Ammoxidation of ethane to acetonitrile over Co-beta zeolite

Yuejin Li and John N. Armor*

Air Products and Chemicals, Inc., 7201 Hamilton Boulevard, Allentown, PA 18195-1501, USA

Co-beta zeolite selectively catalyzes the ammoxidation of ethane to acetonitrile with a rate that is 1–2 orders of magnitude higher than those over typical metal oxide catalysts.

There is considerable interest in converting light alkanes directly to higher value organic chemicals because of the low cost and abundance of the alkanes. On the other hand, alkanes are chemically stable, which poses a tremendous challenge to achieve a high selectivity in their conversions. A commercially successful example of alkane activation is the manufacture of maleic anhydride by selective oxidation of butane[1] using V–P–O based catalyst. Another example is the recently announced production of acrylonitrile by reacting propane with NH_3 and O_2 (ammoxidation) over an Sb–V–Al mixed oxide catalyst.[2] In spite of these commercial advances, limited progress has been made for conversion of other alkanes. There were a few attempts to apply the propane ammoxidation catalysis on ethane to make acetonitrile. However, the propane ammoxidation catalyst, V–Sb–Al, was found ineffective for the ethane ammoxidation to acetonitrile. As postulated by Catani and Centi,[3] different mechanistic pathways are required for these two reactions because of the fundamental difference between propene, an intermediate for propane ammoxidation, and ethene, an intermediate for ethane ammoxidation.

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 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. Here, we report our recent discovery[5] using a metal exchanged zeolite as a superior catalyst for ethane ammoxidation with a very high reaction rate and selectivity to acetonitrile.

Some metal exchanged zeolites are known to activate small alkanes for selective reduction of NO_x.[6] In the case of NO_x reduction with methane over Co-zeolites, CH_4 was activated by abstracting a proton with a NO_2 species which was adsorbed on Co^{2+} sites.[7] Metal cations exchanged in zeolites are atomically dispersed on the coordinately unsaturated sites to balance the negative changes of the zeolite framework. These cations provide unique catalytic centers, as Lewis-acid sites, with a high site density which is usually not achievable by bulk or supported metal oxides.[8] We sought to utilize the unusual properties of metal-zeolite systems to activate ethane for its ammoxidation reaction [eqn. (1)].

$$C_2H_6 + NH_3 + 3/2O_2 \rightarrow CH_3CN + 3H_2O \qquad (1)$$

NH_4-beta zeolite (Si/Al = 14) (20 g) was exchanged with a 2 l, 0.02 M cobalt acetate aqueous solution at 70–80 °C for 24 h. After washing with 1 l of deionized water, the zeolite was dried overnight at 110 °C. Elemental analysis showed that the Co/Al atomic ratio was 0.35 (70% of the cation exchange capacity) or 2.2% Co by mass. The reactions were conducted in a microreactor system operating in a steady-state plug-flow mode at atmospheric pressure. The reactor is a U-shaped quartz tube with 0.25 in od at the inlet section and 0.375 in 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. A typical feed consisted of 5% C_2H_6, 10% NH_3 and 6.5% O_2 in He with a total flow rate of 100 cm^3 mol^{-1}. A 0.2 g catalyst sample sieved between 20/40 mesh was used for each run, which renders a GHSV of 15000 or a contact time of 0.24 s. The reactor effluent was analyzed by two on-line gas chromatograghs in series, each equipped with a thermal conductivity detector.

As shown in Fig. 1, C_2H_6 was selectively converted to acetonitrile over a Co-beta catalyst with a selectivity as high as 76%. The selectivity moderately decreased with increasing temperature. Major by-products for the ethane conversion are CO_2 and C_2H_4. The selectivity of CO_2 was *ca.* 20%, and the selectivity of C_2H_4 was generally low but increased linearly with increasing temperature. The conversion of C_2H_6 was strongly dependent on the reaction temperature and the availability of O_2. The highest conversion was 47% obtained at 475 °C.

An interesting observation for this reaction is that the total C_2 selectivity ($C_2H_4 + CH_3CN$) is relatively constant, $73 \pm 3\%$. The mutually compensating effect between the formations of C_2H_4 and CH_3CN suggests that C_2H_4 is the primary product of this reaction. Indeed, a reference reaction with C_2H_4–NH_3–O_2 under similar conditions tripled the nitrile yield. We believe that C_2H_6 is first converted to C_2H_4 *via* oxidative dehydrogenation on NH_3 moderated Co^{2+} sites. Ammonia is strongly adsorbed on most of the Co^{2+} sites as a Lewis base. The ethene molecule then adds on top of the adsorbed NH_3 forming an adsorbed

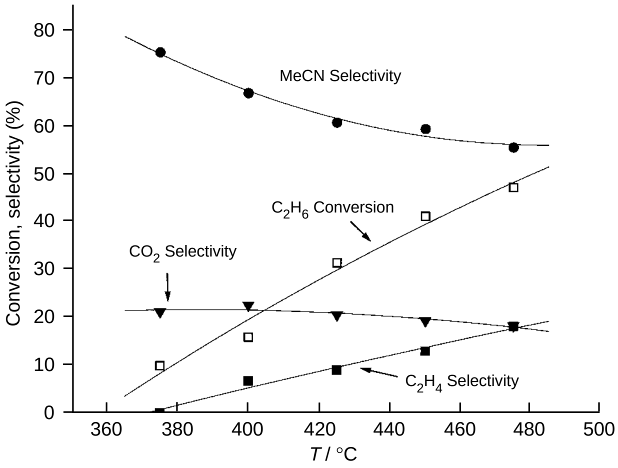

Fig. 1 Ethane ammoxidation to acetonitrile over Co-beta catalyst as a function of temperature

Table 1 Comparison between Co-beta and metal oxides for ethane CH_3CN ammoxidation[a]

Catalyst	Catalyst composition	Ref.	Catalyst mass/g	CH_3CN yield (%)	10^4 CH_3CN production rate/ mol g^{-1} h^{-1}
Co-beta	Si/Al = 14, Co/Al = 0.35	This work	0.2	26.4	160
VPO	P/V = 0.10 (atomic ratio)	9	0.2	0.2	1.2
$SbVO_4$	Sb/V = 1.0 (atomic ratio)	2	0.2	0.06	0.4
Nb–Sb oxides/Al_2O_3	70 mass% Al_2O_3 Nb/Sb = 1 : 5	3	0.5	1.2	3.0
Cr–Zr–Mo oxides	Cr : Zr : Mo = 18.1 : 1 : 31.2	4	0.5	2.6	6.4

[a] All catalysts were tested at 500 °C, except for Co-beta (475 °C), under conditions described within the text.

ethylamine molecule, which is readily dehydrogenated to CH_3CN in the presence of O_2.

The Co-beta catalyst was compared with a variety of metal oxide catalysts for the ethane ammoxidation reaction. As shown in Table 1, the CH_3CN formation rate over Co-beta (at 475 °C) is 1–2 orders of magnitude higher than those over metal oxide catalysts (at 500 °C). Nb–Sb–Al and Cr–Zr–Mo were reported to be active for this reaction.[3,4] However, they were active only with a much longer contact time, 3–19 s. With a shorter contact time (<1 s), the amount of CH_3CN produced was barely detectable. It is obvious that Co-beta, a non-traditional selective ammoxidation catalyst, is superior in terms of reaction rate and selectivity to nitrile. In addition, our Co-zeolite catalysts were tested on stream for 100 h without significant deactivation.

In summary, we have found that Co-beta was a very good catalyst for converting ethane to acetonitrile with high rate and selectivity. We believe this to be a positive step towards utilizing ethane to make valuable chemicals.

Footnote and References

* E-mail: armorjn@apci.com

1 G. Emig and F. Martin, *Catal. Today*, 1987, **1**, 477.
2 A. T. Guttmann, R. K. Grasselli and J. F. Brazdil, *US Pat.*, 4,746,641, 1988.
3 R. Catani and G. Centi, *J. Chem. Soc., Chem. Commun.*, 1991, 1081.
4 S. M. Aliev, V. D. Sokolovskii and G. B. Boreskov, *USSR Pat.*, SU-738 657, 1980.
5 Y. Li and J. N. Armor, *Eur. Pat. Appl.*, EP 0761 654 A2, 1997.
6 Y. Li and J. N. Armor, *Appl. Catal. B*, 1993, **2**, 239.
7 Y. Li, T. L. Slager and J. N. Armor, *J. Catal.*, 1994, **150**, 388.
8 J. N. Armor, in *Science and Technology in Catalysis 1994*, Kodansha Press, Tokyo, 1995, p. 51.
9 P. M. Michalakos, M. C. Kung, I. Jahan and H. H. Kung, *J. Catal.*, 1993, **140**, 226.

Received in Bloomington, IN, USA, 30th May 1997, 7/03788K

Typeset and printed by Black Bear Press Limited, Cambridge, England