A Reaction Pathway for the Ammoxidation of Ethane and Ethylene over Co-ZSM-5 Catalyst

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The ammoxidation of ethane and ethylene to acetonitrile was studied over a Co-ZSM-5 catalyst with an emphasis on the reaction pathway. We found that the adsorption of ammonia on Co-ZSM-5 is stronger than that on H-ZSM-5. C₂H₄ adsorption is weak and readily desorbs below 300°C. While the adsorption of C₂H₃N (a reaction product) is very strong in He, its desorption is accelerated with the presence of NH₃. With a specially designed temperature programmed experiment (reaction between the adsorbed NH₃ and gaseous C₂H₄/O₂/He mixture), we observed C₂H₅NH₂ as a reactive intermediate, and this intermediate was demonstrated to be readily converted to C₂H₃N under the ammoxidation reaction conditions. A detailed pathway is offered, whereby C₂H₄ is thought to add on an adsorbed NH₃, forming an adsorbed ethylamine which is subsequently dehydrogenated to form C₂H₃N. We further speculate that an oxidative environment N₂ comes from N-N pairing between the adsorbed NH_3 and an amine (both on a single Co^{2+} site). © 1998 Air Products and Chemicals. Inc.

INTRODUCTION

Recently, we reported that ethane can be efficiently converted to acetonitrile (Eq. [1]) in the presence of ammonia and oxygen (ammoxidation reaction) over some metal exchanged zeolite catalysts (1, 2). Among the most effective catalysts for this reaction are Co^{2+} exchanged ZSM-5. beta and NU-87. These catalysts have much higher reaction rate and yield versus most oxide-based catalysts for the ammoxidation reactions (1, 3, 4). Based on our earlier reaction studies, we propose a three-step pathway to account the C_2H_6 ammoxidation reaction. The first step is oxidative dehydrogenation of C₂H₆ to C₂H₄; C₂H₄, a reactive hydrocarbon and a major product for the reaction, is further added to an adsorbed NH_3 molecule (on a Co^{2+} site) forming an adsorbed C₂H₅NH₂ intermediate; this amine intermediate is then converted to C₂H₃N. In this contribution, we report data to elaborate and further substantiate this reaction scheme. C₂H₄ was found to be a hydrocarbon intermediate for C_2H_6 ammoxidation. To simplify the discussion regarding the reaction pathway, in this manuscript, we use C_2H_4 , instead of C_2H_6 , as a reactant for the ammoxidation reaction (Eq. [2]).

$$C_2H_6 + NH_3 + 1.5O_2 \rightarrow C_2H_3N + 3H_2O$$
 [1]

$$C_2H_4 + NH_3 + O_2 \rightarrow C_2H_3N + 2H_2O$$
 [2]

Temperature programmed experiments (desorption and reaction) were carried out over a Co-ZSM-5 catalyst to study the adsorption features of NH₃, C_2H_3N , and C_2H_4 . We were able to capture a reactive intermediate, $C_2H_5NH_2$, with a specially designed, *in situ* reaction and confirmed that this intermediate was readily converted to C_2H_3N under the ammoxidation conditions.

EXPERIMENTAL

The Co-ZSM-5 catalyst was prepared by cation exchange of the ammonium form ZSM-5 with cobalt acetate solution at 80°C, and the detailed procedures for this preparation were described earlier (2). The ammoxidation reaction runs with C_2H_4 were conducted using the same apparatus as C_2H_6 ammoxidation (2). The concentration of NH₃ was varied between 2 and 15%, that of hydrocarbon between 5 and 15% and O₂ between 1 and 8%. The catalysts were first pelletized, crushed, and sieved to 20–40 mesh before loading in the reactor. (The apparent density of the catalyst sample is 0.5 g/cm³.) For plug flow reaction studies, the total flow rate was 100 ml/min with 0.05 g catalyst, which renders a space velocity 60000 h⁻¹. A catalyst was routinely pretreated with flowing helium at 500°C for 1 h before a reaction run.

For C_2H_4 ammoxidation the major carbon containing products are C_2H_3N and CO_2 , and the nitrogen containing products are C_2H_3N , N_2 , and small amounts of N_2O . The conversion, selectivity and yield are defined as

Conversion of ethene,
$$X = \left(\sum_{i} y_{i} n_{i}\right) / \left(y_{E} n_{E} + \sum_{i} y_{i} n_{i}\right),$$
[3]

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100

90

80

70

Selectivity of product P_i (carbon basis),

$$S_i = y_i n_i \bigg/ \sum_i y_i n_i, \qquad [4]$$

Yield of product
$$P_i$$
, $Y_i = XS_i$, [5]

where y_i and y_E are the mole fractions of carbon containing product P_i and C_2H_4 , respectively; n_i and n_E are the number of carbon atoms in each molecule of product P_i and ethene, respectively, and all the terms were evaluated for the exit stream.

Selectivity of product *P_i* (nitrogen basis),

$$S_j = y_j n_j \bigg/ \bigg(y_A n_A + \sum_j y_j n_j \bigg),$$
 [6]

where y_i and y_A are the mole fractions of nitrogen containing product P_i and NH₃, respectively; n_i and n_A are the number of nitrogen atoms in each molecule of product P_i and ammonia, respectively.

A residual gas analyzer (or RGA, UTI 100C) was used for all the temperature-programmed experiments. This RGA is capable of monitoring 12 different mass species simultaneously as a function of time. TPD experiments were carried out over Co-ZSM-5 with NH₃, C₂H₃N, C₂H₄, and C₂H₅NH₂, respectively. Co-ZSM-5 (0.1 g) was first pretreated in flowing He at 500°C for 1 h and cooled to an adsorption temperature. The adsorption temperatures are 100°C for NH₃ and C₂H₃N and 25°C for C₂H₄. After the Co-ZSM-5 catalyst was saturated with an adsorbate (in 3000 ppm NH₃/He, 3000 ppm C₂H₄/He, and 1.2% C₂H₃N, respectively), the catalyst was flushed with He at the adsorption temperature with a flow rate of 150 cc/min. When the mass intensity of the species monitored by RGA is below a reasonable level (or at a certain cutoff time, e.g., 20 min for NH₃), the temperature was ramped to 550°C at a ramp rate of 10°C/min. Relevant mass numbers were continuously monitored as a function of time.

For the C₂H₅NH₂ TPD experiment, the Co-ZSM-5 catalyst was contacted with C₂H₅NH₂ vapor at 25°C. (A stream of He (50 cc/min) flowed through a $C_2H_5NH_2$ bubbler at -77° C: then it was further diluted with another stream of He at 50 cc/min just before entering the reactor.) After flushing the system with He (150 cc/min) for about 20 min, a stream of NH₃/O₂/He mixture (3.3% NH₃, 3.9%, O₂) was passed through the catalyst bed at 150 cc/min until the RGA signals were stabilized. The temperature was then raised from 25 to 525°C in flowing the mixture gas (150 cc/min) at a ramp rate of 10°C/min. Mass factions at 2, 17, 18, 27, 28, 41, and 45 were monitored simultaneously.

The temperature-programmed reaction between adsorbed NH₃ and a gaseous mixture of C₂H₄/O₂/He was conducted over Co-ZSM-5. After pretreatment (500°C in He for 1 h) of Co-ZSM-5, NH₃ was first adsorbed on Co-ZSM-5 at 25°C. Then a stream of C_2H_4 (5%)/ O_2 (5%)/He mixture was passed through the catalyst at 150 cc/min. Upon stabilization of the flow, the temperature was ramped to $525^{\circ}C$ at a rate of 10°C/min while monitoring relevant mass species with RGA.

RESULTS

Reaction Studies for C₂H₄ Ammoxidation

When a stream of C₂H₄/NH₃/O₂/He flows through a Co-ZSM-5 catalyst at $T > 350^{\circ}$ C, a mixture of products are produced. Acetonitrile dominates the carbon-containing products, with small amounts of CO₂ formation and trace amounts of CO (<1%), HCN (<1%), and $C_{3}H_{5}N$ (<1%). In addition, N₂ is a major product of NH₃ conversion with a trace amount of N₂O formation. The conversions and selectivities for the C₂H₄ ammoxidation reaction are presented in Figs. 1–3 as a function of inlet $[C_2H_4]$, $[NH_3]$, and $[O_2]$ in feed.

As shown in Fig. 1, the selectivity of C_2H_4 to C_2H_3N is generally high (50-80%) and increases with $[C_2H_4]$. Conversely, the conversion of C₂H₄ decreases with increasing $[C_2H_4]$. NH₃ has a moderate C_2H_3N selectivity, which is higher at high $[C_2H_4]$. Interestingly, a higher C_2H_4 partial pressure increases the utilization of both NH₃ and C₂H₄. The O₂ is almost completely (not shown in Fig. 1) converted except at the inlet $[C_2H_4]$ of 15% (80% O₂ conversion). Figure 2 shows the [NH₃] dependence. Both C₂H₄ conversion and selectivity increase with increasing $[NH_3]$. The NH_3 conversion and selectivity are slightly lower at higher inlet

Conversion/Selectivity (%) NH₂ conversion 60 50 40 30 C₂H₂ conversion 20 10 NH₃ selectivity to C₂H₃N 0 10 12 16 14 18 [C,H,] (%)

C₂H₄ selectivity to C₂H₃N

FIG. 1. C_2H_4 ammoxidation as a function of $[C_2H_4]$. The reaction run was carried out at 425°C with 0.05 g Co-ZSM-5, F = 100 cc/min, [NH₃] = 10%, and $[O_2] = 6.5\%$.



FIG. 2. C_2H_4 ammoxidation as a function of [NH₃]. The reaction run was carried out at 425°C with 0.05 g Co-ZSM-5, F = 100 cc/min, [C₂H₄] = 10%, and [O₂] = 6.5%.

NH₃ levels. Similar to the C_2H_6 ammoxidation reaction (2), O_2 is a strong driving force for the C_2H_4 ammoxidation reaction, and in the absence of O_2 no reaction occurs. Both NH₃ and C_2H_4 conversion are enhanced at higher [O_2]. The C_2H_4 selectivity only slightly decreased (from 80 to 75% at [O_2] of 3.5 to 8%), while the selectivity of NH₃ is not affected by the O_2 level (Fig. 3). Using these partial pressure dependence data, we obtained the empirical reaction rate (for C_2H_3N) orders of 0.62, 0.74, and 1.0 with respect to [C_2H_4], [NH₃], and [O_2], respectively.



FIG. 3. C_2H_4 ammoxidation as a function of $[O_2]$. The reaction run was carried out at 425°C with 0.05 g Co-ZSM-5, F = 100 cc/min, $[C_2H_4] = 10\%$, and $[NH_3] = 10\%$.



FIG. 4. Comparison of TPD profiles between NH_3 adsorbed on Co-ZSM-5 and H-ZSM-5.

Temperature Programmed Desorption of Ammonia (TPDA)

Temperature programmed desorption of NH₃ over a Co-ZSM-5 catalyst was conducted and compared with H-ZSM-5 (see Fig. 4). The NH₃ adsorption from the proton sites of H-ZSM-5 is represented by the higher temperature peak at $\sim 400^{\circ}$ C. The TPDA profile over the Co-ZSM-5 catalyst shows a very different picture. The high temperature peak is not visible; rather, a continuous desorption occurred starting from the low temperature peak and extended beyond 550°C. This Co-ZSM-5 catalyst was almost fully exchanged with Co^{2+} (Co/Al = 0.49), and IR spectroscopy measured with DRIFTS confirmed that there was no observable acidic OH group (about 3610 cm^{-1}) on this catalyst. To quantify the NH₃ desorption, TPDA experiments were also carried out with a thermogravimetric analysis (TGA) method. The amount of NH₃ desorbed above 285°C was measured as 1 mmol/g (or 0.76 NH₃/bulk Al) and that over Co-ZSM-5 as 1.2 mmol/g (or 1.8 NH_3/Co^{2+}). The IR spectra we collected show that NH₃ adsorbs on Co-ZSM-5 as a Lewis base and Co^{2+} is an excellent Lewis acid center. The above TPD results suggest that two NH₃ molecules can adsorb on a single Co^{2+} .

Temperature Programmed Desorption of Ethylene

Ethylene is a major product of the ammoxidation reaction and is thought to be a primary product of C_2H_6 activation (1, 2). The adsorption of C_2H_4 on Co-ZSM-5 is relatively weak, compared to the adsorption of NH₃. As shown in Fig. 5, most of the adsorbed C_2H_4 molecules desorbed below 300°C with an intensity much lower than that for NH₃. It is conceivable that in the presence of NH₃, or under the ammoxidation conditions (e.g., high temperatures), the



FIG. 5. Comparison of NH₃ TPD and C₂H₄ profiles over Co-ZSM-5.

coverage of C_2H_4 on cobalt sites is insignificant. The adsorption/desorption of C_2H_4 appears to be reversible because no other products were observed.

Temperature Programmed Desorption of Acetonitrile

Acetonitrile is not only a product of the ammoxidation reaction but also an excellent Lewis base due to its exceptional electron donating ability from the N atom. The adsorption and desorption of C_2H_3N was studied on Co-ZSM-5. Figure 6 compares the C_2H_3N TPD profile in He and in a mixture of NH₃/He (3000 ppm NH₃). In a He flow, the adsorption of C_2H_3N is very strong, high intensity desorption was observed throughout the whole temperature range (100–525°C). However, when He was



FIG. 6. Comparison of C_2H_3N TPD in a He flow and in an NH₃/He mixture over Co-ZSM-5.

replaced by a stream of NH₃/He mixture (3000 ppm NH₃) at 100°C, most of the adsorbed C₂H₃N molecules were displaced by NH₃. As shown in Fig. 6, the overall desorption intensity of C₂H₃N was significantly reduced from 1.88 to $0.51 C_2H_3N/Co^{2+}$ —a 73% reduction. In addition, the high temperature desorption peak at 520°C was no longer visible with flowing the NH₃/He mixture. What is remarkable is that all this reduction in C₂H₃N coverage occurred at 100°C with a stream containing only 3000 ppm NH₃.

*Temperature Programmed Reaction (TPRx): NH*₃(*a*)/*C*₂*H*₄/*O*₂

Previously, we reported that $C_2H_5NH_2$ might be a reactive intermediate for C₂H₃N formation (2). An experiment was designed to capture the intermediate during a temperature programmed reaction. After a standard catalyst pretreatment (500°C in He for 1 h), NH₃ was first adsorbed on Co-ZSM-5 at 25° C. Then a stream of C₂H₄ $(5\%)/O_2$ (5%)/He mixture was flowed through the catalyst at 150 cc/min. Upon stabilization of the flow, the temperature was ramped to 525°C at a ramp rate of 10°C/min. The very high space velocity minimizes the over oxidation of any intermediates. Figure 7 shows some of the mass fragments monitored. As the temperature reached 350°C, both O₂ and C₂H₄ consumption began and O₂ was depleted at 450°C. C₂H₃N started appearing at 350°C, peaked at 440°C and then sharply dropped with increasing temperature. At $T > 440^{\circ}$ C, C₂H₅NH₂ was observed, slowly tailing off with increasing temperature. This observation suggests that C₂H₅NH₂ is indeed an intermediate reaction for the ammoxidation reaction. The sharp drop in C₂H₃N intensity beyond 440° C must be caused by the depletion of O_2 , slowing down the dehydrogenation of amine.

Temperature Programmed Desorption/Reaction of Ethylamine in NH₃/O₂

We reported earlier that, under steady-state conditions, $C_2H_5NH_5$ was oxidized to C_2H_3N over a Co-ZSM-5 catalyst. This experiment was intended to show that the adsorbed $C_2H_5NH_2$ is converted to C_2H_3N under reaction conditions. After adsorption of $C_2H_5NH_2$ at room temperature and flushed with He, an NH₃/O₂/He mixture was passed through the catalyst bed while temperature was ramped to 525°C at 10°C/min. As shown in Fig. 8, C_2H_3N was observed and peaked at 320, 390, and 500°C. An $C_2H_5NH_2$ desorption peak can be seen around 300°C with a relatively low intensity.

Ammoxidation of Higher Hydrocarbons

As a way to verify the reaction scheme proposed earlier, ammoxidation reactions with some higher hydrocarbons were conducted over the Co-ZSM-5 catalyst. Table 1 shows propane ammoxidation results over Co-ZSM-5. The



FIG. 7. Temperature programmed reaction between adsorbed NH₃ and gaseous mixture of C₂H₄ and O₂ over a Co-ZSM-5 catalyst.

major products for C_3H_8 ammoxidation are C_2H_3N , C_3H_6 , and CO_2 . Interestingly, only a very small amount of C_3H_5N was formed, even though the feed here was C_3H_8 and the dominant nitrile product is C_2H_3N . The ammoxidation of other hydrocarbons (n- C_4H_{10} , iso- C_4H_{10} , and n- C_5H_{12}) also produced C_2H_3N as a dominant nitrile product with very low quantities of propionitrile formation (5).

DISCUSSION

Acetonitrile Formation Pathway

The elementary steps for C_2H_4 ammoxidation are proposed below (see Fig. 9). First, NH₃ is adsorbed on a hydroxylated Co²⁺ site (Eq. [7]). The NH₃ adsorption is a reversible process, and its equilibrium is dependent on the reaction temperature. However, its adsorption should be the strongest among all the reactants. The second step

2.0 1.5 CH₃CN (m/e=41 ntensity (a.u.) 1.0 0.5 C₂H₅NH₂ (m/e=45)0.0 300 100 200 400 500 Temperature (°C)

FIG. 8. Temperature programmed desorption/reaction of $C_2H_5NH_2$ over Co-ZSM-5 in a $NH_3/O_2/He$ stream.

involves an addition of a gaseous C_2H_4 to the adsorbed NH₃ forming an adsorbed ethylamine molecule (Eq. [8]). The adsorbed amine is dehydrogenated by reacting with its neighboring OH forming an ethylamine anion and H₂O as a by-product (Eq. [9]). This adsorbed amine anion is subsequently oxidized by a gaseous O₂ forming an adsorbed pair of C₂H₃N and OH group and H₂O as a by-product (Eq. [10]). Finally, C₂H₃N is desorbed (Eq. [11]). These steps are further explained below.

The TPDA experiments suggest that NH₃ adsorption is a necessary and important step for the ammoxidation reaction. At the reaction temperatures, NH₃ should cover most of the sites, because of the weak adsorption of C_2H_4 on the Co²⁺ sites. It is logical to assume that a gaseous C_2H_4 molecule would add on the adsorbed NH₃ molecule at our reaction temperatures. Gas phase NH₃ + C_2H_4 addition reaction to form ethylamine is not thermodynamically favorable at our reaction temperatures. However, the strongly adsorbed NH₃ can lower the Gibbs free energy for the formation of an *adsorbed* amine molecule. The formation of the adsorbed ethylamine is supported by the TPRx experiment with the C_2H_4/O_2 mixture flowing through the NH₃

TABLE 1

Propane Ammoxidation^a on Co-ZSM-5

T (°C)	C ₃ H ₈ Conv. (%)	O ₂ Conv. (%)	Sel. to C ₂ H ₃ N (%)	Sel. to CO ₂ (%)	Sel. to C ₃ H ₆ (%)	Sel. to C ₂ H ₄ (%)	Sel. to C ₃ H ₅ N (%)
375	19	86	25	26	42	5	1
400	26	97	28	28	35	6	2
425	29	100	29	28	34	6	1
450	31	100	29	30	31	7	1

 a Feed composition: 5% hydrocarbon, 10% NH3, 6.5% O2; 0.2 g catalyst, F=100 cc/min.

FIG. 9. Acetonitrile formation pathway.

adsorbed Co-ZSM-5 catalyst (see Fig. 7). The TPR studies in Figs. 7-8 show the onset of the C_2H_4 , NH_3 , O_2 reaction at 350°C with O₂ depletion at 450°C. The drop in O₂ coincides with the sharp drop of acetonitrile formation and mirrors the formation of ethylamine in Fig. 7. Desorption and reaction studies of ethylamine in Fig. 8 show that ethylamine is converted to acetonitrile in the same temperature region; ethylamine was thus considered as a reaction intermediate. A series of sequential dehydrogenation steps are proposed to account for nitrile formation. The H atoms associated with N are thought to be more reactive than the ones on C because of the proximity between N and Co. We speculate that the dehydration between OH and the adsorbed $C_2H_5NH_2$ results in an amine anion adsorbed on Co^{2+} . The Co^{2+} is thus balanced by an negative charge generated from the zeolite lattice and by a negative charge of this amine anion. Subsequent dehydrogenation is proposed to proceed with O₂ insertion and dehydration. Although, we have not identified the adsorbed amine anion as an intermediate for C₂H₃N formation, we do know that C₂H₅NH₂ reacting with O₂ over Co-ZSM-5 does result in C₂H₃N and that when O₂ is depleted C₂H₅NH₂ desorbed. The desorption of C₂H₃N from the Co^{2+} sites is a reversible process. Although the strength of C_2H_3N adsorption on Co^{2+} sites is strong, the adsorption of NH_3 is even stronger. As shown in Fig. 6, a majority of the adsorbed C₂H₃N can be displaced by a low concentration (3000 ppm) of NH₃ at 100°C. Therefore, under the ammoxidation conditions, where a high concentration of NH₃ is available, the desorption of C₂H₃N should readily occur.

This proposed pathway is consistent with the results of ammoxidation of higher alkanes and alkenes. With propane, butane, or butene, we obtained C_2H_3N as a major nitrile product with only trace amounts of higher nitriles. This implies that the NH_3 + olefin addition step follows a Markovnikov orientation; i.e., NH_2 is added to the β -position of the carbon chains. With the formation of $C \equiv N$ and simultaneous breaking of a C-C bond, C_2H_3N is obtained. Thus, C_2H_3N is the most significant nitrile product regardless of hydrocarbon used. The higher hydrocarbon ammoxidation runs support the notion that addition and sequential dehydrogenation are necessary mechanistic steps for the ammoxidation reaction.

Based on the elementary steps (Eqs. [7]–[11]), one can derive a kinetic expression for C_2H_4 ammoxidation to C_2H_3N . For the sake of simplicity, Eqs. [9] and [10] will be combined as Eq. [12],

$$HO-Co-C_2H_5NH_2 + O_2 \rightarrow HO-Co-C_2H_3N + 2H_2O.$$
[12]

For C_2H_4 adsorption, we have the following equilibrium process,

$$C_2H_4 + Co(OH) = C_2H_4 - Co - OH.$$
 [13]

The following assumptions are made: (1) steady-state reaction; (2) Eqs. [7], [8], [11], and [13] are in equilibrium; and (3) adsorption site coverage is conserved as shown in Eq. [14],

$$\theta_{\rm NH_3} + \theta_{\rm C_2H_3N} + \theta_{\rm C_2H_4} + \theta_0 = 1,$$
 [14]

where, θ_{NH_3} , $\theta_{C_2H_3N}$, $\theta_{C_2H_4}$, and θ_0 are fractional coverage for the adsorption of NH₃, C_2H_3N , C_2H_4 , and fraction of vacant sites, respectively. Note, the coverage for $C_2H_5NH_2$ and O_2 are omitted here, assuming that they are too small to be significant. Based on the steady-state assumption, the C_2H_3N formation rate can be expressed as

$$r = r_{12} = k_{12} \theta_{C_2 H_5 N H_2} p_{O_2}.$$
 [15]

Based on the assumption [2], we have

r

$$\theta_{C_2H_5NH_2} = K_8 \theta_{NH_3} p_{C_2H_4}.$$
[16]

Similarly, one can express the coverage of other adsorbates as Eqs. [17]–[19],

$$\theta_{\rm NH_3} = K_7 \theta_0 p_{\rm NH_3}$$
 [17]

$$\theta_{C_2H_3N} = K_{-11}\theta_0 p_{C_2H_3N}$$
[18]

$$\theta_{C_2H_4} = K_{13}\theta_0 p_{C_2H_4};$$
[19]

 K_7 , K_8 , and K_{13} are equilibrium adsorption constant for NH₃, $C_2H_5NH_2$, and C_2H_4 , respectively; and K_{-11} is the desorption equilibrium constant for C_2H_3N . Based on Eq. [14], one obtains Eq. [20],

$$\theta_{\rm NH_3} = 1 - \theta_{\rm C_2H_3N} - \theta_{\rm C_2H_4} - \theta_0.$$
 [20]

Combining Eqs. [17]–[20], one obtains Eq. [21],

$$\theta_0 = \frac{1}{1 + K_7 p_{\rm NH_3} + K_{-11} p_{\rm C_2H_3N} + K_{13} p_{\rm C_2H_4}}.$$
 [21]

Combining Eqs. [21], [15]–[17], we have the following rate expression for C_2H_3N :

$$r = \frac{k_{12}K_8K_7p_{\rm NH_3}p_{\rm C_2H_4}p_{\rm O_2}}{1 + K_7p_{\rm NH_3} + K_{13}p_{\rm C_2H_4} + K_{-11}p_{\rm C_2H_3N}}.$$
 [22]

This resulting rate expression is consistent with our empirical reaction rate orders, fractional orders with respect to C_2H_4 and NH_3 , and first order with respect to $[O_2]$. Our TPD experiments with NH_3 , C_2H_4 , and C_2H_3N show that NH_3 adsorption is by far the strongest and NH_3 should be the dominant adsorbed species on the catalyst.

Nitrogen Formation Pathway

N₂ is a significant by-product for the ammoxidation reaction, and its formation should be minimized. Therefore, it is important to understand how N2 is formed, and we speculate that one obvious N₂ formation step is the NH₃/O₂ reaction (Eq. [23]). After all, NH₃ is the only, original source of nitrogen. A parallel, NH3 oxidation reaction would seem to be a first logical guess. However, a test reaction with NH_3/O_2 $(5\% \text{ NH}_3 \text{ and } 3\% \text{ O}_2 \text{ over } 0.1 \text{ g Co-ZSM-5 at } 450^{\circ}\text{C}) \text{ shows}$ that the rate of N₂ formation (3 mmol/g/h) is only 1/6 of that from the ammoxidation reaction under identical conditions $(+5\% C_2H_4)$. This suggests that NH₃ oxidation alone only accounts for a small fraction of N₂ generated. What about the total oxidation of the adsorbed amine intermediate? Simple stoichiometry tells us that C₂H₅NH₂ oxidation would yield four CO2 molecules for every N2 formed, which is not consistent with our observation that more N2 was produced than CO₂:

$$2NH_3 + 1.5O_2 = N_2 + 3H_2O.$$
 [23]

Obviously, another pathway for N₂ formation must exist, and this pathway may involve amine intermediates. This alternative N₂ formation pathway is proposed below (see the equation in Fig. 10), which involves nitrogen pairing between NH_3 and C_2H_5NH (Eq. [9]) under an oxidative environment. The adsorbed C₂H₅NH₂ can be converted to either C_2H_3N (Eq. [12]) or N_2 in the presence of NH_3/O_2 (Eq. [25]). This N₂ pathway (Eq. [25]) is essentially a N-N pairing step between these two N containing molecules. Since the hydrocarbon part of the amine complex is on top (far away from the Co^{2+} center) most of C_2H_4 is released into gas phase after N_2 is formed. C_2H_4 desorption (Eq. [27]) is thought to be fast, and its desorption is accelerated by the adsorption of NH₃. The gaseous C₂H₄ may then further react with an adsorbed NH₃ forming another adsorbed amine molecule (Eq. [8]). As a result, there is less hydrocar-





bon being totally oxidized compared to N_2 formation. However, there is always some C_2 hydrocarbons being oxidized to CO_2 . This proposal pathway explains our observations that more N_2 than CO_2 is formed during the ammoxidation reaction. The nitrogen pairing between amine and ammonia may be similar to the NH_3 - NH_3 pairing except that the amine intermediate may be more reactive.

Ethane Oxidative Dehydrogenation

For ethane ammoxidation, C_2H_6 needs to be first activated, and its activation is likely to be aided by O_2 . Ethylene is a significant co-product of C_2H_6 ammoxidation and is more reactive compared to C_2H_6 as an ammoxidation reactant. It is obvious that C_2H_4 is a primary product and a reactive intermediate for C_2H_6 ammoxidation. Thus, the first step for C_2H_6 activation would be its oxidative dehydrogenation. Specific steps are proposed in Fig. 11 (Eqs. [28], [29] and [26], [27]). We believe that C_2H_6 is activated by sequential oxidative H abstractions. The first H abstraction is accomplished by dehydration between an OH group and C_2H_6 . The adsorption of C_2H_6 on (with) Co^{2+} is not favorable in the presence of NH₃. However, this process becomes feasible at higher temperatures at which some vacant sites

$$C_2H_6 + \begin{array}{c} OH \\ C_0 \end{array} \longrightarrow \begin{array}{c} HQ \\ C_0 \end{array} \begin{array}{c} C_2H_6 \end{array} (28)$$

$$HQ \underset{Co}{\overset{c}{\longrightarrow}} \begin{array}{c} C_{2}H_{5} \\ C_{0} \end{array} + H_{2}O \qquad (29)$$

$$\begin{array}{c} C_2H_5 \\ C_0 \end{array} + 1/20_2 \longrightarrow HQ C_2H_4 \\ C_0 \end{array}$$
 (26)

$$\begin{array}{ccc} HQ & C_2H_4 & & OH \\ C_0 & & I \\ C_0 & & C_0 \end{array} + C_2H_4 \qquad (27)$$

FIG. 11. Scheme for C_2H_6 activation.

are available by desorbing NH₃. This assumption is consistent with the fact that more C_2H_4 and C_2H_3N are produced at higher temperatures. Assuming that every C_2H_3N formed requires one C_2H_4 molecule, C_2H_6 activation is extremely favored at high temperatures. On the other hand, our earlier report (2) show that the oxidative dehydrogenation of C_2H_6 to C_2H_4 is aided by the presence of NH₃. Thus it is possible that C_2H_6 is also activated on the cobalt sites that are partially coordinated with NH₃. Further studies are needed to depict a detailed picture of the NH₃ promotion.

CONCLUSIONS

The adsorption of NH₃ is very strong on the Co²⁺ sites of the Co-ZSM-5 catalyst, and its adsorption is essential for the formation of a C–N bond. The adsorption of C₂H₃N on the cobalt sites is also strong but can be displaced by a diluted stream of NH₃/He mixture at 100°C. During the ammoxidation reaction, C₂H₄, formed from the oxidative dehydrogenation of C₂H₆, adds to an adsorbed NH₃ species. This reactive intermediate has been identified as $C_2H_5NH_2$, which is readily dehydrogenated to form C_2H_3N . N_2 formation mainly comes from N–N pairing between the adsorbed NH₃ and an amine species (both on a single cobalt site) in an oxidative environment. The parallel NH₃/O₂ reaction only contributes to a minor portion of the N₂ formed.

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