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Acetonitrile Formation from Ethylene and Ammonia over Zn^{2+} and Cd^{2+} Exchanged Y-zeolites

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Zn^{2+} and Cd^{2+} exchanged Y-zeolites are found to be active for acetonitrile formation from ethylene and ammonia. Their catalytic activities are much higher than that on Al_2O_3, which has been known to be an active catalyst for this reaction.

Formation of nitriles in the reaction between an alkene (particularly propene) and ammonia was studied about 40 years ago, e.g., over cobalt catalysts by Teter et al.,1) over molybdenum oxide catalysts by Denton et al.,2) over alumina and nickel catalysts by Kominami et al.,3) and over nickel catalysts by Yamauchi et al.4) Over the molybdenum oxide and alumina catalysts, acetonitrile was predominantly formed.2,3) On the other hand, propionitrile was mainly formed over the nickel catalysts (ca. 90%).3,4) For acetonitrile formation from ethylene (C_2H_4) and ammonia (NH_3), alumina (Al_2O_3) was reported to be an effective catalyst.5) However, few research works on zinc as an active component for the reaction between C_2H_4 and NH_3 have been reported to date. Similarly, few works on the reaction over supported cadmium catalysts have been reported. In the present work, Zn^{2+} and Cd^{2+} exchanged Y-zeolites are found to be active for acetonitrile formation from ethylene and ammonia; their activities are much higher than that on Al_2O_3.

The Zn^{2+} and Cd^{2+} exchanged Y-zeolites were prepared by using a conventional cation exchange method: Powdered NaY-zeolite (Si/Al=2.8, obtained from Tosoh Corp.) was suspended in NH_3 aqueous solution of zinc chloride ($ZnCl_2$) and cadmium chloride - 2.5 water ($CdCl_2 \cdot 2\frac{1}{2}H_2O$), respectively, and the mixture was stirred at 323 K for 12 h. The powder was washed with distilled water and dried at 383 K overnight in an oven. The dried powder was pressed, crushed and then sieved to 20 - 42 mesh. The catalysts for which Al_2O_3 was used as a support were prepared by the usual impregnation method. An apparatus used was a fixed-bed type reactor (a fused silica tube, i.d.=10 mm) with continuous flow, operated at atmospheric pressure. The catalyst (1.00 g) was placed in the reactor and pretreated with oxygen at 773 K for 3 h. The reaction was performed at 673 K with the reaction gas mixture of C_2H_4(20%) -NH_3(20%)-He(60%) (total flow rate = 50 $cm^3 \cdot min^{-1}$). Concentrations of products in the effluent gas stream were determined by gas chromatography.

In the reactions between C_2H_4 and NH_3 over both Zn^{2+}/Y-zeolite and Cd^{2+}/Y-zeolite, acetonitrile was predominantly formed. Changes in the activities with time on stream were small at the reaction temperatures below 723 K. In the present work, the catalytic activity was evaluated by the rate of acetonitrile formation at time on stream of 5 h. The results of the catalytic runs are summarized in Table 1. As shown by run 1, NaY-zeolite showed almost no activity for acetonitrile formation from C_2H_4 and NH_3. On the other hand, HY-zeolite (Si/Al=2.8, Na-exchanged = 68%) was found to be active for this reaction (run

2). By loading of Zn^{2+} or Cd^{2+} species on NaY-zeolite, the activity became appreciable. In addition, the activity increased with an increase in the amounts of Zn^{2+} loaded (runs 3-5) or Cd^{2+} loaded (runs 6-8). Thus, the catalytic activities for acetonitrile formation on Zn^{2+} and Cd^{2+} exchanged Y-zeolites were found to be much higher than that on HY-zeolite.

Table 1. Catalytic Activities of Zinc and Cadmium Catalysts for Acetonitrile Formation from Ethylene and Ammonia

Run No.	Catalyst	Zn^{2+} or Cd^{2+} /wt%	$r_{AN}/10^{-6}$mol $\cdot$min$^{-1}\cdot$g^{-1}
1	NaY	—	—
2	HY	—	0.03
3	Zn^{2+}/NaY	1.0	0.10
4		2.0	0.93
5		3.0	1.43
6	Cd^{2+}/NaY	1.0	0.16
7		2.0	0.38
8		3.0	0.42
9	Al_2O_3	—	0.04
10	Zn^{2+}/Al_2O_3	2.0	0.07
11	Cd^{2+}/Al_2O_3	2.0	0.24

Alumina was known to be an effective catalyst for this reaction.5) In fact, acetonitrile was predominantly formed over Al_2O_3, where almost no deactivation of the catalyst was observed. The activity on Al_2O_3 (run 9) was comparable with that on HY-zeolite. By loading of Zn^{2+} on Al_2O_3, the activity for acetonitrile formation was enhanced (run 10). As shown by run 11, the activity on Cd^{2+}/Al_2O_3 (2.0 wt%) was observed to be much higher than that on Al_2O_3 itself. These results also indicate that zinc and cadmium species on the support are effective to enhance the activity for acetonitrile formation from C_2H_4 and NH_3. On the reaction over Al_2O_3, acid sites at the surface were proposed to be the active sites.5) At the present time, however, we have not clarified the relation between the catalytic activity and the acidic properties of the catalyst.

Zn^{2+} and Cd^{2+}/Y zeolites were thus found to be active catalysts for acetonitrile formation from C_2H_4 and NH_3.

References

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