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The mechanism of nitrogen oxides reduction by hydrocarbons and in other systems

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Abstract

Three aspects of the catalytic reduction of NO_x have been investigated with particular emphasis on Cu-ZSM5. The reaction using methane shows a large kinetic isotope effect which is absent with isobutane. Thus, while abstraction of hydrogen from methane is rate determining, a different step plays that role with higher hydrocarbons. With Cu-ZSM5 and Co-ZSM5 the equilibration step, NO to NO_2, is incomplete below 400°C in the presence and absence of methane. However, conversion of NO_2 to NO is near complete when using isobutane over Cu-ZSM5, possibly due to a process which also maintains the catalyst free of deposited material. Measurements of the further reactions of isocyanic acid, HNCO, over Cu-ZSM5 at 270°C show that its rate of hydrolysis to CO_2 and NH_3 is fast while that with NO to give N_2 and N_2O is absent.

Keywords: Nitrogen oxides; Reduction; Hydrocarbons

1. Introduction

The reports of Iwamoto et al. [1] and of Held et al. [2] showing that Cu-ZSM5 is capable of catalysing the reduction of nitric oxide by hydrocarbons in the presence of oxygen has generated a great deal of work on related systems. Many other catalysts for the reaction are now known. While few, if any, are superior to Cu-ZSM5 in effectiveness, some may suffer less from the deactivation which inhibits its use on vehicles. Cu-ZSM5 is also ineffective with methane as the reductant. Co-ZSM5 [3,4], Co-ferrierite [5] and Ga-ZSM5 [6,7] in particular are much more selective.

The literature contains many suggestions as to the reaction mechanism in these systems but details remain controversial. Two sub-questions are of particular interest. Firstly, what is the initiating step and is it the same with all hydrocarbons and all catalysts? Secondly, what is the step which constructs the bond in the N_2 product? In respect of the former we have recently shown that the rate of the methane/NO/O_2 reaction over Co-ZSM5 is reduced by a factor of two when CD_4 is used in place of CH_4 [8]. This deuterium isotope effect indicates that the slow step is hydrogen abstraction to form a methyl species, which then reacts further with NO_x or oxygen in the selective and unselective paths respectively. In respect of the second, observation of adsorbed NCO [9], of deposits with equal C, N, O atom ratios [10] and of HNCO and HCN as trace gaseous products [11] have led to the supposition that N–N bond

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formation is preceded by formation of a CN-containing species of some type. Subsequent reaction with NO via radical chemistry could then produce N_2. The alternative, recently discussed in some detail by Cho [12], is that the N–N bond forms directly on the catalyst surface after NO dissociation. Certainly the formation of N_2 is uniquely catalytic since the chemistry in the homogeneous hydrocarbon/NO/O_2 system leads only to oxidation and NO_2 formation [13].

Here we describe the results of some experiments which address these questions. The kinetic isotope effect has been determined over Cu-ZSM5 for both methane and isobutane. The corresponding NO/NO_2 ratios in the product gas have also been determined with NO + O_2, and with NO_2 as the oxidants. Finally, we have investigated if isocyanic acid (HNCO) reacts further over Cu-ZSM5. This experiment has been made possible by our recent discovery that HNCO is a substantial product of the reaction of H_2/NO/CO mixtures over Pt/SiO_2 catalysts [14]. This provides a way of generating HNCO in situ and investigating its further reaction over another catalyst downstream.

2. Experimental

Catalytic behaviour was investigated using an improved version of the test system described previously [8]. Samples of mass $\approx$ 0.1 or 0.4 g were contained in Pyrex U-tube reactors (4 or 6 mm ID). The reactant stream was provided from a set of mass flow controllers supplying, respectively, 1% CH_4 in He, 10% O_2 in He, 1% NO (or 0.8% NO_2) in He with UHP grade helium itself as the carrier. The standard mixture used contained 1040 ppm CH_4 (or 595 ppm of C_4H_{10}), 1640 ppm NO (or NO_2) and 2.6% O_2 in helium at a total flow rate of 100 cm^3(STP)/min with the reactor at close to atmospheric pressure. Isotope experiments used matching mixtures of 1% CD_4 or 1% C_4D_{10} (both from CIL Inc. > 99%D) in helium. The exit gas stream from the reactor was periodically sampled by a high speed chromatograph (MTI Model M200) and then flowed through a gas cell in the beam of an FTIR spectrometer (Mattson Cygnus 100 with MCT detector). The chromatograph gave parallel analyses for N_2, O_2, the hydrocarbon and CO (on a molecular sieve 5A column) plus CO_2 and N_2O (on a Porapak U column) with a cycle time of 2 min and with a detection limit of < 3 ppm. All FTIR measurements were carried out at 0.25 cm^{-1} resolution, with accumulation of 64 scans per spectrum. Most measurements used a cell of pathlength 16 cm, which gave an accuracy of $\pm$10 ppm for NO_2 and $\pm$50 ppm for NO using lines at 1630 and 1900 cm^{-1} respectively. Blank tests with an empty reactor showed that the conversion of NO to NO_2 by homogeneous oxidation in the flow system and infrared cell was < 2% with the standard mixture and $\approx$ 4% when the O_2 concentration was raised to 8%. FTIR analyses for HNCO employed a 2.4 m multiple reflection gas cell (Infrared Analysis Inc.) heated to $\approx$ 75°C.

The sample of Co-ZSM5 (SiO_2/Al_2O_3 ratio of 22.4, 110% exchanged) was provided by Dr J.N. Armor and prepared as described elsewhere [3,4]. The Cu-ZSM5 was made by exchange of a Na-ZSM5 with a SiO_2/Al_2O_3 ratio of 23.8 (Tosoh Corp.) with sufficient 0.013 M $Cu(CH_3COO)_2$ to achieve an exchange level of $\approx$ 90%. The samples used for testing were contained in the reactor between plugs of quartz wool and initially pretreated in flowing 10% O_2/He while raising the temperature in stages to 500°C. The Pt/SiO_2 catalyst used to generate HNCO was that designated 40-SiO_2-PtCl-L in the series characterised by Uchiyama et al. [15]. It had been prepared by impregnation and contained 1.1 wt% Pt with a dispersion of 40%. The base HNCO experiments were carried out as described previously [14] using a single 76 mg bed of Pt/SiO_2 packed as above. The sequential bed employed the same mass of Pt/SiO_2, immediately followed by 50 mg of Cu-ZSM5.

3. Results and discussion

3.1. Deuterium kinetic isotope effects with Cu-ZSM5

As shown in Figs. 1 and 2, the activity of Cu-ZSM5 for methane conversion in $CH_4/NO/O_2$ mixtures is similar to that of Co-ZSM5. However, its effectiveness for N_2 production (ie. NO conversion) is much less. The deuterium kinetic isotope effect (KIE) was measured for Cu-ZSM5 in order to see if the rate determining step in both paths is hydrogen abstraction, as previously found for Co-ZSM5 [8]. The results of one such determination, in which CH_4 and CD_4 were interchanged is shown in Fig. 3. It is apparent that production of both CO_2 and N_2 drops sharply when CD_4 is introduced and recovers immediately on reintroduction of CH_4. As may be seen from Table 1, the KIE values, calculated from the rate ratios, are very similar to those for Co-ZSM5 despite the large difference in selectivity. A KIE is excess of 2 at ≈ 375°C can be taken as strong evidence that the rate determining step is the breakage of a CH versus CD bond [16]. Thus, hydrogen abstraction from methane is this step with both catalysts. It cannot be NO dissociation. Nor can it be removal of oxygen deposited by NO dissociation, except in the following indirect way. If the oxygen removal step was

$$OH^- + OH^- \rightarrow H_2O + O^{2-}$$

and this was fast, then its rate could be restricted by formation of OH^- according to

$$Cu^{2+}, O^{2-} + CH_4 \rightarrow CH_3 + OH^- + Cu^+$$

In other words, abstraction from methane is rate limiting, but it arises because the hydrogen ab-

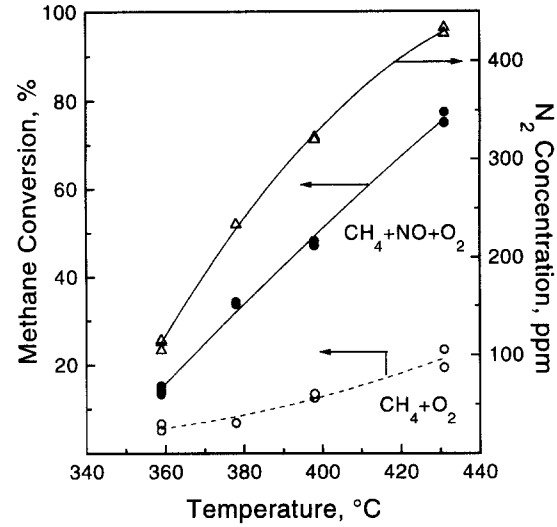

Fig. 2. Methane conversion and N_2 production as a function of temperature under standard conditions with Co-ZSM5.

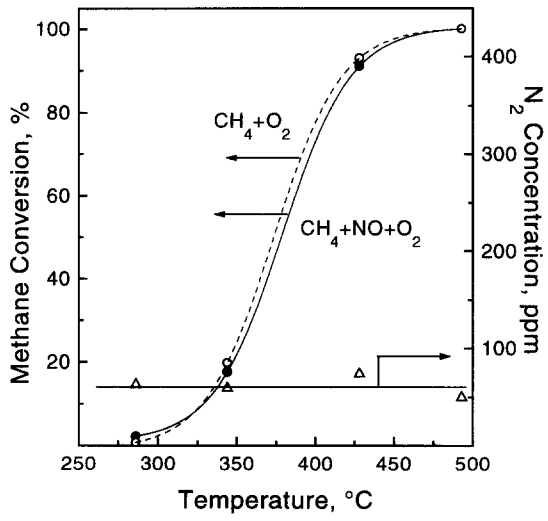

Fig. 1. Methane conversion and N_2 production as a function of temperature under standard conditions with Cu-ZSM5.

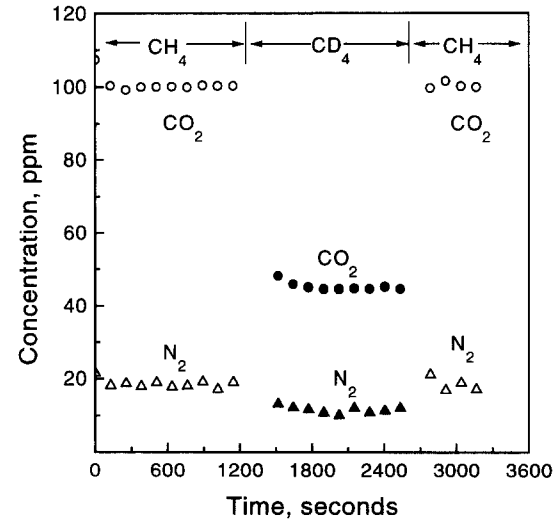

Fig. 3. Effect of replacement of CH_4 by CD_4 on CO_2 and N_2 formation over Cu-ZSM5 at 375°C under standard conditions.

Table 1
Deuterium kinetic isotope effect for the methane/NO/O_2 reaction at 375°C

Catalyst	S [a] (%)	KIE	
		to CO_2	to N_2
Cu-ZSM5 [b]	19	2.33	≈ 1.6
Co-ZSM5 [c]	64	2.37	2.1

[a] S = Selectivity defined as N_2/CO_2 as in Ref. [3].
[b] Standard conditions, 0.070 g Cu-ZSM5.
[c] Data from Ref. [8].

stracted is needed to facilitate removal of surface oxygen to allow continuance of the catalytic cycle.

Whatever the origin, there is no reason to suppose that a fundamental difference in mechanism is the cause of the low selectivity of Cu-ZSM5 for the $CH_4/NO/O_2$ reaction. The probable cause is as follows. The dashed lines in Figs. 1 and 2 are for the CH_4/O_2 reaction. It is apparent that this reaction is much slower than the $CH_4/NO/O_2$ one with Co-ZSM5, but over Cu-ZSM5, the rate of methane combustion is unchanged by the addition of NO. The clear implication is that the activity of Co-ZSM5 for CH_4 combustion is low, that introduction of NO provides additional sites for the reaction of CH_4 and that this step gives N_2. On the other hand, Cu-ZSM5 is relatively active for combustion, so that any sites introduced through the inclusion of NO are competing with those already present. Thus, while the reaction chemistry may be the same with the two catalysts their effectiveness for NO reduction differ markedly.

Kinetic isotope effect measurements are most accurately carried out at low conversions as in Fig. 3, so that rates can be calculated accurately using the differential reactor approximation. It proved difficult to find such conditions when using isobutane with Cu-ZSM5. As shown in Fig. 4, the catalyst was quite stable at 295°C but the hydrocarbon conversion (≈ 87%) was too high for meaningful KIE measurements. At 282°C, the activity fell steeply with time, presumably due to deposition of carbonaceous matter of some type. The CO/CO_2 ratio also rose.

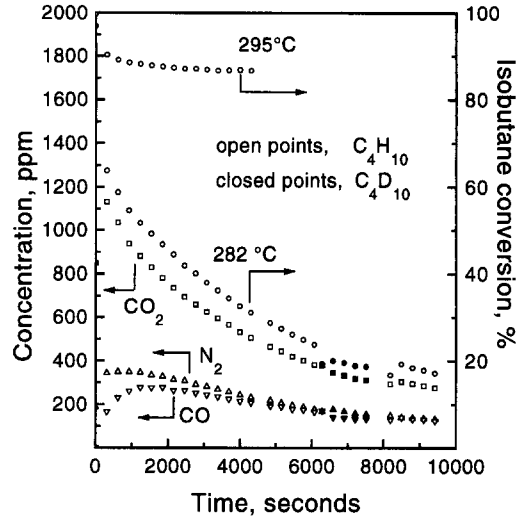

Fig. 4. Effect of replacement of C_4H_{10} by C_4D_{10} over Cu-ZSM5 when using NO and O_2 under standard conditions at 282°C.

A substitution of C_4D_{10} for C_4H_{10} when the conversion reached 20% showed no change in the rates of production of N_2, CO_2 or CO. Thus the KIE is close to unity under these conditions. The experiment was repeated at 282°C using NO_2 in place of NO, as shown in Fig. 5. Unlike the NO reaction at the same temperature, the catalyst shows little deactivation. Substitution of C_4D_{10} now causes a small drop in product formation but the KIE is still low (≈ 1.1). Thus,

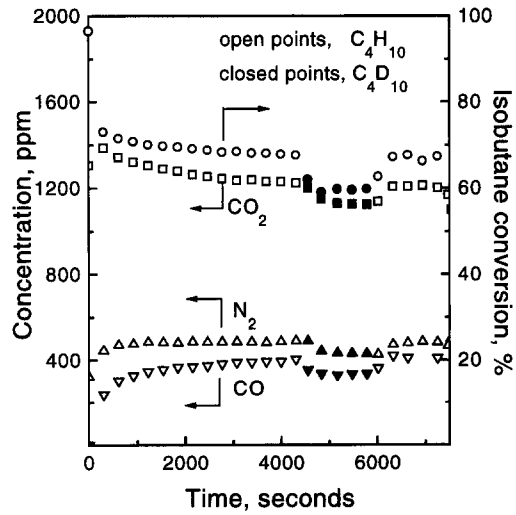

Fig. 5. Effect of replacement of C_4H_{10} by C_4D_{10} over Cu-ZSM5 when using NO_2/O_2 under standard conditions at 282°C.

unlike the situation with methane, the reaction with isobutane is not limited by the rate of hydrogen abstraction. The actual rate-determining step cannot be specified but NO dissociation or removal of largely carbonaceous material are two possibilities. It is also clear that NO_2 is able to maintain catalyst stability at 282°C under the conditions of Figs. 4 and 5 in a way which NO cannot.

3.2. NO/NO_2 equilibration

Fig. 6 shows the $NO_2/(NO + NO_2)$ ratios for a range of measurements carried out with and without methane in the feed and with NO or NO_2. Below 400°C, all points using NO are below the equilibrium line while those starting from NO_2 (solid) are above it. The points using $NO + O_2$ alone (open) are closer to the line than those with CH_4 also present (cross-hatched). It is also apparent that Cu-ZSM5 (circles) achieves greater equilibration than Co-ZSM5 (squares) despite a five-fold smaller mass. All points above 400°C are close to equilibrium, with the exception of the least active system (the $CH_4/NO/O_2$ reaction over Co-ZSM5).

The conclusion from the above is that both catalysts have modest activity for $NO + O_2 \rightleftharpoons$

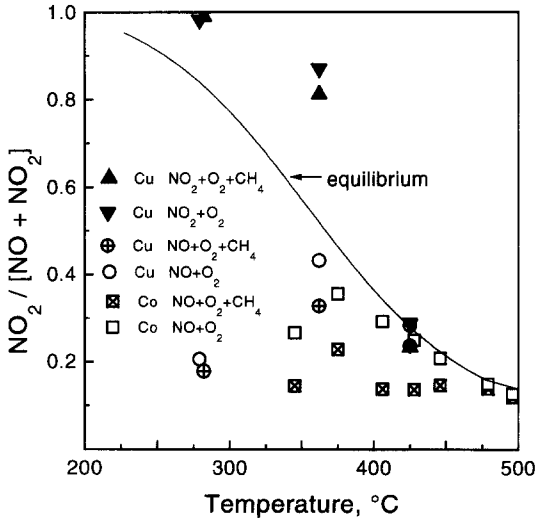

Fig. 6. $NO_2/(NO+NO_2)$ ratio in the product stream with and without methane using Cu-ZSM5 (70 mg) and Co-ZSM5 (380 mg).

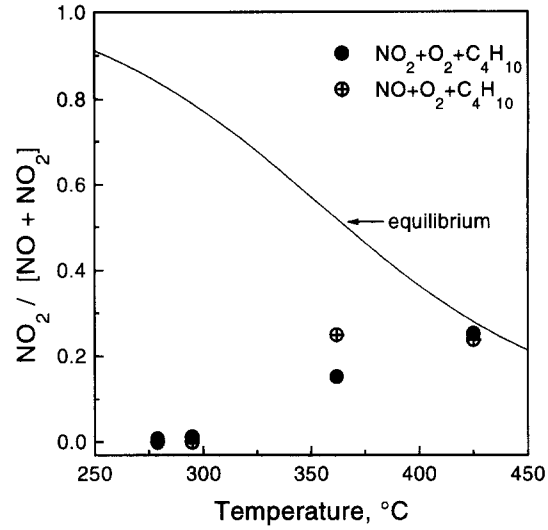

Fig. 7. $NO_2/(NO+NO_2)$ ratio in the product stream when using isobutane over Cu-ZSM5 (70 mg) under standard conditions.

NO_2 equilibration below 400°C and that this activity is inhibited to some extent when methane is present. The picture with isobutane over Cu-ZSM5 is very different as shown in Fig. 7. The $NO_2/(NO + NO_2)$ ratio is below equilibrium regardless of whether NO_2 or NO is employed. Thus this system contains a way to rapidly convert NO_2 to NO which is very effective even at the lowest temperature. The probable cause is a step in which deposited carbonaceous matter, or a precursor to it, is oxidised by NO_2 with evolution of NO, ie.

$$NO_2 + CH_x \rightarrow NO + CO_2 + H_2O$$

It is the existence of this process which enables stable operation with NO_2 under conditions which produce rapid deactivation with NO. Bethke et al. [17] have recently reported a similarly rapid conversion of NO_2 to NO for the corresponding reactions of propane and propene over Cu/ZrO_2 and Cu-ZSM5 catalysts.

3.3. Reactions of HNCO over Cu-ZSM5

Several findings [9–11] suggest that isocyanate species may be involved in the hydrocarbon/NO_x reaction over zeolites. Perhaps the most persuasive is that of Radkte et al. [11] showing that isocyanic acid, HNCO, is present

in small amounts (< 15 ppm) in the product stream from the reaction using propene over Cu-ZSM5. In recent work we have shown that HNCO can be formed in much larger amounts (200 ppm and more) during the reaction of $H_2/NO/CO$ mixtures over Pt/SiO_2 catalysts [14]. This can be explained on the basis that dissociation of NO forms N adatoms which, on a largely CO covered surface, can give rise to small amounts of Pt–NCO groups via the equilibrium reaction

$$N_a + CO_a \rightleftharpoons NCO_a$$

Reaction of these NCO groups with hydrogen adatoms then results in evolution of HNCO. While this chemistry has no direct relevance to the hydrocarbon/NO_x reaction, it is relevant that HNCO was absent from the product stream when using Pt/Al_2O_3 or a sequential bed comprising Pt/SiO_2 followed by Al_2O_3. All HNCO was then hydrolysed to CO_2 and NH_3 which raises the question as to whether Cu-ZSM5 would behave similarly.

This has been tested as shown in Fig. 8. The top panel (A) shows the FTIR spectrum of the product gas from the reaction of $H_2/NO/CO$

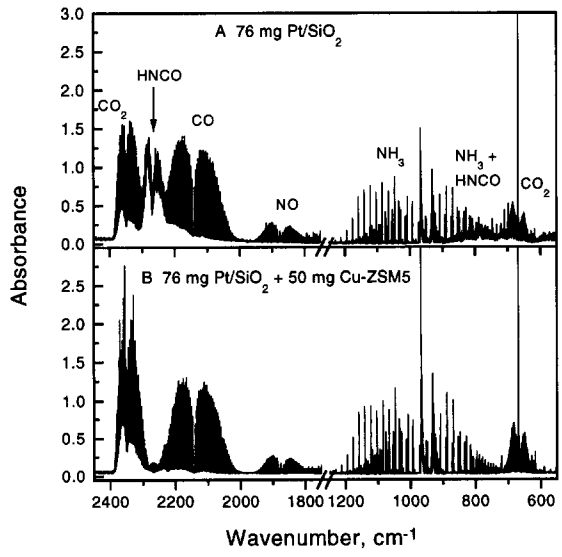

Fig. 8. FTIR spectrum of product stream: A, using 1000 ppm H_2, 4000 ppm CO and 1000 ppm NO over 76 mg Pt/SiO_2 at 270°C; B, as for A but with 50 mg Cu-ZSM5 downstream.

Table 2
Exit gas composition from the reaction of 1000 ppm H_2, 4000 ppm CO and 1000 ppm NO at 270°C under the conditions of Fig. 8

Catalyst	CO	NO	CO_2	N_2	N_2O	HNCO
Pt/SiO_2 alone	3500	300	400	40	39	280
Pt/SiO_2 + Cu-ZSM5	3460	320	660	40	36	< 10

over 76 mg of Pt/SiO_2 at 270°C. The conversions of H_2, NO and CO were > 98%, 70% and 15% respectively. The formation of HNCO is clearly demonstrated by a pronounced P–R band contour centred at 2267 cm^{-1} and a complex structure of lines which underlie strong lines due to NH_3 in the region 900 to 700 cm^{-1}. Fig. 8B is for an identical experiment with the same Pt/SiO_2 sample with 50 mg of Cu-ZSM5 packed immediately downstream in the same reactor. The bands due to HNCO have completely disappeared while those arising from CO_2 and NH_3 are clearly more intense. (The small residual absorption at ≈ 2270 cm^{-1} is due to N_2O not HNCO). The concentrations in the exit streams from the two experiments are shown in Table 2. The increase in CO_2 concentration when Cu-ZSM5 is present matches the loss of HNCO. The changes in NH_3 and H_2O concentrations were also in qualitative agreement with that expected for hydrolysis but the calibrations were not accurate enough for quantitative comparisons. Most significantly, there is no increase in N_2 concentration, or loss of NO, when the Cu-ZSM5 is included. Thus HNCO, or NCO groups derived from it, do not react with NO under the conditions used.

We have shown in other work [18] that HNCO is rapidly deposited as Al–NCO groups on Pt/Al_2O_3 and that the hydrolysis process involves these groups. A similar situation seems likely with Cu-ZSM5. If this is true, then the present results count against the supposition that surface isocyanate species are intermediates in NO reduction, at least at the low test temperatures used here. Clearly, they do react easily with NO to make N_2 (Table 2). Correspondingly, if they were present in large amounts,

then hydrolysis should give rise to much ammonia but this has never been reported as other than a minor product in hydrocarbon/NO_x systems [11]. The situation could be different at higher temperatures with methane if NCO radicals, generated in the gas phase through the reaction of methyl radicals with NO_x, reacted homogeneously with NO. It should also be remembered that the present experiments were carried out in the absence of O_2 and this might have some influence. Further experiments along the present lines but with the Cu-ZSM5 bed operated under conditions different from the HNCO generation step are required to sort out these possibilities

4. Conclusions

1. The existence of a large KIE in methane/NO_x systems shows that hydrogen abstraction is the rate limiting step. The absence of such an effect with isobutane indicates that a different slow step is operative with higher hydrocarbons.
2. NO to NO_2 interconversion is not equilibrated below 400°C in the absence or presence of methane. Nonetheless, there is a rapid path which converts almost all NO_2 to NO when isobutane is used. This process may be linked to the absence of deactivation under conditions which cause loss of activity when using NO rather than NO_2.
3. At 270°C, isocyanic acid reacts much faster with water on Cu-ZSM5 (to give CO_2 and NH_3) than with NO (to give N_2). It seems unlikely that surface isocyanates can be major intermediates under such conditions.

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References

[1] M. Iwamoto, H. Yahiro, Y. Shundo, Y. Yu-U and N. Mizumo, Shokubai, 32 (1990) 430.
[2] W. Held, A. Konig, T. Richter and L. Puppe, SAE Tech. Paper 900496.
[3] Y. Li and J.N. Armor, Appl. Catal. B, 1 (1992) L31.
[4] Y. Li and J.N. Armor, Appl. Catal. B, 2 (1993) 239.
[5] Y. Li and J.N. Armor, Appl. Catal. B, 3 (1994) L1.
[6] Y. Li and J.N. Armor, J. Catal., 150 (1994) 376.
[7] E. Kikuchi and K. Yogo, Catal. Today, 22 (1994) 73.
[8] A.D. Cowan, R. Dümpelmann and N.W. Cant, J. Catal., 151 (1995) 356.
[9] H. Yasada, T. Miyamoto, C. Yokoyama and M. Misono, Shokubai, 35 (1993) 386.
[10] C. Yokoyama and M. Misono, J. Catal., 150 (1994) 9.
[11] C. Radtke, R.A. Koeppel and A. Baiker, J. Chem. Soc., Chem. Commun., 427 (1995).
[12] B.K. Cho, J. Catal., 155 (1995) 184.
[13] J.H. Bromley, F.J. Barnes, R. Mandycszewski, T.J. Edwards and B.S. Haynes, Proc. 24th Int. Symp. Comb., The Combustion Institute, Pittsburgh, 1994, p. 899.
[14] R. Dümpelmann, N.W. Cant and D.L. Trimm, Appl. Catal. B, 6 (1995) L291.
[15] T. Uchiyama, J.M. Hermann, Y. Inoue, R.L. Burwell, J.B. Butt and J.B. Cohen, J. Catal., 50 (1977) 464.
[16] L. Melander, Isotope Effects on Reaction Rates, Ronald Press, New York, 1960.
[17] K.A. Bethke, C. Li, M.C. Kung, B. Yang and H.H. Kung, Catal. Lett., 31 (1995) 287.
[18] R. Dümpelmann, N.W. Cant and A.D. Cowan, submitted for publication.