Ammonoxidation of Ethane to Acetonitrile and Ethylene: Reaction Transient Analysis for the Co/HZSM-5 Catalyst

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ABSTRACT: Ethane ammonoxidation to acetonitrile and ethylene over the Co/HZSM-5 catalysts was revisited based on both transient and steady-state performance evaluation to elucidate the structure/reactivity relationships. We suggested that the exchanged Co$^{2+}$ cation encapsulated in the zeolite favors the formation of acetonitrile and ethylene, whereas nanosized cobalt oxide particles without close proximity with the HZSM-5 only favor CO$_2$ formation. Excess Bronsted acid sites of the zeolites may act as a reservoir for NH$_3$, which inhibits the CO$_2$ formation through the NH$_3$-mediated oxidative dehydrogenation mechanism. According to the transient kinetic analysis, the time constants $\tau$ from the back-transient decay for NH$_3$ and CO$_2$ are both 7.7 min, which decreased to 2.7 min for acetonitrile and further decreased to 3–4 s for ethane, ethylene, and O$_2$. Assuming first-order reaction kinetics, the rate constants for the formation of acetonitrile and CO$_2$ are 0.37 and 0.13 min$^{-1}$, respectively, from their corresponding reactive intermediates.

1. INTRODUCTION

The current shale gas revolution has revitalized research interests on the catalytic conversion of light C$_1$–C$_3$ alkanes. While significant attention has been devoted to methane and propane conversion, a catalytic process for ethane conversion has been relatively less concerned probably due to the fact that it is difficult to compete with the well-established steam cracking process (although it is high carbon and energy-intensive). The catalytic processes for ethane conversion include oxidative/nonoxidative dehydrogenation (ODH),$^{1,2}$ aromatization,$^{3,4}$ ammonoxidation, partial oxidation, reforming, and so forth.$^{5,6}$ The advantages and disadvantages of these catalytic processes are summarized in Table 1. In the present paper, we revisited the Co/HZSM-5 catalyzed ethane ammonoxidation because such a catalytic system produces acetonitrile and ethylene simultaneously with inhibited CO$_2$ formation (compared to the ODH) because of the presence of NH$_3$.$^{7,8}$

The ammonoxidation reaction was initially invented in 1959 by Standard Oil of Ohio (the SOHIO Process) for the production of acrylonitrile from propylene, NH$_3$, and O$_2$.$^{9,10}$ The ethane ammonoxidation was then investigated about 20 years later by Aliev and Sokolovskii with a Cr–Sc–Mo–O catalyst.$^{11,12}$ However, the selectivity to acetonitrile (<30%) was limited because of the formation of CO$_2$ and HCN over such a mixed metal oxide catalyst. It is quite surprising that the formation of ethylene was not mentioned in the early study.$^{13}$ Other mixed metal oxide catalysts investigated for ethane ammonoxidation include Nb–Sb–O/Al$_2$O$_3$,$^{14}$ V–Mo–Nb–O,$^{15}$ Ni–Nb–O,$^{16,17}$ and Mo–V–Te–Nb–O.$^{18}$ However, the selectivity to acetonitrile over these mixed oxide catalysts was low (<30%) and the typical propylene and propane ammonoxidation catalyst V–Sb–Al–O seems to be not effective in the ethane ammonoxidation.$^{19}$

The most effective catalyst for ethane ammonoxidation was the cobalt-modified zeolites (prepared through an aqueous solution or solid-state ion-exchange) initially developed by Li and Armor.$^{20,21}$ The rate of acetonitrile formation over the Co$^{2+}$ catalyst at 475 °C was 1–2 orders of magnitude higher than the mixed metal oxide catalysts at 500 °C.$^{22}$ Li and co-workers then investigated systematically the effect of zeolite topology, types of metal cations, and the effect of reaction conditions (temperature and reactants partial pressure) on the catalytic activity and selectivity, as well as the reaction pathways and mechanism.$^{23,24}$ Among various zeolite topologies investigated, the Co-modified MFI (ZSM-5) and BEA (β) catalysts seem to be more effective: ethane conversion up to 35% and acetonitrile selectivity around 50% was obtained at 450 °C. Although Co–Y has the highest acetonitrile selectivity (60%), the conversion of ethane was only 8.4%, which increased significantly after dealumination treatment.$^{25}$ Besides the zeolites, Co/silica-alumina and CoO/Al$_2$O$_3$ were also investigated for ethane ammonoxidation, which showed significantly lower activity and selectivity than the Co-ZSM-5 and

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Co-β catalysts, indicating the importance of the zeolites framework structure. Later studies on the effect of acidity further indicated that the negative charge of the zeolite framework and the accessibility of the reactants to the exchanged cobalt cations to be the decisive factors for controlling the activity. With respect to the effect of metal cations, Co²⁺ has been found to be the most effective one. The catalytic activity for other metal cations, such as Ni²⁺, Fe³⁺, and Mn³⁺ was significantly lower than that of Co²⁺, whereas the Cu⁺, Pd⁺, Ag⁺, Rh⁺, and Pt-modified ZSM-5 catalysts were found to be totally inactive in acetonitrile formation (produce mainly ethylene and CO₂). In terms of the catalytically active sites, Li and Armor suggested that acetonitrile, ethylene, and CO₂ can all be produced over the exchanged Co²⁺ cation; however, the formation of acetonitrile and ethylene was favored. Although Li and co-workers have carried out extensive studies on the Co/zeolites catalysts, such a catalytic system has been frequently revisited recently for both ethane and ethylene ammoxidation by others for the purpose of further improving the catalytic performance or understanding the catalytic mechanism.

Table 1. Advantages and Disadvantages of Various Catalytic Processes for Ethane Conversion

| processes          | products                  | catalysts                          | advantages                                 | disadvantages                               |
|--------------------|---------------------------|------------------------------------|--------------------------------------------|---------------------------------------------|
| aromatization      | ethylene + aromatics      | metal-modified HZSM-5              | high conversion, high total selectivity    | low stability, high reaction temperature,   |
| ODH                | ethylene                  | mixed metal oxides                 | lower reaction temperature, higher stability| low selectivity at high ethane conversion   |
| dehydrogenation    | ethylene                  | Pt-based                           | high selectivity                           | low stability, high reaction temperature, conversion is equilibrium-limited |
| ammoxidation       | ethylene + acetonitrile   | metal-modified zeolites or mixed metal oxide | lower reaction temperature, higher stability, lower CO₂ formation than ODH | low selectivity at a high ethane conversion; NH₃ can also be oxidized to NOₓ. |
| partial oxidation  | oxygenates                | metal-modified HZSM-5 or metal oxides | lower reaction temperature, higher stability | low conversion, high operation pressure, or use H₂O₂. |
| reforming          | H₂ + CO                   | transition metal-based             | industrial application is feasible         | products need to be converted through FT or methanol synthesis and so forth. |

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Although Li and co-workers have carried out extensive studies on the Co/zeolites catalysts, such a catalytic system has been frequently revisited recently for both ethane and ethylene ammoxidation by others for the purpose of further improving the catalytic performance or understanding the catalytic mechanism. For example, Essid et al. recently reported that the activity and selectivity of ethane ammoxidation both improved if [Co(NH₃)⁶]²⁺ was impregnated into
the BEA zeolite instead of $[\text{Co(OH}_2\text{)}]^{2+}$. The improved catalytic performance was attributed to the formation of $\text{Co}_3\text{N}$ with the presence of NH$_3$ during the activation or impregnation.$^{15}$

In this work, a series of Co modified HZSM-5 catalysts were prepared for ethane ammoxidation through incipient wetness impregnation, ion-exchange, and physical mixing. The effect of Co loading, SiO$_2$/Al$_2$O$_3$ ratio, and various reaction conditions on the catalytic performance has been investigated. Specifically, the kinetics and mechanism of such catalytic systems have been discussed based on the early-stage reaction transient analysis as well as the back-transient kinetics. The physicochemical properties of the catalysts were extensively characterized by N$_2$ physisorption, transmission electron microscopy (TEM), scanning TEM–energy-dispersive X-ray spectroscopy (STEM–EDX), X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), ultraviolet–visible diffuse reflectance spectroscopy (UV–vis-DRS), and NH$_3$ and $n$-propylamine temperature-programmed desorption (TPD). The effect of catalyst preparation, Co loading, and the Si/Al$_2$ ratio of the zeolite host on the physicochemical properties and their relationships to the catalytic performance was discussed. We anticipate that a balance between the function of Co species and the Bronsted acid density of the HZSM-5 is crucial in the ethane ammoxidation.

### 2. RESULTS AND DISCUSSION

#### 2.1. Catalytic Results

##### 2.1.1. Effect of the Catalyst Preparation

We first did the blank test of the reactor system, which only produces a negligible amount of CO$_2$ ($\sim0.2\%$). Other products were not observed during the blank test. While pure HZSM-5 seems to be active in ethane ammoxidation, the rates of acetonitrile, ethylene, and CO$_2$ were negligible in comparison to the Co-modified HZSM-5 catalyst (see Figure S1). The catalytic performance of ethane ammoxidation over the cobalt-modified HZSM-5 (Si/Al$_2$ = 30) catalysts prepared through ion-exchange, impregnation, and physical mixing is shown in Figure 1a,b. As we can see, all of the three catalysts are quite active in ethane ammoxidation for acetonitrile and ethylene. The cobalt-exchanged HZSM-5 (Co-IE) prepared according to Li and Armor$^{18}$ shows slightly higher activity (in terms of ethane conversion) and relatively lower selectivity to acetonitrile than the catalysts prepared through impregnation (Co-IM-2 wt %). However, the catalyst prepared through physical mixing (Co-PM-2 wt %) shows relatively higher CO$_2$ selectivity and lower activity than the Co-IE and Co-PM-2 wt %. The rates for the formation of acetonitrile, ethylene, and CO$_2$ are shown in Figure 1b. The Co-PM-2 wt % catalyst clearly shows a lower rate in terms of acetonitrile and ethylene. We anticipate that over the Co-PM-2 wt %, the catalytically active sites (exchanged Co$^{2+}$ cation) were formed during the activation and ongoing reaction process through the solid-state ion-exchange (see STEM–EDX characterization for evidence). Hence, all three catalysts finally show similar selectivity after reaching the steady state. However, the Co-PM-2 wt % catalyst takes a longer induction period before reaching the steady state (see Figure S2), which also provides evidence for the occurrence of solid-state ion-exchange during the reaction process. It must be noted that for all of the catalysts, the NH$_3$ conversion is typically 50%, which is significantly higher than the ethane conversion (10−20%). Such different reaction rates regarding NH$_3$ and ethane conversion suggested that large amounts of NH$_3$ were nonselectively oxidized into NO$_x$ instead of forming acetonitrile. [The mass spectrometer signal of NO$_x$ (m/z = 30) was clearly identified, but quantification of NO$_x$ is quite difficult]. The acetonitrile selectivity based on NH$_3$ is 25−30%, which is similar to the results reported by Li and Armor.$^{33,34}$

##### 2.1.2. Effect of the Si/Al$_2$ Ratio

Using the impregnation method for catalysts preparation, we then investigated the effect of the Si/Al$_2$ ratio and Co loading on the catalytic performance. As shown in Figure 1c, both ethane conversion and acetonitrile selectivity decrease with the increasing Si/Al$_2$ ratio. Accordingly, the selectivity to CO$_2$ increases significantly and ethylene selectivity increases slightly. Specifically, the ethane conversion was decreased from 18% to almost zero with increasing Si/Al$_2$ ratio from 30 to 80. However, the conversion of NH$_3$ and O$_2$ decreased with increasing Si/Al$_2$ from 30 to 50 and then increased with further increasing Si/Al$_2$ from 50 to 80. In terms of the rates for the formation of acetonitrile, ethylene, and CO$_2$ (see Figure 1d), they all decreased almost linearly with the increasing Si/Al$_2$ ratio from 30 to 80 or decreasing the Bronsted acids of the zeolite host. Therefore, the acid properties of the zeolite host are important for such a catalytic system. According to our recent study,$^{44}$ the Bronsted acidities of the HZSM-5 with Si/Al$_2$ ratio of 30, 50, and 80 are 351, 387, and 224 μmol/g, respectively. Because the exchanged Co$^{2+}$ cation has been considered as the catalytic active sites for ethane ammoxidation$^{17}$ and for the zeolite host with a higher Bronsted acid density, the concentration of the Co$^{2+}$ active sites should also be higher. Without sufficient Bronsted acid sites (for high Si/Al$_2$ ratio zeolite), excessive cobalt species will most likely form cobalt oxide particles without close proximity with the zeolite (see STEM–EDX characterization), which will result in the formation of CO$_2$ and NO$_x$. Consequently, NH$_3$ and O$_2$ conversion further increased with the increasing Si/Al$_2$ ratio from 50 to 80.

##### 2.1.3. Effect of Co Loading

Because it has been generally accepted that the exchanged Co$^{2+}$ cation is responsible for the ethane ammoxidation,$^{29−35}$ the effect of Co loading on the HZSM-5 (Si/Al$_2$ = 30) host was investigated. The Co loading was varied from 0.5 to 10 wt %, which represents the excess amount of either H$^+$ or Co$^{2+}$ [assuming bridge-type-exchanged Co$^{2+}$ cations (...Al−O−Co−O−Al...)]. As shown in Figure 1e, the acetonitrile selectivity decreases, CO$_2$ selectivity increases, and ethylene selectivity remain almost unchanged with increasing Co loading from 0.5 to 10 wt %. The conversion of all three reactants increased almost linearly with increasing Co loading from 0.5 to 2 wt %. With further increase of the Co loading from 2 to 10 wt %, the conversion of ethane and NH$_3$ remain unchanged, but the conversion of O$_2$ further increased. From the involved reaction stoichiometry, such further increased O$_2$ conversion is likely related to the increased CO$_2$ selectivity because the conversion of ethane and NH$_3$ conversion remain unchanged. In terms of the formation rate of different products, as shown in Figure 1f, the maximum rate for acetonitrile was obtained at 2 wt % Co loading. When the Co loading was further increased from 2 to 10 wt %, the rate of acetonitrile decreased; meanwhile, the rate of CO$_2$ further increased and the rate of ethylene remains almost unchanged. As already mentioned, excessive cobalt species will form cobalt oxide particles without close proximity with the zeolite (see STEM–EDX characterization), which is undesired for ethane ammoxidation. Therefore, we suggested that 2 wt % be the optimal Co loading for the ethane ammoxidation. Although for the 2 wt % loading sample Co is deficient compared to the
stoichiometric Co/Al ratio, the excessive Bronsted acid sites could act as a reservoir for NH₃. Actually, if we normalize the rate by the Co loading instead of the mass of the catalyst, the rates for all three products decreased continuously with increased Co loading (see Figure S3), which indicated that the excessive Bronsted acid sites could have a beneficial effect to the ammoxidation.

2.2. Catalyst Characterization. The characterization results of the selected Co-modified HZSM-5 catalysts were measured by means of N₂-physisorption, XRD, XPS, STEM−EDX, NH₃-TPD, and n-propylamine-TPDec. As shown in Table 2, the physical properties of the catalysts are clearly influenced by the method of catalyst preparation and the Co loading. The Co-IE and Co-PM samples show lower total and microsurface area than the Co-IM samples because of the partially blocked micropores. Additionally, with increasing Co loading for the Co-IM samples, the total and microsurface area and pore volume are also clearly decreased. The XRD patterns (see Figure 2a) of the Co-modified HZSM-5 catalysts with different Co loadings show almost identical diffraction patterns for the MFI type of zeolites. The diffraction of Co species was completely absent for Co loading ≤2 wt %, indicating very high dispersion of the Co species in the HZSM-5 zeolite. The Co species underwent significant solid-state ion-exchange during the high-temperature pretreatment to form the exchanged Co²⁺ cation. When the Co loading ≥5 wt %, the diffraction of Co₃O₄ (311) was identified at 2θ of 36.8° (JCPDS no. 42-1467), indicating that nanosize Co₃O₄ particles are formed when the Co loading is higher than the nominal amount (assuming Co/Al = 0.5, the Co loading for the ion-exchanged sample is 3.1 wt %). Such oxidic Co particles usually do not have close proximity with the zeolites (see Figure 3i) and could be responsible for the nonselective ODH and NH₃ oxidation to NOₓ on the high Co-loading catalyst.

The bulk XRD characterization was further complemented by the results from XPS surface analyses. The Co 2p spectra of the samples are displayed in Figure 2b, while the calculated Co and Al ratios from the spectra are shown in Table 3. There are

### Table 2. Physical Properties for Co-IM, Co-IE, and Co-PM Samples

| Sample     | Pore size (nm) | External surface area (m² g⁻¹) | Surface area (m² g⁻¹) | Total surface area (m² g⁻¹) | Microsurface area (m² g⁻¹) | Pore volume (cm³ g⁻¹) | Total pore volume (cm³ g⁻¹) | Micro pore volume (cm³ g⁻¹) |
|------------|----------------|--------------------------------|-----------------------|-----------------------------|-----------------------------|------------------------|-----------------------------|----------------------------|
| Co-IE      | 4.00           | 70.1                           | 239.7                 | 169.7                       | 0.24                        | 0.08                   |                             |                            |
| Co-PM      | 4.00           | 72.0                           | 241.1                 | 169.1                       | 0.24                        | 0.08                   |                             |                            |
| Co-IM-0.5 wt % | 2.61           | 91.1                           | 337.1                 | 246.1                       | 0.22                        | 0.11                   |                             |                            |
| Co-IM-1 wt % | 2.63           | 86.0                           | 321.4                 | 235.4                       | 0.21                        | 0.11                   |                             |                            |
| Co-IM-2 wt % | 2.62           | 85.6                           | 324.6                 | 239.0                       | 0.22                        | 0.11                   |                             |                            |
| Co-IM-5 wt % | 2.69           | 73.2                           | 295.0                 | 221.8                       | 0.20                        | 0.10                   |                             |                            |
| Co-IM-10 wt %| 2.63           | 67.3                           | 275.2                 | 208.0                       | 0.18                        | 0.10                   |                             |                            |

![Figure 2](image_url)

**Figure 2.** Characterizations of the Co-modified HZSM-5 catalyst. (a) XRD patterns; (b) Co 2p XPS spectra; (c) NH₃-TPD profiles; and (d) n-propylamine-TPD, rate of propylene desorption.
no apparent peaks present at the Co 2p spectra for both Co-IE and Co-IM-0.5 wt %, indicating that the concentration of Co species on the surface of the zeolite is too low to be detected by the XPS. The peaks start to emerge for other samples and increases with increasing Co loading. The Co 2p spectrum of Co-IM-2 wt % contains a peak at $\sim 782$ eV which is usually ascribed to a divalent Co$^{2+}$. The peak shifted to $\sim 780$ eV for the Co-IM-5 wt %, indicating the presence of Co$^{3+}$, which formed the spinel-type Co$_3$O$_4$ particles as identified by the XRD. Compared to the fresh catalyst, the Co 2p intensity of the Co-IM-2 wt % after ethane ammoxidation further attenuates. During the reaction process, the migration of the Co$^{2+}$ into the inner pores of the zeolites is likely happening which prevents the detection of the Co species by the XPS measurement.

While the Co species was largely absent from the XPS spectra for the samples with low Co loading, the presence of Co was clearly observed from both UV--vis-DRS spectra and the STEM--EDX mapping. As shown in Figure 3, the UV--vis-DRS spectra clearly show Co($II$) ions at wavenumbers of 12 000--24 000 cm$^{-1}$ for the Co-IE and Co-IM (with Co loading $\leq 2$ wt %) samples. Additionally, the peak at 31 000 cm$^{-1}$, which can be assigned to the CoO$_x$ species, was almost absent from the UV--vis-DRS spectra, indicating that most of the cobalt species are coordinately with framework aluminum located in the pores of zeolites.$^{51}$ The TEM image and STEM--EDX chemical mappings of the Co-IM-2 wt % (on HZSM-5 with Si/Al$_2 = 30$) catalyst are shown in Figure 4 a--c. A comparison of the Co $K\alpha$ and Al $K\alpha$ mappings of the catalyst both before and after reaction demonstrated the homogenous distribution of the cobalt species on the zeolite. Aggregated CoO$_x$ nanoparticles were not observed from the TEM, which again confirmed the formation of exchanged Co$^{2+}$ cations. Different from the catalyst prepared through impregnation, the Co-PM-2 wt % catalyst after the reaction showed nanosized particles supported on the HZSM-5 (Figure 4 d). Additionally, the occurrence of solid-state ion-exchange during the activation and reaction process was proved by the STEM--EDX characterization. As shown in Figure 4 f, homogeneously distributed Co species were clearly identified in the selected region (see Figure 4 e), where nanosized particles are absent. While Co and zeolite in close proximity

| Table 3. Effect of Co Loading on the Chemical Properties of the Catalysts |
|-------------------|----------------|----------------|----------------|
|                  | Co/Al bulk   | Co (at %)     | Al (at %)     | total acid   | Bronsted   |
|                  | ratio$^a$    | surface$^b$   | surface$^b$  | (μmol/g)     | acid (μmol/g) |
| HZSM-5           | 1225.0        | 531.0          |             |             |             |
| Co-IE            | 0.50          | 0.3            | 1.5          | 741.1        | 381.7        |
| Co-IM-0.5 wt %   | 0.08          | 0.5            | 1.6          | 555.1        | 369.8        |
| Co-IM-1 wt %     | 0.16          | 555.1          | 369.8        | 542.7        | 321.3        |
| Co-IM-2 wt %     | 0.32          | 0.4            | 1.4          | 555.9        | 262.4        |
| Co-IM-5 wt %     | 0.80          | 1.1            | 1.6          | 381.1        | 221.6        |
| Co-IM-10 wt %    | 1.61          |                |              |             |             |

$^a$Nominal Co/Al ratio based on Co loading. $^b$Surface concentration measured by XPS.

Figure 4. TEM and STEM--EDX of different catalysts. (a,b) Fresh catalyst after activation, (c--i) catalyst after reaction at 475 °C. (a) TEM image of Co-IM-2 wt % on Si/Al$_2 = 30$, (b,c) STEM--EDX chemical mapping of Co-IM-2 wt % on Si/Al$_2 = 30$ before and after the reaction, (d,e) TEM images of Co-PM 2 wt %, (f) STEM--EDX chemical mapping of image (e), (g,h) TEM image of Co-IM-2 wt % on Si/Al$_2 = 280$ and the corresponding STEM--EDX mapping, (i) TEM image of Co-IM-10 wt %.

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Brønsted acid sites (H+) of the host HZSM-5 were largely catalysts. With increasing Co loading, the intensity of the high-aromatization), the formation of secondary products from such methods, was decomposed to NH₃ and propylene according to the reaction of the propylene. However, over the present Co-IM-2 wt % at 475 °C. As shown in Figure 4g,h, aggregated Co species without close proximity with the zeolite host was too high because of the off-ratio of the Co/H⁺. As shown in Figure 4g,h, aggregated Co species without close proximity with the zeolite were clearly identified for the catalyst with Si/Al₂ = 280 (Co loading 2 wt %). The same aggregated Co species were found for the Co-IM-10 wt % (Si/Al₂ = 30) catalyst (see Figure 4i).

The effect of Co loading on the acidity of the catalysts was characterized by NH₃- and n-propilamine-TPD. As shown in Figure 2c, two distinct NH₃ desorption peaks at 280 and 490 °C are assigned to NH₃ desorbed from weak acid sites and strong acid sites, respectively. The total acid sites quantified by NH₃-TPD are varied from 381 to 741 μmol/g for different catalysts. With increasing Co loading, the intensity of the high-temperature peak decreased, which suggested that the Brønsted acid sites (H⁺) of the host HZSM-5 were largely replaced by the exchanged Co²⁺ cation. Evidence for the decreased Brønsted acid density can also be found from the n-propylamine-TPD results (Figure 2-d), which provide quantitative results of the Brønsted acid density.

In such methods, "C₃H₇-NH₃"...ZSM-5" was formed between propylene and the Brønsted acid site of the zeolite, which was decomposed to NH₃ and propylene according to the Hofman-elimination type of mechanism at ~400 °C. In our previous paper, the desorption of NH₃ was employed to quantify the Brønsted acid sites because of the secondary reaction of the propylene. However, over the present Co-modified HZSM-5 catalyst (not a typical catalyst for aromatization), the formation of secondary products from propylene was insignificant. Therefore, propylene desorption during the propylamine-TPD was employed for quantification as suggested by the literature. The Brønsted acid density of the catalysts was quantified to be 381.7 μmol/gcat for Co-IM-0.5 wt % and decreased to 221.6 μmol/gcat for the Co-IM-10 wt % catalyst. The Brønsted acid sites only slightly decreased when the Co/Al ratio exceeds significantly the stoichiometric ratio for ion-exchange, indicating that part of the Brønsted acid sites (most probably the sinusoidal channels) is inaccessible for solid-state ion-exchange.

2.3. Transient Kinetics Analysis and Mechanism. Relaxation-type transient kinetic analysis provides important information about how the steady-state reaction was reached upon introducing perturbation, which was realized by fast partial pressure step changes for the reactor influent gases in the present study. During the early-stage transient, the reactor flux was changed abruptly from Ar to the reactant mixture. Information about how a clean surface catalyst reaches the steady-state ammoxidation was obtained. The results over the optimal Co-IM-2 wt % catalyst are shown in Figure 5a. The normalized (with respect to the steady-state outlet molar flow rate) outlet flow of reactants and products take about 2 min to reach 1, which means the ethane ammoxidation over such catalysts takes 2 min to reach the steady state. The reactants ethane and O₂ appear almost immediately in the outflow gas phase and reach the maximum at 0.3 min after switching from Ar to the reactant mixture. Ammonia, however, appears in the gas phase with clear delay (0.25 min) and it takes about 2 min to reach the maximum. Significant delay of NH₃ with respect to ethane and O₂, indicating the strong chemisorption of NH₃ on the (Lewis and Brønsted) acid sites of the catalyst. Additionally, ethane and O₂ reach a maximum that exceeds their steady-state level at 0.2−0.5 min, which is most probably because of the increase of partial pressure caused by the consumption of NH₃ through chemisorption. The O₂ then decreased to below steady-state when acetonitrile was largely produced. Such early-stage features of delay were totally absent during the blank test (see Figure S4a,b), in which the influence of the reactor system on the delay can be excluded. Additionally, delay of NH₃ over the HZSM-5 sample (without Co function) is similar to the Co/HZSM-5 catalysts, indicating that the initial delay of NH₃ (~0.25 min) mainly originated from the chemisorption on the acid sites of the zeolite.
In terms of product formation, ethylene and CO$_2$ were produced simultaneously when ethane appeared in the gas phase. Both reached a maximum at 5 s and decreased immediately to a minimum after 20–30 s. They both take about 1 min to reach the steady-state level. The peaks of ethylene and CO$_2$ showed up before the full appearance of NH$_3$ in the gas phase, which suggested that the clean catalyst surface without NH$_3$ is active for ethane ODH to ethylene (mainly produces CO$_2$ rather than ethylene). Such a nonselective ODH mechanism was replaced by NH$_3$-mediated ODH (ammoxidation) when the catalytical active sites were occupied by NH$_3$. Different from the production of ethylene and CO$_2$, ammoxidation involves two different mechanisms during the early-stage run-in period: the formation of acetonitrile dependent exclusively upon the chemisorption of NH$_3$ on the catalytic active sites. Ethylene and CO$_2$ appear immediately in the gas based on the nonselective ODH mechanism, whereas the formation of acetonitrile was delayed (the same as NH$_3$) because it requires building a catalytically active surface through NH$_3$ pre-chemisorption. The production of acetonitrile reaches the steady-state at 1.5 min. Quite similar features of delay on acetonitrile and NH$_3$ were also observed for the Co-IE and Co-PM-2 wt % catalysts (see Figure S5b,d). However, the delay of O$_2$ as well as the quantitative information of such early-stage features for different reactants and products, seem to be affected by the catalyst preparation.

The back-transient kinetics was initiated by changing the reactor flux from the reactant mixture back to the inert gas (Ar). Kinetics information about the reactivity of the chemisorbed intermediates (on the catalyst surface) can be obtained from the time constants of the product decay. Assuming first-order reaction kinetics on single-type catalytically active sites, the rate for the formation of final products during the extended back-transient can be expressed as $\ln(\text{rate}_{\text{transient}}) = \ln(\text{rate}_{\text{steady-state}}) - t/\tau$ (or $\ln(\text{rate}_{\text{transient}}) = \ln(\text{rate}_{\text{steady-state}}) - kt$). Details about the derivation of such a linear equation can be found in our previous paper.$^{50}$ The entire back-transient behavior of the normalized outlet flow for both reactants and products is shown in Figure 5b. The time constant $\tau$ for the decay of NH$_3$ and CO$_2$ is 7.7 min, which decreased to 2.7 min for acetonitrile and further decreased to only 3–4 s for ethane, ethylene, and O$_2$. The time constant (3–4 s) is close to the reactor response of the inert gas (2 s) and the response of the blank test (see Figure S4a). During the entire back-transient process, the first few minutes after removal of reactants were considered as the near steady-state behavior (see Figure 5c). It takes only about a few seconds for the complete decay of O$_2$, while the decay of ethane and ethylene take slightly longer than that for O$_2$. They all disappeared from the gas phase within about 10 s, which is similar to the time required for the complete appearance of Ar in the gas phase. Therefore, we suggested that the chemisorbed surface intermediates do not lead to the formation of ethylene in the absence of gas-phase ethane and NH$_3$. Additionally, ethane and O$_2$ either chemisorbed weakly (completes poorly with NH$_3$) on the catalyst or the chemisorbed ethane and O$_2$ converted immediately to another type of intermediates (presumably the most abundant reactive intermediates or MARI). The decay of acetonitrile, CO$_2$, and NH$_3$ requires a longer time than that for ethane and ethylene. The rate constant for the formation of acetonitrile and CO$_2$ is 0.37 and 0.13 min$^{-1}$, respectively, (see Figure 5d) from their corresponding reactive intermediates. A strict linear relation between $\ln(\text{rate}_{\text{transient}})$ and time during the extended back-transient indicates that such reactions follow the first-order kinetics. The near steady-state back-transient also shows a sudden decay of acetonitrile, NH$_3$, and CO$_2$ within the initial 30 s, which then level-off for various time periods before the final first-order decay. Such unique behavior is most probably because of the formation of two different types of catalytically active sites, presumably Co oxide particles located on the external surface of the HZSM-5 zeolite and exchanged Co$^{2+}$ cations inside the pores of the zeolite. Additionally, the time constant for the decay of NH$_3$, CO$_2$, and acetonitrile over the Co-IE and Co-PM-2 wt % catalysts (see Figure S5a,c) was quite similar to that over the optimal Co-IM-2 wt % catalyst, indicating that the same type of reactive intermediates and catalytically active sites are involved. It must be noted that the decay of CO$_2$ over the HZSM-5 sample (Figure S4c) is significantly faster than that over the Co-modified HZSM-5 catalysts (note that the activity of the HZSM-5 sample is very low in ethane ammoxidation, see Figure S1), indicating the formation of CO$_2$-related species (probably formates or carbonates) on the Co sites.

In terms of the reaction pathways and mechanism, we suggested that ammonia mediated the initial step ethane ODH. The C–N bond was formed immediately after the initial C–H bond activation, which acts as an intermediate for acetonitrile. Meanwhile, such an intermediate can also be decomposed into ethylene and NH$_3$, which might be partially oxidized into CO$_2$ and NO$_x$, respectively. The overall kinetic expression for the rate of acetonitrile has been proposed by Li and Armor.31 They suggested that the formation of the C–N bond between ethylene and chemisorbed NH$_3$ on the Co–OH sites could produce the ethylamine-type intermediate, whereas the formation of ethylene from ethane ODH was proposed on a clean Co–OH site in the absence of NH$_3$, which is less likely under the ammoxidation conditions because NH$_3$ terminates such chemisorption on Lewis acid Co sites. Li and Armor also proposed the formation of N$_2$ from the ethylamine-type intermediate with an additional chemisorbed NH$_3$. However, the formation of NO$_x$, which was clearly observed from our study, was not considered. With respect to the catalytic active sites, Li and Armor suggested that the exchanged Co$^{2+}$ cations to be responsible for the formation of all products from ethane ammoxidation. We anticipate that CO$_2$ may originate from the ethylene oxidation, and such a reaction was particularly favored because of the presence of the Co nanoparticles without close proximity with the zeolites. The efficient formation of acetonitrile may also be related to the remaining Brønsted acid sites of the zeolite host, which could provide protonated NH$_3$ in the first step, followed by the formation of “C$_2$H$_5$NH$_3$$^{+}$”–“ZSM-5$^{-}$” (as the reactive intermediate) through a mechanism similar to the reverse Hofman-elimination. Therefore, supported by our catalytic results, we suggested that a proper balance between the exchanged CO$_2$ cations and the Brønsted acidity density would adjust and optimize the activity/selectivity to acetonitrile in this catalytic system.

3. CONCLUSIONS

While the cobalt-modified HZSM-5 catalyst has been extensively studied for the ethane ammoxidation since the later 1990s, more detailed discussion about the structure/performance relationships and the kinetics of the reaction mechanism has been less concerned. We present here our
understanding of these questions based on the performance of the catalyst with tuned metal/acid functions. Such steady-state catalytic performance was complemented with the early-stage transient analysis and the back-transient kinetics of the product decay study. We identified that the catalyst prepared through simple impregnation shows similar catalytic performance with that prepared through the ion-exchange method. The same type of the active site, namely, the exchanged Co\(^{2+}\) cation was formed by two preparation methods after activation. The catalyst prepared through physical mixing also leads to the formation of exchanged Co\(^{2+}\) sites (with the co-presence of nanosized Co oxide particles), showing similar product selectivity. The effect of the Si/Al\(_2\) ratio and Co loading on the activity and selectivity suggested that excess Co amounts or deficient Brønsted acid sites density resulted in the formation of CO\(_2\) rather than acetonitrile and ethylene, which most probably due to the formation of aggregated cobalt oxide particles as identified by the STEM–EDX, XRD, XPS, and UV–vis–DRS. We suggested that the excess Brønsted acid sites of the zeolites might act as a reservoir for NH\(_3\), which promotes the formation of acetonitrile while inhibiting the CO\(_2\) formation. The early-stage catalytic behavior during the transient kinetic analysis indicated that NH\(_3\) mediated the initial ODH of ethane. Ammonia and acetonitrile appear in the product stream simultaneously before building the NH\(_3\) reservoir, whereas CO\(_2\) was mainly produced. According to the back-transient kinetic analysis, the decay of NH\(_3\) and CO\(_2\) shows the same large time constant \(\tau\) for 7.7 min, indicating that the presence of NH\(_3\) strongly reduced the rate of CO\(_2\) formation from its intermediate precursor. The time constant for acetonitrile was decreased to 2.7 min and further decreased to only 3–4 s for ethane, ethylene, and O\(_2\). Finally, the kinetics from the back-transient analysis suggested the first-order reactions for the formation of acetonitrile and CO\(_2\) from their corresponding reactive intermediates. Their rate constants are 0.37 and 0.13 min\(^{-1}\), respectively.

4. EXPERIMENTAL SECTION

4.1. Catalyst Preparation. Co/HZSM-5 with different Co loadings was prepared through incipient wetness impregnation. The NH\(_4\)-HZSM-5 zeolites were purchased from VWR International \((S_{\text{BET}} \approx 400 \text{ m}^2/\text{g})\). Before impregnation, the NH\(_4\)-HZSM-5 zeolites were converted into proton-type through calcination at 550 °C under air for 6 h. For a typical impregnation process, 6 mL of an aqueous solution of cobalt nitrate (Sigma-Aldrich) was added dropwise to the calcined HZSM-5 (3 g). The obtained sample was kept in air for 12 h at 60 °C. Finally, the sample was calcined under flow of air in a muffle furnace at 560 °C for 4 h. The obtained samples were named as Co-IM \# wt %, where the \# represents the nominal metal-based Co loading. The obtained powder samples were pressed into pellets and sieved to obtain a particle size of 20–45 mesh for characterization and catalytic performance tests.

For the purpose of comparison, Co-modified HZSM-5 catalysts were also prepared through ion-exchange (named as Co-IE) and physical mixing (named as Co-PM). For ion-exchange, 3 g of NH\(_4\)-HZSM-5 zeolite was exchanged with 0.05 M cobalt nitrate aqueous solution at 80 °C for 6 h and repeated three times. The obtained slurry was centrifuged and washed with distilled water three times. For physical mixing, 0.534 g of cobalt nitrate was mixed with 3 g NH\(_4\)-HZSM-5 using a Fritsch Pulverisette ball mill for 5 min. The obtained sample was finally dried and calcined according to the same procedure described above.

4.2. Catalyst Characterization. Nitrogen adsorption/desorption isotherms were measured at –195.8 °C on a TriStar II 3020 gas adsorption analyzer of Micromeritics. Prior to the measurement, the sample was degassed under high vacuum at 300 °C for 8 h. The total surface area was calculated from the adsorption branch in the range of relative pressure from 0.05 to 0.25 by the Brunauer–Emmett–Teller (BET) method, whereas the total pore volume was estimated at a nitrogen relative pressure of 0.99. The micropore volume and external surface area were calculated from the isotherms by the \(t\)-plot method; the micropore surface area was obtained from the difference between the total surface area and external surface area.

Ammonia-TPD and n-propylamine-TPD experiments were performed in a quartz reactor with a volume of 2 mL (ID, \(\Phi = 1/2 \text{ in}\)). Prior to NH\(_3\) and n-propylamine adsorption, the catalysts (0.1 g for NH\(_3\)-TPD and 0.06 g for C\(_3\)H\(_7\)NH\(_2\)-TPD) were pretreated in Ar at 650 °C for 20 min. Adsorption of NH\(_3\) or n-propylamine was carried out at 120 °C under pure NH\(_3\) for 30 min or through pulsing n-propylamine injection until saturation, respectively. For both experiments, the samples after pre-adsorption were flushed with Ar (at 120 °C for NH\(_3\) and 200 °C for n-propylamine) for 2 h to remove the physically adsorbed NH\(_3\) and n-propylamine. Finally, the temperature of the sample was increased to 620 °C at a ramp of 10 °C/min under the flow of Ar at 20 mL/min. Desorption of NH\(_3\) \((m/z = 17)\) was measured during the NH\(_3\)-TPD by an online mass spectrometer (Agilent 5973). In the C\(_3\)H\(_7\)NH\(_2\)-TPD experiment, the desorption signals of NH\(_3\) \((m/z = 17)\), C\(_3\)H\(_6\) \((m/z = 41)\), benzene \((m/z = 78)\), toluene \((m/z = 92)\), and xylene \((m/z = 106)\) were measured with the same mass spectrometer. More detailed experimental procedures for NH\(_3\)- and n-propylamine-TPD have been described in our previous work.\(^{24}\)

The solid-phase composition prepared by different methods and various cobalt loading percentages was identified by X-ray powder diffraction with a scanning rate of 4° min\(^{-1}\) in the range of 20 from 4 to 50°. The purity and crystallinity of zeolites of the sample obtained by pressing the powder into chisolate were measured by the X-ray diffractometer on the Rigaku Ultima III XRD system with Cu Ka radiation (154.06 pm, 40 kV, and 44 mA).

TEM/STEM–EDX characterization of the sample was performed on a JEOL 2100TEM (accelerating voltage 200 kV) equipped with a Gatan camera.

The surface chemistry and composition of the catalysts were measured using a PHI Quantum 2000 XPS. The samples were crushed and pressed into indium metal foils, which were then mounted on the XPS sample holders. A monochromated Al K\(_\alpha\) radiation (1486.6 eV) at an operating power of 18 kV was used for the analysis. The core-level spectra were monitored by employing a pass energy of 23 eV for the high-resolution scans and 123 eV for the survey scans. The C 1s line at 284.8 eV of adventitious carbon was taken as an energy reference between the total surface area and external surface area. The spectra obtained were processed and analyzed using the CasaXPS software.

The ultraviolet–visible diffuse reflectance spectra (UV–vis–DRS) were collected on a Cary 5000 UV–vis–NIR spectrophotometer (Agilent) equipped with a diffuse reflectance attachment with a polytetrafluoroethylene integrating
sphere. Before each measurement, the hydrated Co-ZSM-5 samples were transformed to their dehydrated form under 10⁻¹ Pa and 400 °C for 7 h, which were then transferred into a sample cell in a glovebox (O₂ < 0.1 ppm; H₂O < 0.1 ppm). Operated at a scan speed of 10 nm s⁻¹, a step length of 1 nm, and a slim width of 5 nm, the UV–vis-DRS were collected in a differential mode referenced to their parent H-ZSM-5 zeolites.

4.3. Catalytic Testing. The ammoxidation of ethane was conducted in a home-made U-shape quartz reactor equipped with an on-line Agilent 5973 mass spectrometer. The manifold reactor setup has two parallel gas lines, switched by a four-way valve, connecting to the reactor. The reactor influent gas can be abruptly switched from inert (Ar) to the reactant mixture (C₂H₆/NH₃/O₂) and vice versa, which provides the dynamic information for both the early-stage transient period and the back-transient reaction fade away. Typically, 0.2 g of the catalyst was loaded in the reactor and pretreated in Ar (20 mL/min) at 650 °C (ramp 10 °C/min) for 20 min to remove the impurities adsorbed on the catalyst. The temperature of the reactor was then cooled to 475 °C for the reaction. Prior to each experiment, bypass feed spectra were recorded for mass spectrometer calibration and used as a reference for activity calculation. Finally, the reaction was initiated abruptly by switching the influent gas from Ar to the reactant mixture (10% C₂H₆, 10% NH₃, and 6.4% O₂, balance with Ar) at a total flow of 80 mL/min. The corresponding gas hourly space velocity is 32 000 h⁻¹. All of the connection gas lines between the reactor and mass spectrometry were heated to 150 °C to avoid the condensation of acetonitrile and water.

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