Ammoxidation of Ethane to Acetonitrile over Metal–Zeolite Catalysts

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Ammoxidation of ethane to acetonitrile was studied over a variety of metal ion exchanged zeolite catalysts. We discovered that ethane can be efficiently converted to acetonitrile over some Co-zeolite catalysts. The type of zeolite is very important. In this regard, ZSM-5, beta, and NU-87 are superior to others. Among various transition metal cations, Co^{2+} is most active for acetonitrile formation. Kinetic studies on Co-ZSM-5 show that the nitrile formation rate is first order in NH_3, 0.5 order in C_2H_6, and 0.8 order in O_2. In the absence of O_2, no reaction occurs. A reaction scheme is proposed, whereby C_2H_4, a reactive intermediate, is thought to add to a strongly adsorbed NH_3 forming an adsorbed ethylamine, which is subsequently dehydrogenated to form C_2H_3N. © 1998 Academic Press

INTRODUCTION

There has been a great deal of interest in converting the relatively inert but inexpensive alkanes to value-added chemicals, such as olefins (via dehydrogenation), oxygenates (via oxidation), and higher hydrocarbons (via oxidative methane coupling). One commercially successful example of alkane conversion is the production of maleic anhydride by selective oxidation of butane over V−P−O-based catalyst (1). An alkane reacting with ammonia in the presence of oxygen (ammoxidation) can also form a carbon-nitrogen bond. In this regard, the recently announced acrylonitrile process by propane ammoxidation presents a breakthrough in alkane conversion. In this process, acrylonitrile, a unsaturated C_3 nitrile, is produced over V−Sb−Al based oxide catalyst (2). However, this type of catalysis has not been successfully extended to ethane. Acetonitrile, a saturated C_2 nitrile, cannot be efficiently produced using the catalysts that are effective for propane ammoxidation (3).

A few attempts by others were reported to carry out the ethane ammoxidation reaction using metal oxide catalysts. Using Al_2O_3 supported Nb−Sb oxides, Catani and Centi investigated ethane ammoxidation between 480 and 540°C with a contact time of 2.6 s (3). They obtained ethane to acetonitrile selectivity of 50%, CO selectivity of >20%,

and variable selectivities for CO_2 formation. HCN was also formed during this reaction with a relative constant selectivity of ~5%. Earlier, a USSR patent (4) disclosed that ethane was converted to acetonitrile with a maximum yield of 10% over a Cr−Nb−Mo oxide catalyst at 350–500°C with a contact time of 19 s. By-products of this reaction were not specified.

Recently, we reported (5) that Co-beta zeolite catalyst was very efficient for C_2H_6 ammoxidation to C_2H_3N (Eq. [1])

$$C_2H_6 + NH_3 + \tfrac{3}{2}O_2 = C_2H_3N + 3H_2O. \qquad [1]$$
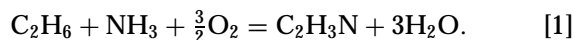
The C_2H_3N formation rate over Co-beta catalyst was 1–2 orders of magnitude higher than many metal oxide catalysts that are normally used for alkane oxidation or ammoxidation reactions, e.g., VPO, $SbVO_4$ and those used in Refs. (3) and (4). In this paper, we present a more complete picture of using metal-exchanged zeolites to catalyze the C_2H_6 ammoxidation reaction. Our interest in using metal-exchanged zeolites as catalysts to activate alkanes derives from our earlier experience (6, 7) with the $NO_x/CH_4/O_2$ reaction over Co-zeolite catalysts, where an alkane, CH_4, is activated by the adsorbed NO_x species on the Co^{2+} sites. Here, we wish to show that metal cations, especially Co^{2+}, when stabilized in a zeolite environment, have unusual catalytic properties that are not commonly seen with traditional metal oxide systems. The way the alkane is activated in this case is quite different from the $NO_x/CH_4/O_2$ reaction, and a reaction scheme is proposed for C_2H_6 ammoxidation over Co-zeolite catalysts.

EXPERIMENTAL

The metal–zeolite catalysts were prepared by the cation exchange method. Typically, an NH_4-zeolite was exchanged with a metal cation in an aqueous solution, e.g. cobalt acetate solution, at an elevated temperature. As an example, the preparation of Co-ZSM-5 is described in detailed here, and other catalysts can be found in our earlier publications (8–10). A 10-g NH_4-ZSM-5 sample obtained from VAW Aluminum AG, Germany (Si/Al = 12), was exchanged with 1 liter of 0.01 M cobalt acetate aqueous solution (pH = ~6) at 70–80°C for 24 h. After two identical exchanges, the

resulting zeolite slurry was filtered, washed with 1 liter de-ionized water, and then filtered again. Finally, the zeolite was dried at 110°C overnight. Elemental analysis showed that the Co/Al atomic ratio of this catalyst was 0.49, or 98% of the cation exchange capacity. (Note that for divalent cations, such as Co^{2+}, a Co/Al atomic ratio of 0.5 is equivalent to 100% of its theoretical exchange capacity.) The cobalt loading of this catalyst was 3.8% by weight.

Some zeolites were obtained commercially and others were prepared in-house. Zeolite H-beta (Si/Al = 13) was obtained from PQ Corporation, Na-mordenite (LZ-M5), Na-Y (LZ Y-52) (Si/Al = 2.5), and Na-A from Union Carbide, and K, Na-ferrierite from Tosoh. ZSM-11, chabazite, offretite, and NU-87 were synthesized according to the published procedures (11–14). Na or K zeolites were first converted to NH_4-zeolite (10) prior to metal ion exchange.

The Co/alumina-silica catalyst was prepared by exchanging amorphous silica-alumina (12 wt% Al, obtained from W.R. Grace & Co., Davison Division) with Co^{2+} in a 1-liter, 0.02 M cobalt acetate solution. This catalyst had a cobalt loading of 2.98 wt%. The CoO/Al_2O_3 catalyst was prepared by impregnating γ-alumina with a cobalt nitrate solution using the incipient wetness technique; the preparation was dried at 110°C and subsequently calcined in 10% O_2/He mixture at 500°C for 1 h. The Co loading was calculated as 10 wt%.

The reaction runs were made using a microreactor system operating in a steady state, plug-flow mode at atmospheric pressure. The reactor was a U-shaped quartz tube with 1/4″ OD at the inlet section and 3/8″ OD at the outlet section. The catalyst was located in the outlet section at the center of the electrical furnace which surrounds the reactor tube. Quartz wool plugs were used to support and secure the catalyst bed. The feed delivery system consists of four flow channels (NH_3, C_2H_6, O_2/He mixture, and He), each controlled by an independent mass flow controller, and these channels merged before proceeding to the reactor inlet. Typically, a total flow rate of 100 ml/min and a catalyst weight of 0.2 g were used for each run. A catalyst was normally pretreated with flowing helium at 500°C for 1 h before a reaction run. The reactor effluent was analyzed by two gas chromatographs in series, both equipped with a thermal conductivity detector (TCD). Hydrocarbons, nitriles, CO_2, and N_2O were separated by a Porapak Q column, while N_2, O_2, and CO were separated by a molecular sieve 5A column. The reactor system was also connected to an on-line mass spectrometer to confirm the product identification. All routine product analyses were carrier out with the GC technique. The conversion and selectivity are defined as:

Conversion of C_2H_6,

$$X = \left(\sum_i y_i n_i \right) \bigg/ \left(y_A n_A + \sum_i y_i n_i \right), \qquad [1]$$

Selectivity of product,

$$P_i, S_i = y_i n_i \bigg/ \sum_i y_i n_i, \qquad [2]$$

where y_i and y_A are the mole fractions of products P_i and C_2H_6, respectively; n_i and n_A are the number of carbon atoms in each molecule of product P_i and C_2H_3N, respectively, and all the terms were evaluated for the exit stream. The major products of C_2H_6 ammoxidation reaction over Co-zeolite catalysts are C_2H_3N, C_2H_4, CO_2, and N_2. Other by-products also produced were very small quantities of N_2O, C_3H_5N (propionitrile), and HCN, and these by-products are insignificant, compared to the major products. For the conversion and selectivity calculations, all products and by-products were included.

RESULTS

Effect of Zeolite Topology

The effect of zeolite topology on the catalytic activity and selectivity was tested over a variety of cobalt-exchanged zeolites. The reaction results (conversion and selectivities) along with catalyst compositions are summarized in Table 1. Cobalt exchanged amorphous silica-alumina and impregnated CoO on γ-alumina are also included for comparison. Dramatic differences in catalytic performance were observed for these zeolite catalysts. At 450°C, Co^{2+} exchanged ZSM-5, beta, and NU-87 have comparable C_2H_6 conversions (27–38%) and C_2H_3N selectivities (46–51%). Co-ZSM-11 has only a fraction the conversion (11%), compared to the first three catalysts, and the conversion over Co−Y is even lower (8%). Co-mordenite has a moderate C_2H_6 conversion and C_2H_3N selectivity, 24 and 28%, respectively. Interestingly, Co-ferrierite, the catalysts most active for $NO/CH_4/O_2$ reaction (10), is a poor catalyst for the C_2H_6 ammoxidation reaction (conversion = 2%, selectivity = 19% at 450°C). Co-offretite showed a moderate conversion, but a low selectivity, to C_2H_3N. For most of these zeolite catalysts, the selectivity to CO_2 is normally low (<20%) and that to total C_2 ($C_2H_4 + C_2H_3N$) is >70%.

However, on Co-A zeolite, a high selectivity to CO_2 was observed, and the selectivity to C_2H_3N is low. As a reference, a nonzeolite catalyst, Co^{2+} exchanged silica-alumina, was tested for this reaction and found to be moderately selective and somewhat active. The Al_2O_3 supported CoO, however, did not produce any detectable amount of C_2H_3N.

Effect of Metal Cation

The effect of metal cation on the catalytic performance is summarized in Table 2. Cu-ZSM-5 is inactive for nitrile

TABLE 1

Ethane Ammoxidation[a] over Co-Zeolites

Catalyst name	Catalyst comp.[b]	Temp (°C)	Conv. of C_2H_6 (%)	Sel. to C_2H_3N (%)	Sel. to C_2H_4 (%)	Sel. to CO_2 (%)	Total C_2[c] sel. (%)	Apparent TOF[d] $\times 1000$ sec^{-1}
Co-ZSM-5	11.0; 0.49 3.83%	450	38.2	48.7	28.5	20.6	77.2	5.3
Co-beta	12.9; 0.42 2.32%	450	35.3	50.8	22.9	22.1	73.7	8.5
Co-NU-87	16.9; 0.49 2.85%	450	26.7	46.3	35.6	14.1	81.9	4.8
Co-ZSM-11	30.2; 0.39 1.79%	450	11.1	39.2	44.6	12.2	83.8	2.7
Co–Y	2.5; 0.58 13.2%	450	8.4	60.0	17.8	15.6	77.8	0.4
Co-mordenite	5.2; 0.40 4.89%	450	23.6	27.5	55.0	15.4	82.5	1.5
Co-ferrierite	8.3; 0.50 4.3%	450	2.2	18.9	63.0	18.0	81.9	0.1
Co-offretite	2.8; 0.39 8.9%	450	33.7	7.9	59.5	26.9	67.4	0.3
Co-Linde A	1.0; 0.31 10.2%	400	1.6	28.6	14.3	57.1	42.9	0.05
		450	38.6	9.3	43.8	46.3	53.1	0.4
Co-silica-alumina	4.7; 0.22 3.0%	500	10.6	24.5	65.4	9.9	89.9	1.0
CoO/Al_2O_3	—; — 10%	450	4.6	0.0	65.1	30.2	65.1	0

[a] Feed: 5% C_2H_6, 10% NH_3, and 6.5% O_2, He balance; F = 100 cc/min; 0.2 g catalyst.
[b] The numbers are Si/Al ratio, Co/Al ratio, and Co loading as weight percent, respectively.
[c] Total C_2 = acetonitrile + ethylene.
[d] The apparent TOFs are calculated based on the assumption that 100% of the cobalt is dispersed and each cobalt center is on an active site.

formation, with C_2H_4 and CO_2 being the major products. Ni^{2+}, Mn^{2+}, and Fe^{3+} exchanged ZSM-5 resulted in moderate acetonitrile selectivities (10–20%) and C_2H_6 conversions compared to Co-ZSM-5. The relatively low conversion of Fe-ZSM-5 compared to Mn-ZSM-5 and Ni-ZSM-5 is probably due to its lower Fe content (1.0% by weight). These differences are clearly apparent by looking at the column of apparent TOFs (turnover frequencies) in Table 2. Ag-ZSM-5 and the precious metal-ZSM-5 catalysts are basically inactive for nitrile formation. For Ag-ZSM-5, the reaction products are C_2H_4 and CO_2. Pd-ZSM-5 and Pt-ZSM-5 produce primarily CO_2 by ethane combustion with moderate conversions ~20%. Rh-ZSM-5 showed surprising results; the conversion of C_2H_6 is extremely low (2%) at 450°C. Upon careful analysis of all products, including N_2 formation, we found ammonia oxidation to N_2 and H_2O was a dominant reaction with Rh-ZSM-5, which resulted in a complete depletion of O_2. Thus, C_2H_6 remained essentially intact; there was very little CO_2 formation. This is consistent with our earlier report that Rh-ZSM-5 is an effective catalyst for removing NH_3 in wet streams at low

temperatures (15). It is obvious that Co is a metal of choice for this ammoxidation reaction.

Reaction Studies on Co-ZSM-5 Catalyst

Figure 1 shows the catalytic performance of Co-ZSM-5 as a function of temperature. The conversion of C_2H_6 increases with temperature at low temperatures but levels-off at $T > 425$°C. The level-off of conversion is apparently due to the depletion of O_2 in the reactor as evidenced by the complete conversion of O_2 at $T \geq 425$°C. The selectivity to acetonitrile mildly decreases with increasing temperature (from 60% at 350°C to 45% at 475°C). The selectivity to C_2H_4 slightly increases with temperature at $T < 400$°C and tends to level-off at high temperatures. Interestingly, the CO_2 formation is relatively constant between 350 and 475°C, and its selectivity is ~20%.

The catalysts are very stable under the ammoxidation conditions. A 5-day continuous run over a Co-ZSM-5 catalyst revealed no appreciable change in catalytic performance. Further, we discovered that water did not have any

TABLE 2

Ethane Ammoxidation[a] over Metal-ZSM-5 Catalysts

Metal	Catalyst comp.[b]	Reaction temp. (°C)	Conv. of C_2H_6 (%)	Sel. to C_2H_3N (%)	Sel. to C_2H_4 (%)	Sel. to CO_2 (%)	Total C_2[c] sel. (%)	Apparent TOF[d] $\times 1000$ sec^{-1}
Co	11.0; 0.49 3.83%	450	38.2	48.7	28.5	20.6	77.2	5.3
Cu	13.5; 0.65 4.46%	450	15.0	0.8	65.6	33.6	66.4	0.03
Ni	11.0; 0.50 3.92%	450	11.9	19.4	50.5	30.1	69.9	0.6
Fe	14.4; 0.17 1.0%	450	9.2	16.2	39.3	42.1	55.5	1.6
Mn	12.7; 0.31 3.34%	450	26.9	11.7	12.6	60.2	24.3	1.0
Pd	11.1; 0.37 4.54%	400	20.3	1.2	7.5	91.2	8.7	0.1
Ag	14.1; 0.71 6.96%	450	13.7	0.0	42.0	54.3	42.0	0
Rh	11.5; 0.23 2.66%	450	2.0	0.0	0.0	100.0	0.0	0
Pt	14.2; 0.12 2.55%	450	21.0	2.0	0.0	98.0	2.0	0.6

[a] Reaction conditions: The feed consisted of 5% C_2H_6, 10% NH_3, and 6.5% O_2, balance by He. The total flow rate was 100 cc/min. A 0.2 g sample was used for all runs.

[b] The numbers are Si/Al atomic ratio, metal/Al atomic ratio, and metal loading as weight percent.

[c] Total $C_2 = C_2H_3N + C_2H_4$.

[d] The apparent TOFs are calculated based on the assumption that 100% of the cobalt is dispersed and each cobalt center is on an active site.

influence on this reaction. Addition of 5% H_2O in the middle of a normal reaction run (with 10% NH_3, 5% C_2H_6, and 6.5% O_2 as a feed) did not produce any change in catalytic performance. Note, under our normal reaction conditions,
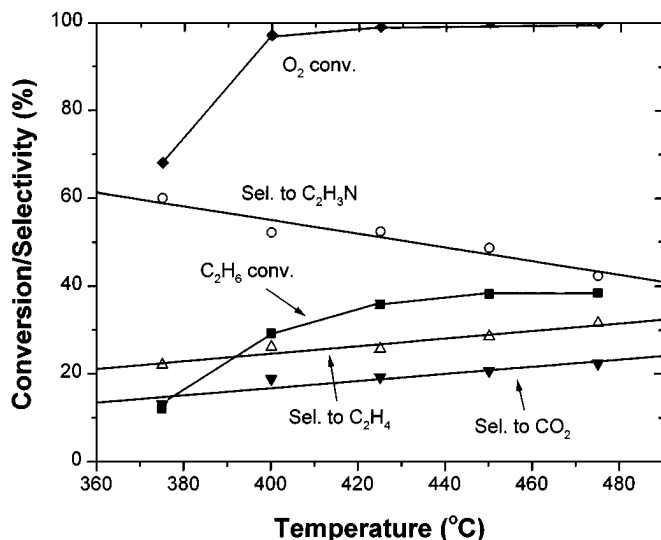

FIG. 1. Ethane ammoxidation over Co-ZSM-5 as a function of reaction temperature. The feed consists of 10% NH_3, 5% C_2H_6, 6.5% O_2 balanced in He.

more than 10% H_2O is produced as a by-product. The lack of water inhibition for this reaction is not surprising. As will be discussed later, ammonia adsorption is a necessary step for the C_2H_6 ammoxidation reaction, and water is a much weaker Lewis base than ammonia and cannot compete with ammonia for adsorption sites.

As shown in Fig. 2, the dependence of conversion and selectivity on the C_2H_6 partial pressure was carried out at 400°C with 0.1 g Co-ZSM-5 catalyst, where the partial pressure of C_2H_6 was systematically varied with other concentrations (10% NH_3, 6.5% O_2) and total flow rate (100 cc/min) was kept constant. Under this set of conditions, all the reactants are in sufficiently high concentrations during the course of the reaction so that the reaction rate is not restricted by the availability of other reactants, except C_2H_6. The C_2H_6 conversion decreases with increasing $[C_2H_6]$. The selectivity to C_2H_3N is relatively constant (~45%), while the C_2H_4 and CO_2 selectivities decrease and increase, respectively, with increasing $[C_2H_6]$.

The C_2H_3N formation rate (mmol/g/h) was calculated as a function of $[C_2H_6]$ from its log–log plot. Based on the expression of the reaction rate,

$$r = d[C_2H_3N]/dt = k[C_2H_6]^n[NH_3]^m[O_2]^p, \quad [3]$$

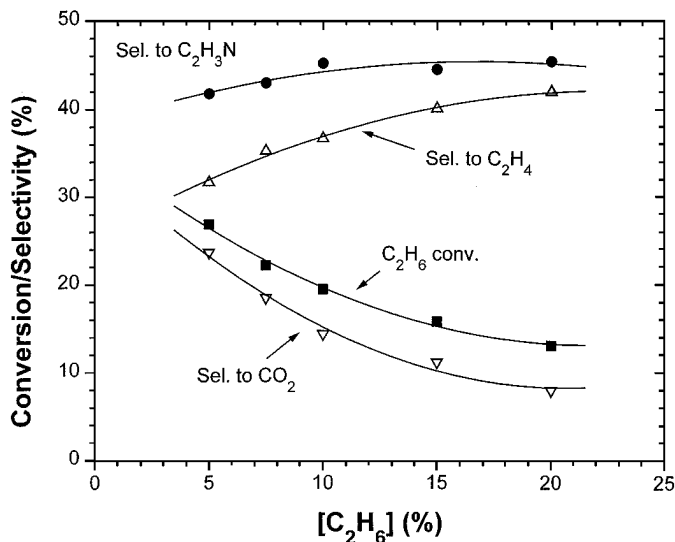the empirical reaction order for C_2H_3N rate with respect

FIG. 2. Ethane ammoxidation over Co-ZSM-5 as a function of C_2H_6 partial pressure. The feed consists of 10% NH_3, 6.5% O_2, and variable levels of C_2H_6.

FIG. 4. Ethane ammoxidation over Co-ZSM-5 as a function of O_2 partial pressure. The feed consists of 5% C_2H_6, 10% NH_3, and variable levels of O_2.

C_2H_6 partial pressure (n) was found to be 0.5. Similar to the C_2H_3N rate, the order for the C_2H_4 formation rate is 0.62 and that for the CO_2 rate is a negative number.

Figure 3 shows the C_2H_6 conversion and product selectivities as a function of [NH_3]. C_2H_6 conversion increase monotonically with [NH_3], and the increase appears linear below [NH_3] < 10%. Similarly, the C_2H_3N selectivity increases with the [NH_3] in the feed. In contrast, the C_2H_4 selectivity is relatively constant with the change of NH_3 concentration. With increasing [NH_3], the CO_2 selectivity

becomes lower. The C_2H_3N rate was found to be first order in [NH_3] ($m = 1$). The CO_2 rate change is parallel to that of C_2H_6 at [NH_3] < 10%, but decreases at higher NH_3 levels. It is interesting to note that the ethene production rate increases quite dramatically with increasing [NH_3] by an order of 0.78.

In the absence of O_2, no reaction products were observed. Upon introducing O_2 into the reacting system, C_2H_4 and C_2H_3N were produced along with some CO_2 (see Fig. 4). The C_2H_6 conversion increases quite linearly with the O_2 level (6% at [O_2] = 1%, 18% at [O_2] = 6.5%). The selectivity to C_2H_3N reaches the maximum at [O_2] = 4–5%. The selectivity to C_2H_4 decreases with O_2 level at low [O_2] but stabilizes at relatively high [O_2]. CO_2 selectivity increases with the O_2 level in the feed. The empirical reaction orders of the products in O_2 partial pressure are interesting. The C_2H_3N and C_2H_4 formation rates are fractional order in O_2, 0.69, and 0.43, respectively, and the rate of CO_2 formation increases rapidly with increasing the O_2 level.

To check the possibility that C_2H_4 might be an intermediate hydrocarbon for the C_2H_6 ammoxidation, an experiment with an $C_2H_4/NH_3/O_2$ feed mixture was conducted under the same conditions. In the case of C_2H_4 ammoxidation, two major products are formed, C_2H_3N and CO_2, with C_2H_3N being the dominant product (~80%). As shown in Table 3, C_2H_4 ammoxidation is more efficient than C_2H_6 ammoxidation; the C_2H_3N yield for the C_2H_4 ammoxidation reaction is more than twice of that for the C_2H_6 ammoxidation reaction.

As a control experiment, we tested oxidative dehydrogenation of C_2H_6 to C_2H_4 ($C_2H_6 + \frac{1}{2}O_2 \rightarrow C_2H_4 + H_2O$) over the same catalyst (Co-ZSM-5) under the same reaction conditions, except no NH_3 was added (see Table 4). We
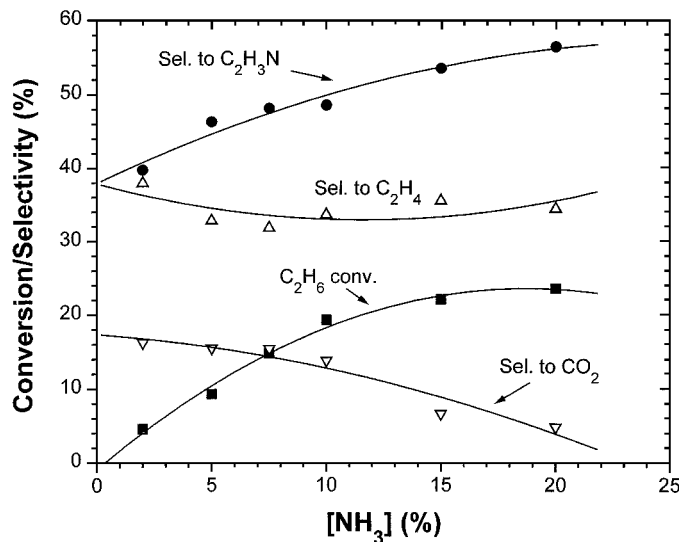

FIG. 3. Ethane ammoxidation over Co-ZSM-5 as a function of NH_3 partial pressure. The feed consists of 5% C_2H_6, 6.5% O_2, and variable levels of NH_3.
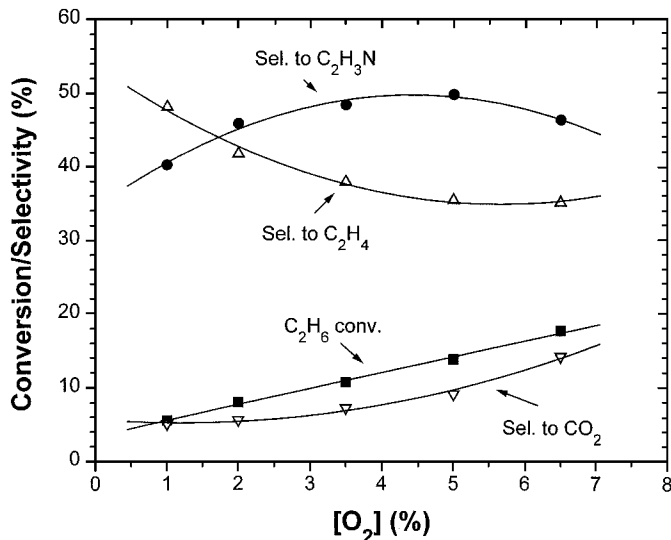
TABLE 3

Ethylene Ammoxidation[a] on Co-ZSM-5

Reaction temperature (°C)	Conversion of C_2H_4 (%)	Selectivity to C_2H_3N (%)	Selectivity to CO_2 (%)	C_2H_3N yield (%)
400	48.4	81.4	17.2	39.4
425	53.4	79.8	18.8	42.6
450	57.7	77.0	21.4	44.4

[a] Reaction conditions: The feed consisted of 5% C_2H_4, 10% NH_3, and 6.5% O_2; balance by He. The total flow rate was 100 cc/min. A 0.2 g sample was used for all runs.

found a very low C_2H_4 yield (3.6% at 450°C). Interestingly, upon the addition of a small amount of NH_3, in addition to C_2H_3N formation, the C_2H_4 yield increased to 10.9%. It appears that the presence of NH_3 promotes the oxidative dehydrogenation of C_2H_6 to C_2H_4.

DISCUSSION

Efficient conversion of C_2H_6 to C_2H_3N has not been demonstrated over metal oxide catalysts that are typically used for C_3H_6 or C_3H_8 ammoxidation to acrylonitrile. Perhaps, this can be attributed to the fundamental difference in molecular structure between acrylonitrile and acetonitrile and the tendency of the oxide catalysts to dehydrogenate C_3 hydrocarbons. We have shown that for the C_2H_6 ammoxidation reaction, some metal-exchanged zeolite catalysts (e.g., Co-beta) are much more efficient that metal oxide catalysts (5). Therefore, metal exchanged zeolites must exhibit some suitable properties to catalyze the C_2H_6 ammoxidation. However, as shown in Table 1, not all zeolites are equal; dramatic differences in catalytic performance were found when they are used as supports for Co^{2+}. These differences are clearly apparent by looking at the column of apparent TOFs.

The three catalysts (Co-ZSM-5, Co-beta, and Co-NU-87), most effective for the ammoxidation reaction, share some common features in zeolite topology, i.e., multidimen-

TABLE 4

Ethane Oxidation[a] (a Reference Reaction) over Co-ZSM-5

Reaction temp. (°C)	Conversion of C_2H_6 (%)	Selectivity to C_2H_4 (%)	Selectivity to CO_2 (%)	Yield of C_2H_4 (%)	C_2H_4 yield for $C_2H_6/NH_3/O_2$[b] (%)
400	15.6	22.4	76.7	3.5	7.6
450	49.6	7.3	76.7	3.6	10.9

[a] Feed composition: 5% C_2H_6, 6.5% O_2, balance by He; total flow rate = 100 cc/min. A 0.2 g catalyst was used for the runs.
[b] Feed composition: 5% C_2H_6, 6.5% O_2, and 5% NH_3.

sional channel structures with channel openings of either 10- or 12-member rings (or 10-ring, 12-ring, in short), and it appears that these features are important for the catalysis of the C_2H_6 ammoxidation reaction. ZSM-5 is a three-dimensional zeolite with an intersecting, 10-ring channel system between the straight (5.3 × 5.6 Å) and the sinusoidal (5.1 × 5.5 Å) channels. Beta is a three-dimensional zeolite with mutually perpendicular intersecting 12-ring channels (5.5 × 5.5 and 7.6 × 6.4 Å) (16). NU-87 has a two-dimensional, 10-ring channel system. But these 10-rings are not intersecting. Adjacent one-dimensional 10-ring channels are linked by short 12-ring channels to create a two-dimensional network, but access to these bridging sections is possible only via the 10-ring windows (17). The dimensions of the 10-ring channels normal to [201] are alternatively 4.6 × 6.2 and 4.8 × 5.9 Å along each channel, and the 12-ring linkage is approximately 5.3 × 6.8 Å. The above zeolite catalysts have Si/Al ratios between 11–17 with comparable Co^{2+} exchange levels (84–98%).

Co-ZSM-11 and Co–Y are two catalysts that fall in the above structure category (multidimensional structure with 10- or 12-ring channels) but showed lower activities than expected. The topology of ZSM-11 resembles that of ZSM-5, except that the intersecting, 10-ring channels are straight in both directions. The lower activity of this Co-ZSM-11 catalyst may be due to the much smaller number of Co^{2+} sites in this zeolite, compared to the ZSM-5 catalyst (because of its higher Si/Al ratio). The low activity of Co–Y catalyst is not yet understood despite its three-dimensional open structure and abundant Co^{2+} cations in the zeolite. This suggests that some other factors are also important for this reaction.

Co-zeolites that do not exhibit the above structural features and showed lower activity include Co-OFF, Co-MOR, Co-FER, and Co-A. Offretite has a three-dimensional, intersecting 12-ring (6.7 × 6.8 Å), 8-ring (4.9 × 3.6 Å) channel systems, and mordenite is a one-dimensional 12-ring (6.5 × 7.0 Å) channel system (not including the 8-membered side pocket). Diffusional limitation may offer one possible explanation of the low activity of these Co-zeolites. Reaction 1 is a very fast reaction occurring on the exchanged cation sites and requires the availability of three reactants, C_2H_6, NH_3, and O_2, within the zeolite channels. The 8-rings, because of lower molecular diffusivity in these channels, may slow down the overall diffusivity, exerting a rate-limiting influence. When this happens, the zeolite is effectively a one-dimensional structure as far as the reaction is concerned. A one-dimensional channel structure does not permit effective mixing of the reactants which are necessary for this reaction. Therefore, it is not difficult to understand that Co-ferrierite is the least active catalyst. For Co-A (a three-dimensional, 8-ring, cage structure), at 400°C the conversion is very low, <2%, and at 450°C the conversion increased, but the selectivity decreased. We suspect

that at 450°C the framework of zeolite A was already substantially dealuminated and, perhaps, partially collapsed under the ammoxidation conditions, where several percentages of H_2O may exist as a product. Consequently, the activity shown at this temperature on Co-A may have been due to the catalysis that occurred at the exterior or the amorphous part of the zeolite, resulting in largely CO_2 and C_2H_4.

Zeolites, with appropriate structural and compositional features, are excellent supports for Co^{2+}, e.g. ZSM-5, beta, and NU-87, but are not unique for C_2H_6 ammoxidation. Co^{2+} exchanged into amorphous silica-alumina gave a low C_2H_3N yield. Its conversion was barely detectable at 450°C and only 11% at 500°C. On the other hand, alumina-supported CoO is inactive for producing C_2H_3N, suggesting a fundamental difference between the cobalt species in a zeolite environment and that on a conventional oxide support.
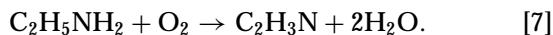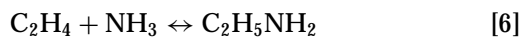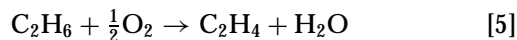
While the support phase is important for the ammoxidation reaction, an effective metal cation as a catalytic center is essential. The very different reaction results obtained over a number of metal cations illustrate the importance of intrinsic selectivity of a metal cation. Na and H-ZSM-5 are inert for the production of nitrile. Some metals, e.g., Rh, preferentially catalyze the NH_3 oxidation reaction to mainly N_2 and, because of this parallel reaction, the formation of the C–N bond is discouraged over these metal catalysts. In this regard, Co^{2+} proved to be the most active and selective species. It should also be pointed out that the chemical state of cobalt, as an isolated divalent cation, is also important. When cobalt exists as an oxide (CoO or Co_3O_4), it does not provide any activity for C_2H_3N production.

An important observation is that a large amount of C_2H_4 is formed during the ammoxidation reaction, and the total C_2 ($C_2H_4 + C_2H_3N$) selectivity is relatively constant (~80%) over a variety Co-zeolite catalysts. Because of the inactive nature of alkanes versus alkenes, we believe that the reactive hydrocarbon is C_2H_4 and that converting C_2H_6 to C_2H_4 via oxidative dehydrogenation is the first step of its activation. This notion was further reinforced by the results of the C_2H_4 ammoxidation reaction. The data in Table 3 show that a higher concentration of C_2H_4 (compared to instantaneous $[C_2H_4]$ during the $C_2H_6/NH_3/O_2$ reaction) results in a higher C_2H_3N formation rate, which is entirely consistent with the mechanistic scheme (*vide infra*).

Thus, the oxidative dehydrogenation of C_2H_6 to C_2H_4 is a necessary step for its ammoxidation reaction. However, as shown in Table 4, NH_3 plays a very important promoting role in this step. In the absence of NH_3, the C_2H_6/O_2 reaction produced mostly CO_2 (77%) and carbon deposition on the catalyst was found, as evidenced by the blackening of the catalyst sample. A dramatic change was observed when 5% NH_3 was added to the feed. In addition to the formation of C_2H_3N, a much larger amount of C_2H_4 was found. If C_2H_3N is formed through the C_2H_4 intermediate, the total amount

of C_2H_4 formed (consumed + unconsumed) will be even larger. The origin of this positive effect by NH_3 addition is not yet understood.

Based on the product analyses and control reaction tests, the following key reaction steps are proposed for C_2H_3N formation (Eqs. [5]–[7]). The first step is oxidative dehydrogenation of C_2H_6 to C_2H_4. This reaction is promoted by NH_3 and is relatively fast. This reaction step is evidenced by the substantial amount of C_2H_4 observed. The second step is the addition of C_2H_4 to adsorbed NH_3 forming adsorbed ethylamine, $C_2H_5NH_2$, as a reactive intermediate. This intermediate is quickly consumed by further reacting with O_2 (oxidative dehydrogenation) forming a more stable product, C_2H_3N (Eq. [7]),
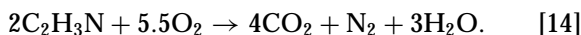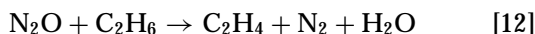
$$C_2H_6 + \tfrac{1}{2}O_2 \rightarrow C_2H_4 + H_2O \qquad [5]$$

$$C_2H_4 + NH_3 \leftrightarrow C_2H_5NH_2 \qquad [6]$$

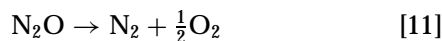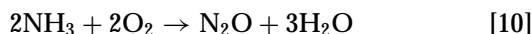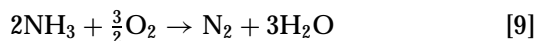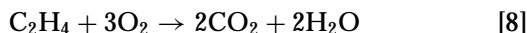$$C_2H_5NH_2 + O_2 \rightarrow C_2H_3N + 2H_2O. \qquad [7]$$

To check the validity of the last step, oxidation of monoethylamine was also carried out over the same Co-ZSM-5 catalyst. A feed consisting of ~2% monoethylamine and 7.5% O_2 (balance by He) was passed over the catalyst at 375 and 400°C at a flow rate of 150 cc/min. Acetonitrile was observed as a dominant product. Thus, this experiment supports the proposal that ethylamine is a reactive intermediate for nitrile formation. (Note, additional evidence for ethylamine will be reported in a subsequent manuscript (18).)

The origin of the CO_2 poses another interesting question. CO_2 could come from the combustion of ethane, ethene, or acetonitrile. Because C_2H_4 is more reactive than C_2H_6, we believe that CO_2 is likely a secondary product rather than a reaction product of C_2H_6 combustion. It is postulated that C_2H_4, a primary product, undergoes parallel reactions: to C_2H_3N via ammoxidation (Eqs. [6] and [7]) and to CO_2 via combustion (Eq. [8]). This postulation is supported by the kinetic results, where the CO_2 selectivity decreases with increasing $[NH_3]$. Higher $[NH_3]$ favors reaction [6] (C_2H_4/NH_3 addition reaction) and discourages the parallel C_2H_4 combustion reaction (Eq. [8]). In addition, high concentrations of NH_3 (a strong Lewis base) would cover most of the reactive sites with adsorbed NH_3 and minimize the number of vacant sites for C_2H_4 combustion. On the other hand, we also demonstrated that the C_2H_3N/O_2 reaction also produced some CO_2 at $T > 400$°C. However, we believe that only a small portion of the CO_2 is produced via this route under ammoxidation conditions.

On the basis of large amount of C_2H_4 formation, we believe the oxidative dehydrogenation of C_2H_6 to C_2H_4 can be easily carried out over Co-ZSM-5 under our reaction conditions. The last step, converting amine to nitrile, is a thermodynamically favored reaction and was demonstrated

over Co-ZSM-5 catalysts. Therefore, neither of these reactions can be a rate-limiting step. The second step (Eq. [6]), amine formation on adsorption sites, is thus likely a rate-determining step for this ammoxidation reaction. This reaction is a reversible reaction and is shifted to the right side with instantaneous removal of amine product via its conversion to nitrile.

Other reactions also occur during the ammoxidation process (Eqs. [8]–[14]). Ammonia oxidation to N_2 and H_2O is a most significant side reaction (Eq. [9]). On a Co-ZSM-5 catalyst ~50% of the NH_3 consumed goes to N_2 at $T > 400°C$. On some catalysts, e.g. Rh-ZSM-5, NH_3 oxidation to N_2 is a dominant reaction, which depletes all the O_2 in the feed, therefore shutting down the ammoxidation reaction. Reaction [11] is known to occur on Co-ZSM-5 (9) and is expected to take place in this ammoxidation process. Trace amounts of HCN (22 ppm at 450°C on Co-ZSM-5) were observed, and it may serve as an intermediate for propionitrile formation (Eq. [13]).

$$C_2H_4 + 3O_2 \rightarrow 2CO_2 + 2H_2O \quad [8]$$

$$2NH_3 + \tfrac{3}{2}O_2 \rightarrow N_2 + 3H_2O \quad [9]$$

$$2NH_3 + 2O_2 \rightarrow N_2O + 3H_2O \quad [10]$$

$$N_2O \rightarrow N_2 + \tfrac{1}{2}O_2 \quad [11]$$

$$N_2O + C_2H_6 \rightarrow C_2H_4 + N_2 + H_2O \quad [12]$$

$$C_2H_4 + HCN \rightarrow C_3H_5N \quad [13]$$

$$2C_2H_3N + 5.5O_2 \rightarrow 4CO_2 + N_2 + 3H_2O. \quad [14]$$

CONCLUSIONS

We discovered that some metal-exchanged zeolites were efficient catalysts for the ammoxidation of C_2H_6 to C_2H_3N. The effectiveness of a Co-zeolite catalyst is greatly influenced by the zeolite topology. Zeolite structures with multidimensionality, proper channel opening (10- and 12-member rings), and sufficient ion exchange capacity are essential requirements. ZSM-5, beta, and NU-87 are the best zeolite hosts. The active centers for this catalysis are the metal cations, and Co^{2+} is found to be the most effective one among the many transition metal ions studied. Over a Co-ZSM-5 catalyst, all three feed components are essential for C_2H_3N formation, and O_2 is a driving force for the ammoxidation reaction. Without the presence of NH_3, CO_2 is the dominant product. We propose that C_2H_3N is formed via three key reaction steps, whereby C_2H_4, an reactive intermediate, is formed by oxidative dehydrogenation of C_2H_6 and then adds onto an adsorbed NH_3 molecule to form an adsorbed amine species, which subsequently dehydrogenates to C_2H_3N.

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