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The Rate-Determining Step in the Selective Reduction of Nitric Oxide by Methane over a Co–ZSM5 Catalyst in the Presence of Oxygen

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The relative reaction rates of CH_4 and CD_4 with NO in the presence of excess oxygen over a Co-ZSM5 catalyst have been determined. The rate ratio, CH_4 consumption versus CD_4 consumption, is nearly 2.4 when using a dry feed at 375°C. Experiments at 431°C using a feed containing 1.6% H_2O show a rate ratio of 2.05. These values are close to those expected for a primary kinetic isotope effect at the respective temperatures, and it is therefore concluded that the rate-determining step is the breaking of a carbon hydrogen bond. The kinetic isotope effect is slightly less for the selective reaction with NO than for the concurrent direct oxidation of methane by oxygen. The two reactions have very similar kinetic orders in methane, suggesting that a common intermediate is involved in the two pathways. Hydrogen–deuterium exchange between CD_4 and H_2O to make CH_3D is negligible under reaction conditions. Similarly, mixed feeds of CH_4 and CD_4 show very little exchange. One interpretation consistent with the results is that the rate-determining step involves detachment of hydrogen from methane by adsorbed nitrogen dioxide to form a methyl species which reacts further with a nitrogen oxide in one pathway but with oxygen in the other. © 1995 Academic Press, Inc.

INTRODUCTION

The reports of Held *et al.* (1) and Iwamoto *et al.* (2, 3) showing that hydrocarbons can selectively reduce nitric oxide in the presence of oxygen have stimulated a great deal of work on this reaction with a view to NO_x control for mobile and other sources. It would appear that Cu–ZSM5 is the most effective catalyst, and its behaviour has been investigated in considerable detail for a number of hydrocarbons. These include ethylene (4), propylene (4–8), propane (8, 9), and isobutane (10, 11). As yet no clear picture of the reaction mechanism operating in these reductions has emerged. However, there is some agreement that the rate-limiting step is not nitric oxide decomposition or a direct reaction between the hydrocarbon and a nitrogen oxide. One view is that the reaction proceeds via a partially reacted derivative of the hydrocarbon, variously suggested as a purely carbonaceous residue (6), or a partial oxidation product containing oxygen (9). There is also evidence to suggest that nitrogen dioxide rather than nitric oxide is the nitrogen-containing species involved in the subsequent steps (9, 10).

While Cu–ZSM5 is a very effective catalyst with C_{2+} hydrocarbons, it has little activity when methane is used. By contrast, recent work by Li, Armor, and co-workers (12–14) shows that Co–ZSM5 exhibits high performance with this hydrocarbon. Oxygen is required for the selective reaction which involves CH_4, NO, and O_2 in a 1 : 2 : 1 ratio to give equimolar amounts of CO_2 and N_2. There is some additional combustion of methane, the extent of which depends on reactant concentrations, temperature, and catalyst formulation (12, 13).

The primary aim of the present work was to determine if CH_4 and CD_4 react at different rates over Co–ZSM5. A large difference in rate (a factor of 2 or more) would demonstrate the existence of a primary deuterium kinetic isotope effect (15) and provide *prima facie* evidence that the rate-determining step involves the breaking of a carbon–hydrogen bond in methane. Such knowledge may be of assistance for the development of more efficient catalysts for this simplest example of a most complex class of reactions.

EXPERIMENTAL

The catalytic measurements were carried out using a single-pass flow system. The gas mixture was made by blending four separate streams comprising helium alone, 1% CH_4/He, 1% NO/He, and 5% (or 10%) O_2/He supplied by separate electronic flow controllers (Brooks Model 5850E). A matching CD_4/He mixture was prepared by pressurising a 0.5-litre cylinder containing a known pressure of CD_4 (MSD Isotopes > 99% D) with helium. This was supplied either in place of CH_4/He, via a three-way valve upstream of the flow controller, or in addition to

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CH_4/He in place of the make-up helium carrier. Separate analyses showed that the CH_4 and CD_4 concentrations were matched to within 5%.

The standard mixture used in most experiments contained 1040 ppm methane, 1640 ppm nitric oxide, and 2.5% oxygen at a total flow rate of 100 cm^3/min (NTP). This was passed downflow over a sample (usually 0.4 g) of Co–ZSM5 contained in a 6-mm-i.d. Pyrex tube giving GHSV of 7500 h^{-1} at STP. The section of tube containing the catalyst was fitted inside an aluminum block located at the centre of a tube furnace. The temperature was controlled from a thermocouple located in this block. A second thermocouple with its tip immediately below the sample bed was used to monitor the catalyst temperature. The Co–ZSM5 catalyst (Si/Al ratio of 11.2, 4.2 wt% Co) was supplied as a fine powder by Dr. J. Armor of Air Products and Chemicals. The cobalt content is equivalent to a Co/Al atom ratio of 0.55, implying an exchange level which is 110% of theoretical. Further details of its preparation and properties can be found elsewhere (12–14). For the present purposes it was pressed at 200 MPa for 1 min. The resultant discs were crushed and sieved to obtain a 300- to 600-μm particle fraction. The test samples were dried under a stream of helium at 110°C and heated to 500°C (at 5 K/min) in a 10% O_2/He stream. After a minimum of 1 h at 500°C they were cooled to reaction temperature under helium alone. A pressure transducer located upstream of the bed showed that the back pressure exerted by the catalyst bed under reaction conditions was less than 7% of atmospheric pressure under all conditions.

The exit stream from the reactor was passed to the gas sampling valve of a Shimadzu GC4A gas chromatograph fitted with a 1.8-m CTR-1 concentric molecular sieve and Porapak Q column (Alltech Associates) operated at 50°C. This provided baseline separation of N_2, O_2, methane, and CO_2 in less than 8 min with a detectability limit of about 10 ppm using a thermal conductivity detector. The system was capable of analysing for CO and N_2O with similar detectability limits but none were observed. Analysis for NO was also possible but it was accurate only in the absence of O_2. The product stream leaving the gas sampling valve was diluted with nitrogen to a known extent and passed to a chemiluminescent NO/NO_2 analyser (Monitor Labs Model 9841). This provided separate readouts of NO alone and NO plus NO_2 combined. The difference between NO plus NO_2 in bypass and product streams gave a good check on NO conversions calculated from the gas chromatographic analyses for N_2. Most experiments were carried out with NO and CH_4 conversions <35%. Rates were then calculated from the product analyses using the differential reactor approximation, i.e.,

$$\text{rate (mol g}^{-1}\text{s}^{-1}) = F \cdot y_i / W,$$

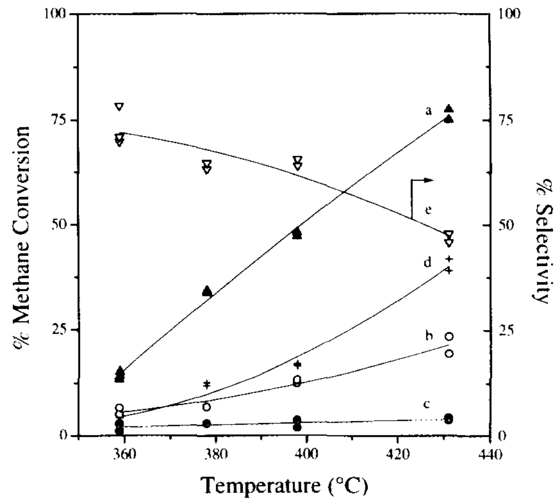


FIG. 1. Methane conversion and selectivity as a function of temperature for reaction over 0.4 g Co–ZSM5 under standard conditions: (a) CH_4/NO/O_2; (b) CH_4/O_2; (c) CH_4/NO; (d) reaction [2] alone when using CH_4/NO/O_2 mixtures; (e) selectivity of the CH_4/NO/O_2 reaction.

where F is the total molar flow rate in mol/s, y_i is the molar fraction of product (CO_2 or N_2) expressed in ppm × 10^{-6}, and W is the weight of the catalyst in grams.

In some experiments with CD_4, the line between reactor and gas chromatograph was sampled into a quadrupole mass spectrometer (Vacuum Generators Model SX300). This stream was trapped with dry ice to remove water and deuterated water and to enable accurate determination of the CHD_3 and CD_4 concentrations using signals at m/e = 19 and 20, respectively.

RESULTS

Li and Armor (12–14) have already given details of the CH_4/NO/O_2 reaction over Co–ZSM5 under conditions of practical interest (moderate to high conversions). Rate comparisons, as between CH_4 and CD_4 here, are best made at lower conversions, and initial experiments were directed at establishing reaction characteristics (activation energies, reaction orders, etc.) under such conditions. Figure 1 shows methane conversions, calculated as [ppm CO_2/(ppm CO_2 + ppm CH_4)]$_{out}$, as a function of temperature for the CH_4/NO/O_2 reaction in comparison with those of CH_4/NO and CH_4/O_2. It is apparent that the ternary mixture (Fig. 1a) reacts much faster than either binary one (Figs. 1b and 1c respectively). As shown previously (12–14), the ternary reaction is largely represented by

$$CH_4 + 2NO + O_2 \rightarrow CO_2 + N_2 + 2H_2O. \quad [1]$$

However, if this were the only reaction then CH_4 and NO

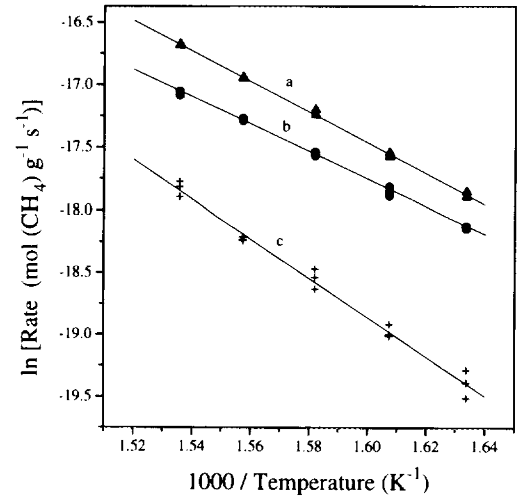


FIG. 2. Arrhenius plots for the reaction of $CH_4/NO/O_2$ mixtures over 0.4 g Co–ZSM5 under standard conditions: (a) CO_2 production; (b) N_2 production (reaction [1]); (c) difference between CO_2 production and N_2 production (reaction [2]).

would react in a 1 : 2 ratio and produce equimolar amounts of CO_2 and N_2. In practice there is some excess CO_2 production due to concurrent methane combustion:

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O. \qquad [2]$$

The extent of reaction [1] is given directly by the measured N_2 production, while that of reaction [2] is simply the difference between CO_2 and N_2 production. It is interesting to note that at temperatures above 370°C the rate of reaction [2] when NO is present, Fig. 1d, is faster than when CH_4/O_2 mixtures are tested alone, Fig. 1b.

The selectivity of methane utilisation when using $CH_4/NO/O_2$ (i.e., reaction [1] as a percentage of reactions [1] and [2]) is defined by

$$S = \frac{[N_2] \times 100}{[CO_2]}$$

and has values of 45 to 75% as shown in Fig. 1e. As noted earlier there was always good agreement between the overall conversion of NO_x (measured as the loss of NO + NO_2 by the chemiluminescent monitor) and that calculated from N_2 production as determined by gas chromatography. The extent of conversion of NO to NO_2, which took place largely on the catalyst, varied with temperature but was always some distance from equilibrium.

Activation energies were determined from additional tests under near differential conditions (conversions less than 25%) over the temperature range 340 to 380°C. Arrhenius plots for CO_2 production (i.e., the sum of [1] and [2]), N_2 production (reaction [1]), and the difference between CO_2 and N_2 production (reaction [2]) are given in Fig. 2. As shown in Table 1, the apparent activation energy for reaction [2] is greater than that for the overall reaction, and for the selective one [1], which explains why selectivity falls with increase in temperature.

TABLE 1

Kinetic Parameters for the $CH_4/NO/O_2$ Reaction over Co–ZSM5[a]

	Overall reaction[b]	Reaction [1][c]	Reaction [2][d]
E_a (kJ/mol)	102 ± 1	91 ± 1	132 ± 4
Order in CH_4	0.70 ± 0.02	0.68 ± 0.02	0.75 ± 0.08
Order in NO	−0.06 ± 0.03	0.11 ± 0.03	−0.47 ± 0.08
Order in O_2	0.27 ± 0.01	0.18 ± 0.01	0.52 ± 0.05

[a] Measured under conditions shown in Figs. 2, 3, 4, and 5; error estimates are one standard deviation.

[b] Total CO_2 production.

[c] N_2 production.

[d] Difference between CO_2 and N_2 production.

Figures 3, 4, and 5 show the dependencies of the various reaction rates on methane, nitric oxide, and oxygen concentrations at 360°C. The corresponding kinetic orders, evaluated from log–log plots, are included in Table 1. The apparent orders in methane are about 0.7 for both reactions [1] and [2]. It is possible that these values are slightly affected by inhibition due to product water at the relatively low temperature used (14). However similar results were obtained in tests at 430°C with 1.8% water in the feed. The selective reaction [1] exhibits a slightly positive (~0.1) order in nitric oxide. It appears that this

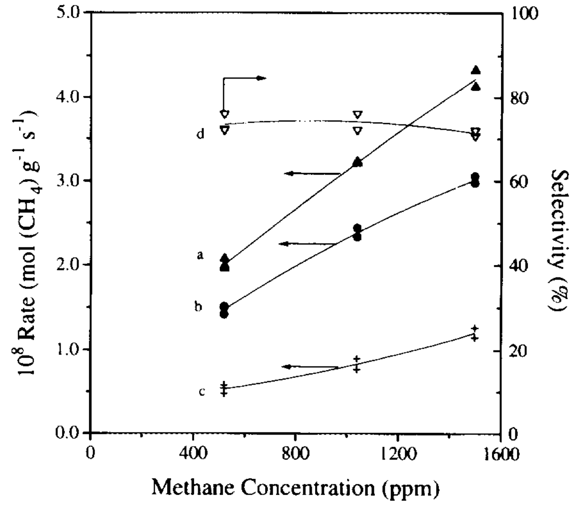


FIG. 3. Dependence of reaction rate and selectivity on methane concentration for CH_4/NO (1640 ppm)/O_2 (2.5%) mixtures over 0.4 g Co–ZSM5 at 360°C; (a) CO_2 production; (b) N_2 production (reaction [1]); (c) difference between CO_2 and N_2 production (reaction [2]); (d) selectivity.

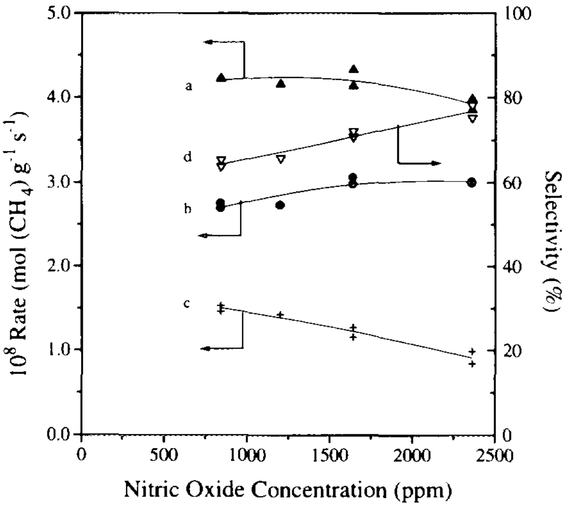


FIG. 4. Dependence of reaction rate and selectivity on nitric oxide concentration for CH_4(1040 ppm)/NO/O_2 (2.5%) mixtures over 0.4 g Co-ZSM5 at 360°C: (a) CO_2 production; (b) N_2 production (reaction [1]); (c) difference between CO_2 and N_2 production (reaction [2]); (d) selectivity.

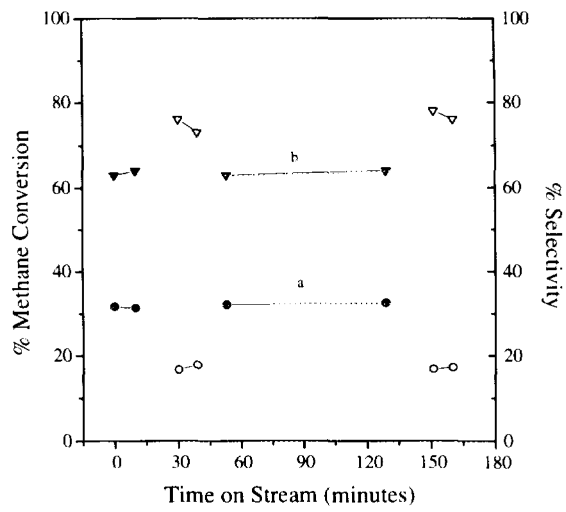


FIG. 6. Methane conversion and selectivity for the reaction of methane/NO (1640 ppm)/O_2 (2.5%) mixtures over 0.4 g Co-ZSM5 with total flowrate of 100 cm^3/min: (a) conversion (●) CH_4, (○) CD_4; (b) selectivity (▼) CH_4, (▽) CD_4.

order is temperature dependent since Li *et al.* (14) reported a value of 0.42 for the reaction at 400°C and additional measurements made as part of this work have given a value of 0.50 in tests at 450°C. The nonselective methane combustion reaction [2] has a higher order in oxygen than the selective one and a distinctly negative order in NO. This indicates that competition between the two oxidants has some influence on the distribution between the pathways.

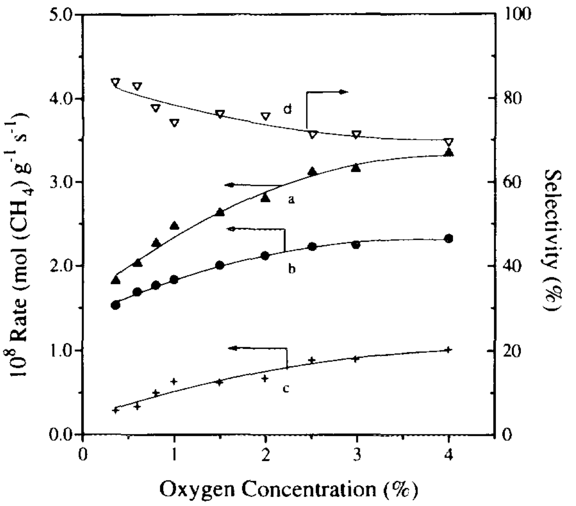


FIG. 5. Dependence of reaction rate and selectivity on oxygen concentration for CH_4(1000 ppm)/NO (1640 ppm)/O_2 mixtures over 0.4 g Co-ZSM5 at 360°C: (a) CO_2 production; (b) N_2 production (reaction [1]); (c) difference between CO_2 and N_2 production (reaction [2]); (d) selectivity.

On the basis of the above information the kinetic isotope effect determinations were carried out at 375°C with methane, NO, and O_2 concentrations of 1040 ppm, 1640 ppm, and 2.5%, respectively. With the standard flow rate this gave a CH_4 conversion of approximately 30% which was the best compromise in terms of the accuracy of product analyses versus the need to rely on the differential reactor approximation to calculate rates. Figure 6 shows the results of a sequence of experiments in which CH_4 and CD_4 were fed alternately over an extended period. It is apparent that the conversion with CD_4 is about half that with CH_4 while the selectivity is slightly higher. Additional experiments were carried out with different flow rates to facilitate comparisons at near identical conversions. Table 2 summarises the calculated rates for all experiments with values for the overall reaction, and reactions [1] and [2], shown separately.

To a first approximation the deuterium kinetic isotope effect can be estimated directly as the rate ratio at constant conversion. As shown in the top two rows of Table 3A the values for the overall reaction are 2.37 and 2.40. The values for the selective reaction [1] are slightly lower, while those for methane combustion are rather higher. One can also attempt to estimate the isotope effect from the constant flow rate (100 cm^3/min) experiments by calculating a rate constant ratio using the kinetic expression

$$\text{rate} = k\,[CH_4]^x[NO]^y[O_2]^z,$$

taking the kinetic orders in Table 1 as the values for x,

TABLE 2

Conversions and Rates for the $CH_4/NO/O_2$ and $CD_4/NO/O_2$ Reactions over 0.4 g Co–ZSM5[a] at 375°C

Methane used	Flow rate (cm^3/min)	Conversions (%)		10^8 rates (mol (methane) g^{-1} s^{-1})[b]		
		Methane	NO	Overall[c]	Reaction [1][d]	Reaction [2][e]
(A) 375°C dry feed						
CH_4	100	32.5	26.5	5.83	3.70	2.12
CD_4	100	17.5	15.5	3.01	2.23	0.78
CH_4	186	20.5	18	7.23	4.77	2.47
CD_4	49	30	23	2.49	1.69	0.80
(B) 431°C 1.6% H_2O added						
CH_4	100	31.5	16.5	6.48	2.63	3.83
CD_4	100	16	11	3.24	1.71	1.53
CH_4	53.4	29.5	17	3.16	1.39	1.77

[a] With standard mixture (i.e., methane 1040 ppm, NO 1640 ppm, 2.5% oxygen).

[b] Averages of at least two analyses.

[c,d,e] As per footnotes *b*, *c*, and *d* to Table 1.

y, and *z* and using the average of inlet and outlet concentrations. As shown in Table 3A, the values so obtained are rather lower than those calculated from the variable flow rate experiments. This difference is attributable to the known effects of water inhibition (14), which will depress the rate more in the CH_4 case because the conversion is higher than when using CD_4.

The constant conversion calculations do assume that D_2O inhibits to the same extent as H_2O. This latter assumption was avoided by repeating the determinations with feeds containing an excess of H_2O (1.6%). It was necessary to carry out these experiments at higher temperature (431°C rather than 375°C) because of the inhibition effect. The rate data obtained are shown in Table 2B and the kinetic isotope values in Table 3B. The latter are similar to, but slightly less than, those for the reaction in the absence of water because of the higher temperature used (see below). The constant conversion and constant flow rate estimates are reasonably close since, unlike the latter situation in the dry feed case, the inhibition by water is constant throughout.

The data in Tables 2 and 3 strongly indicate that the rate-determining step in the methane/NO/O_2 reaction over Co–ZSM5 is the breaking of a CH bond. The expected values for a primary kinetic isotope effect, calculated on the basis of the zero point energy difference between the symmetric stretching frequencies of CH_4 (2917 cm^{-1}) and CD_4 (2109 cm^{-1}) are 2.44 at 375°C and 2.27 at 431°C. These values are close to the experimental ones for the reaction in the absence and presence of water at those temperatures. The experimental values are slightly higher than that found in a study of the reaction between methane

TABLE 3

Deuterium Kinetic Isotope Effects for the Methane/NO/O_2 Reaction over Co–ZSM5 with Dry and Wet Feeds

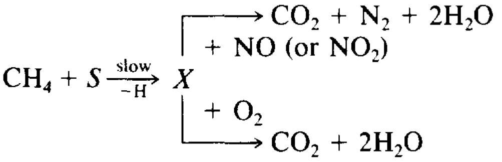
Ratio	Methane conversion (%)	Kinetic isotope effect		
		Overall	Reaction [1]	Reaction [2]
(A) 375°C, dry feed[a]				
Rate (CH_4)/rate (CD_4)	≃19	2.40	2.1	3.2
Rate (CH_4)/rate (CD_4)	≃30	2.37	2.2	2.7
k_{CH_4}/k_{CD_4}	32(CH_4), 17(CD_4)	2.08	1.8	2.8
(B) 431°C 1.6% H_2O added[b]				
Rate (CH_4)/rate (CD_4)	≃31	2.03	1.8	2.2
k_{CH_4}/k_{CD_4}	31(CH_4), 16(CD_4)	2.10	1.6	2.6

[a] Conditions as per Table 2.

[b] Conditions as per Table 4.

and NO (in the absence of oxygen) over RH/Al_2O_3 at 320°C in which it was suggested that methane dissociation was rate limiting (16). They are also slightly higher than the value (1.82) determined in the classic study of Adams and Jennings (17) which established that the rate determining step in the conversion of propene to acrolein over a bismuth molybdate catalyst at 450°C is hydrogen abstraction from the methyl group to form an allyl species. Similarly, the oxidative coupling of methane to ethane exhibits a kinetic isotope effect, 1.5 to 1.8 at 750°C, which is consistent with the view that the slow step in that reaction is the breaking of the carbon–hydrogen bond in methane (18, 19). The present results indicate that hydrogen abstraction is also the rate determining step in the methane/NO/O_2 reaction over Co–ZSM5.

The similarity in apparent kinetic orders in methane for the selective and nonselective reactions (0.68 and 0.75, respectively), and their similar kinetic isotope effects, indicate that a common intermediate is involved. The scheme



$$CH_4 + S \xrightarrow[-H]{\text{slow}} X \begin{cases} \xrightarrow{+\,NO\ (\text{or } NO_2)} CO_2 + N_2 + 2H_2O \\ \xrightarrow{+\,O_2} CO_2 + 2H_2O \end{cases}$$

is suggested in which a surface species S abstracts hydrogen to form an intermediate X which reacts further in two different ways. In such a model the apparent kinetic orders in nitric oxide and in oxygen will reflect the competitive behaviour after the slow step. For example, their kinetic orders for the major pathway (the selective reaction to N_2) will be close to those for the overall methane loss because of the high selectivity. However, one expects the extent of the minor pathway to be positive order in oxygen (since the probability of the intermediate reacting with oxygen will be increased) but negative order in nitric oxide (since this syphons the limited supply of X into the major pathway). This agrees with experimental observations (Table 1). The slight difference in apparent kinetic isotope effect for the two pathways can then be interpreted as a small discrimination effect in which the nonselective reaction is retarded relative to the selective one when CD_4 is used in place of CH_4. Such behaviour could arise, for example, if the reaction of X in the former path was a strict addition, whereas it had elements of a further abstraction in the second path and thus exhibited a small kinetic isotope effect.

At this time the nature of surface site S, and the intermediate X, is a matter of speculation. Li *et al.* (20) have proposed that adsorbed NO_2 is involved in the rate determining step and it is possible that this species is the abstraction site. In the case of the methane coupling reaction the intermediate formed is firmly established as a gas-phase methyl radical (21) although it is not entirely clear if the actual abstraction step is homolytic or heterolytic (22). One possibility in the present case is that the intermediate X is also a CH_3 species in which case the slow step could be formulated as

$$CH_4 + NO_2(\text{ads}) \rightarrow CH_3 + HNO_2(\text{ads}).$$

The subsequent course of reaction would then depend on whether the methyl species reacted with NO (or NO_2) to produce the selective reaction, or with O_2 to give the nonselective one. The orders in NO for the two reactions (slightly positive and slightly negative, respectively) imply that the concentration of adsorbed NO_2 is nearly independent of the NO concentration at the temperature used. The higher rate of the nonselective reaction [2] in $CH_4/NO/O_2$ mixtures than when using CH_4/O_2 alone (Fig. 1d versus Fig. 1b) is consistent with this scheme. The presence of adsorbed NO_2 increases the throughput of methane to such an extent that the subsequent diversion of CH_3 to CO_2 through reaction with O_2 can exceed the reaction rate of CH_4 with O_2 alone present.

Formation of a methylperoxy species and its subsequent oxidation, or direct oxidation of methyl radicals as observed with some oxides (23), are reasonable pathways for the progress of the nonselective component of the overall reaction. While much less certain, there is some recent work which indicates how nitrogen could be formed in the selective pathway. Herschberger and coworkers have shown that the gas-phase reaction of CN with NO_2 gives NCO + NO (24), while that between NCO and NO has CO_2 and N_2 as major products (25). FTIR studies have established that HCN is a product of the reaction between alkenes and NO_x over Cu-ZSM5 (26) and that HNCO is formed during the homogeneous reaction of methane/NO_x mixtures (27). Both surface NCO and CN species have been detected on catalysts active for the hydrocarbon/NO_x reaction (28, 29). Thus it seems that nitrogen could arise by radical processes involving intermediates with carbon–nitrogen bonds. The exact step which forms this bond to begin with is not obvious. Possibly CH_3 and NO_2 combine directly to form nitromethane which reacts further as suggested in the recent work of Tanaka *et al.* (30).

While the conclusion that direct hydrogen abstraction from methane is the rate-determining step is certainly the most reasonable explanation for the present observations, it is difficult to totally exclude other possibilities. Kung (31) has recently explained how a deuterium kinetic isotope effect might arise when a shortage of surface oxygen is coupled to a situation in which two competing reactions have very different stoichiometric requirements for oxygen. This is unlikely to apply in the present case since

TABLE 4

Hydrogen Deuterium Exchange during Reactions of $CD_4/NO/O_2/H_2O$, $CH_4/CD_4/NO/O_2$, and $CH_4/CD_2/O_2$ Mixtures over 0.4 g Co–ZSM5

Feed	Conditions	Flow rate (cm^3/min)	CHD_3/CD_4 Ratio
$CD_4/NO/O_2/H_2O$[a]	Bypass	100	0.015
$CD_4/NO/O_2/H_2O$[a]	Co–ZSM5, 431°C	100	0.028
$CD_4/NO/O_2/H_2O$[a]	Co–ZSM5, 431°C	49	0.063
$CH_4/CD_4/NO/O_2$[b]	Bypass	100	0.015
$CH_4CD_4/NO/O_2$[b]	Co–ZSM5, 375°C	100	0.017
$CH_4/CD_4/O_2$[c]	Co–ZSM5, 375°C	100	0.019

[a] Composition as per footnote to Table 2.

[b] CH_4 520 ppm, CD_4 520 ppm, NO 1640 ppm, O_2 3.9%.

[c] As for footnote [b] but with NO deleted.

the oxygen requirements of reactions [1] and [2] are the same. In theory an isotope effect could arise in the present case if the rate-determining hydrogen abstraction was from oxygen (e.g., during water elimination from surface hydroxyl groups). The persistence of the kinetic isotope effect when using CD_4 in the presence of a substantial excess of H_2O rules against this possibility.

One might also envisage a situation in which the rate-determining abstraction comes after a series of equilibration steps so that the carbon–hydrogen bond then broken is not in methane itself. An absence of hydrogen–deuterium exchange into and out of methane would indicate that such preequilibration does not occur. Table 4 gives CHD_3/CD_4 ratios determined by mass spectrometry during the $CD_4/NO/O_2/H_2O$ runs described earlier and in additional experiments using equimolar CH_4/CD_4 mixtures without added water. A small amount of exchange (1.3 to 4.8%) is evident for the wet feed at 431°C but the extent is only one-tenth or so of the methane conversion due to the reaction itself (16 to 32%). Exchange was negligible for the mixed feed at 375°C whether or not NO was present. Thus there is no evidence for a preequilibration step prior to the reaction. It is therefore most likely that the rate determining abstraction is from methane itself.

As a side point it was possible to calculate the kinetic isotope effect from the mixed feed experiments using the different CH_4 and CD_4 conversions as determined mass spectrometrically. The value obtained, which is for the overall reaction, was 2.33, which is in good agreement with that calculated from the constant conversion experiments with the dry feed (Table 3). The kinetic isotope effect for methane/O_2 mixtures (i.e., without NO) could be similarly calculated from data obtained in the last experiment as noted in Table 4. The estimate, which is much less accurate than those for the NO-containing mixtures due to a lower conversion, was also slightly above 2.

CONCLUSIONS

1. The reaction of methane and nitric oxide in the presence of oxygen over Co–ZSM5 catalysts exhibits a substantial deuterium kinetic isotope effect. This persists when the reaction is carried out in the presence of excess water. The most probable explanation is that the rate-determining step involves hydrogen abstraction from methane itself.

2. The observed reaction orders, and the existence of a slightly lower apparent kinetic isotope effect for nitrogen production than for the concurrent direct oxidation of methane, suggest that a common intermediate is involved in both reactions. This intermediate could be a methyl species which further reacts with NO (or NO_2) in one path but with O_2 in the other.

3. Hydrogen–deuterium exchange between CD_4 and H_2O, and between CH_4 and CD_4, is much slower than methane oxidation during the methane/NO/O_2 reaction over Co–ZSM5 so a dissociative preequilibrium step prior to the primary bond breakage can be excluded.

ACKNOWLEDGMENTS

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REFERENCES

1. Held, W., Konig, A., Richter, T., and Puppe, L., SAE Paper No. 900496, 1990.
2. Iwamoto, M., Yahiro, H., Shundo, Y., Yu-U., Y., and Mizumo, N., *Shokubai* **32,** 430 (1990).
3. Iwamoto, M., and Hamada, H., *Catal. Today* **10,** 57 (1991).
4. Cho, B. K., *J. Catal.* **142,** 418 (1993).
5. Bennett, C. J., Bennett, P. S., Golunski, S. E., Hayes, J. W., Rajaram, R. R., Truex, T. J., and Walker, A. P., *Appl. Catal. A* **86,** L1 (1992).
6. Ansell, G. P., Diwell, A. F., Golunski, S. E., Hayes, J. W., Rajaram, R. R., Truex, T. J., and Walker, A. P., *Appl. Catal. B* **2,** 81 (1993).
7. Burch, R., and Millington, P. J., *Appl. Catal. B* **2,** 101 (1993).
8. D'Itri, J. L., and Sachtler, W. M. H., *Appl. Catal. B* **2,** L7 (1993).
9. Sasaki, M., Hamada, H., Kintaichi, Y., and Ito, T., *Catal. Lett.* **15,** 297 (1992).
10. Petunchi, J. O., and Hall, W. K., *Appl. Catal. B* **2,** L17 (1993).
11. Petunchi, J. O., Sill, G. A., and Hall, W. K., *Appl. Catal. B* **2,** 303 (1993).
12. Li, Y., and Armor, J. N., *Appl. Catal. B* **1,** L31 (1992).
13. Li, Y., and Armor, J. N., *Appl. Catal. B* **2,** L30 (1992).
14. Li, Y., Battavio, P. J., and Armor, J. N., *J. Catal.* **142,** 561 (1993).
15. Melander, L., "Isotope Effects on Reaction Rates." Ronald Press, New York, 1960.
16. Hardee, J. R., and Hightower, J. W., *J. Catal.* **86,** 137 (1984).
17. Adams, C. R., and Jennings, T. S., *J. Catal.* **3,** 549 (1964).
18. Cant, N. W., Lukey, C. A., Nelson, P. F., and Tyler, R. J., *J. Chem. Soc. Chem. Commun,* 766 (1988).

19. Nelson, P. F., Lukey, C. A., and Cant, N. W., *J. Catal.* **120,** 216 (1989).
20. Li, Y., Slager, T. L., and Armor, J. N., *J. Catal.* **150,** 388 (1994).
21. Campbell, K. D., Morales, E., and Lunsford, J. H., *J. Am. Chem. Soc.* **109,** 7900 (1987).
22. Maitra, A. M., *Appl. Catal. A* **104,** 11 (1993).
23. Tong, Y., Rosynek, M. P., and Lunsford, J. H., *J. Phys. Chem.* **93,** 2896 (1989).
24. Park, J., and Herschberger, J. F., *J. Chem. Phys.* **99,** 3488 (1993).
25. Cooper, W. F., Park, J., and Herschberger, J. F., *J. Phys. Chem.* **97,** 3283 (1993).
26. Radkte, F., Koeppel, R. E., and Baiker, A., *Appl. Catal. A* **107,** L125 (1994).
27. Nelson, P. F., and Haynes, B. S., accepted for presentation at the 25th Combustion Institute Symposium, Irvine, July 1994.
28. Ukiso, Y., Sato, S., Abe, A., and Yoshida, K., *Appl. Catal. B* **2,** 147 (1993).
29. Hayes, N. W., Grünert, W., Hutchings, G. J., Joyner, R. W., and Shpiro, E. S., *J. Chem. Soc. Chem. Commun.*, 531 (1994).
30. Tanaka, T., Okuhara, T., and Misono, M., *Appl. Catal. B* **4,** L1 (1994).
31. Kung, H. H., *J. Catal.* **134,** 691 (1992).