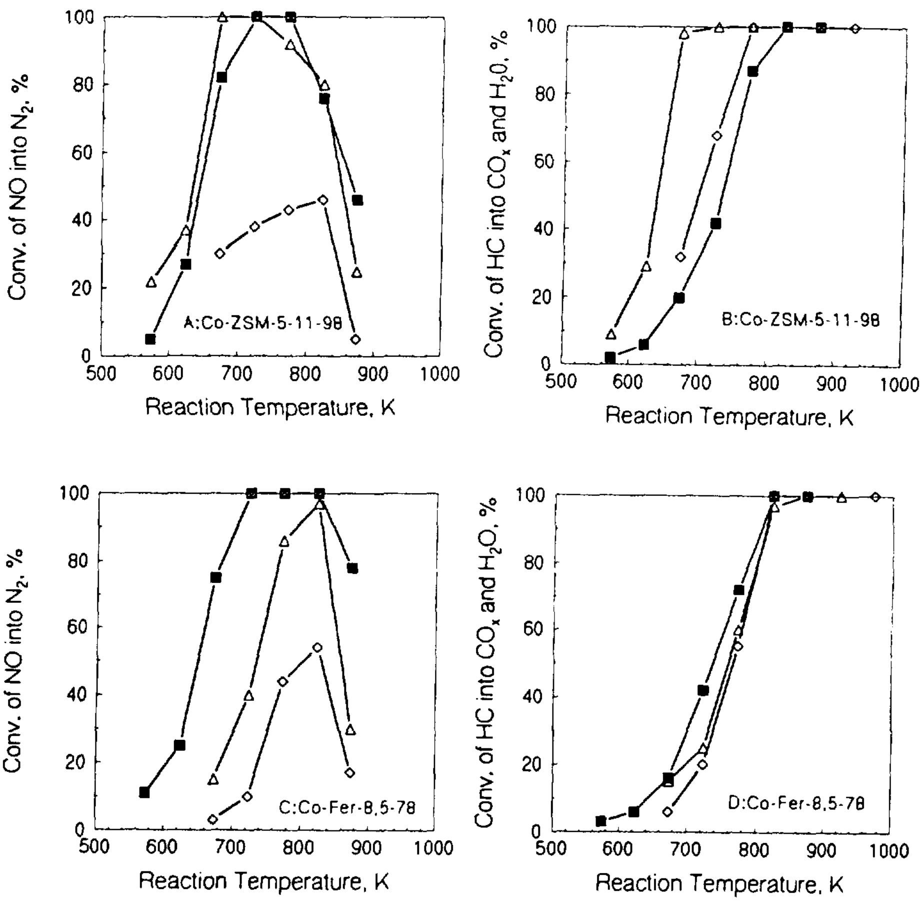

FIG. 5. Comparison of CoZSM-5-11-98 (A & B) and Fer-8.5-78 (C & D) in the SCR and combustion reactions at various temperatures using different reducing agents: 0.8% CH_4 (■), 0.2% i-C_4H_{10} (△), and 0.09% neononane (◇). 0.2% NO and 10% O_2 were the oxidants.

pieces can then diffuse inward. Alternatively, if free radicals were formed in the decomposition process, the reaction thus initiated could then become homogeneous, i.e., boil off into the gas phase. The smaller molecules, NO, O_2, and NO_2, can of course readily enter the pore system, where NO can be converted to NO_2 at the redox centers and reappear in the gas phase. As pointed out earlier (3, 4), and as shown again in this work, NO_2 is a more effective oxidizing agent than NO, although not as effective as a mixture of either NO or NO_2 with O_2. Possibly the SCR can be best characterized as a wall-initiated selective combustion. Perhaps the shape selectivity makes possible the efficient formation of NO_2 which may be an essential intermediate.

At present, we have no indisputable evidence to support the above speculation except chemical logic. Consider the following: a typical reaction mixture such as used in the present work can be stored in a vessel at room temperature in the dark for many months without any sign of reaction. Analyses of the gas before and after this storage period are essentially identical. When the temperature is raised, however, the mixture will undergo combustion homogeneously when the so-called "light-off" temperature is reached. It may be assumed, therefore, that the catalysts employed in the present work simply lower this critical temperature and that a wall-catalyzed combustion reaction ensues. Three oxidizing agents are present: NO, NO_2, and O_2. Although strong evidence does not exist, this speculative mechanism is plausible and should be investigated further. Should it prove correct, new avenues for catalyst development would ensue. Thus, it might be better to look at SCR as a competitive co-oxidation of the hydrocarbon by NO_x and O_2, rather than as a selective reduction of NO in the presence of O_2. If nothing more, it provides a different perspective of the reaction chemistry than do earlier ideas.

The results presented in Figs. 1C and 1D suggest that the H-zeolite is more selective than CoZSM-5, and it may be. Figures 3 and 4 seem to support this view. (The slope of these figures measures the selectivity.) Note then that the selectivity decreases as the conversion increases and

TABLE 3

Results of Blank Experiments at Various Temperatures[a]

Temp. (K)	Conv. of No. into N_2 %			Conv. of HC into CO_x and H_2O		
	CH_4	i-C_4H_{10}	neo-C_9H_{20}	CH_4	i-C_4H_{10}	neo-C_9H_{20}
973	0	0	0	100	100	100
873	0	0	0	15	100	88
823	0	0	0	0	68	34
773	0	0	0	0	2	1
723	0	0	0	0	0	0

[a] 0.8% CH_4, 0.2% i-C_4H_{10} or 0.09% 3,3-diethylpentane + 0.2% NO + 10% O_2 with balance to 1 atm He was fed at 75 cc/min. No conversion to N_2 was observed at any temperature, but light-off of homogeneous combustion is seen at temperatures as low as 773 K.

that initially the selectivity is very high in all cases. These two catalyst systems (HZSM-5 and CoZSM-5) are not really comparable: the former has an H^+/AlO_2^- ratio close to unity, whereas the CoZSM-5 has a CO^{2+}/AlO_2^- ratio of about 0.175. Catalysts with CO^{2+}/AlO_2^- ratios of 0.5 or greater are much more active giving complete conversion over a range of temperatures between 673 and 773 K (11). From these and other reasons, it would be premature to conclude that HZSM-5 is a superior catalyst. It certainly would be expected to be less durable to hydrothermal treatment and therefore not very useful as a catalyst for NO_x removed from combustion streams (20).

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