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Comments on the Mechanism of Ammoxidation of Propylene to Acrylonitrile

In the preceding letter Menon (*1*) has developed some interesting suggestions concerning the participation of nitric oxide in the conventional process of ammoxidation of propylene into acrylonitrile by the reaction of NH_3 and O_2 in the mixture. The suggested mechanism is postulated at least for Bi–Mo–O-type catalysts and is based mainly on the experimental fact that pure NO can convert propylene into acrylonitrile with good selectivity on NiO-type catalysts (*2*, *3*) and on the findings that bismuth molybdate has the highest activity among molybdates for the oxidation of NH_3 (*4*). The proposed scheme involves the addition of NO (formed by oxidation of ammonia) to the adsorbed allyl radical (formed from propylene) and the intermediate formation of *trans*- and *cis*-allyl oxime. The former gives acrylonitrile and water with or without a Beckmann rearrangement, whereas the latter is split into acetyldehyde and hydrocyanic acid or, through a Beckmann rearrangement, into acetonitrile and formaldehyde.

The present authors have experimental evidence that this mechanism cannot be generalized to catalysts of the conventional ammoxidation of propylene (with $NH_3 + O_2$) of the type Sb–Sn–O, nor to catalysts for the conversion of propylene to nitriles by NO of the type NiO/Al_2O_3 or $NiO/SiO_2–Al_2O_3$.

Considering first the oxidation of ammonia into nitric oxide on oxide catalysts at temperatures lower than 500°C it is known that the main products are N_2, some N_2O, and only a very small amount of NO (*5*). In particular, for various molybdenum-based mixed-oxide catalysts (and for Bi–Mo–O among others), the amount of NO produced is almost nil (*6*). The main product is N_2 (98–100%) and N_2O represents the difference (2–0%). The best results concerning the formation of NO (5%) are obtained with Sb–Sn–O-type catalysts at 473°C. Now, when a mixture of NO and propylene is reacted over a Sb–Sn–O catalyst, only a small selectivity (29%) toward acrylonitrile is observed (*3*), whereas with the conventional mixture ($NH_3 + O_2$) this catalyst gives a selectivity toward acrylonitrile at 460°C of the order of 80% (*7*). The mechanism proposed for the conventional ammoxidation involves the intermediate formation of propyleneimine and its oxidative dehydrogenation into acrylonitrile (*6–8*).

Another point deserving discussion is the problem of the acidity of catalysts employed in the ammoxidation, because this acidity favors a Beckmann rearrangement of allyl oximes which, in turn, would favor the formation of side products like acetonitrile and formaldehyde when this rearrangement concerns the *cis*-allyl oxime (*1*).

The Sb–Sn–O catalyst discussed above is not acidic. Indeed, a mixture of isopropanol, air, and ammonia is converted, on this catalyst at 460°C (*9a,b*), into acetone (oxidation reaction) with a selectivity of 52% and into propylene (de-

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hydration reaction) with a selectivity of 17%. By comparison Bi–Mo–O catalyst should be more acidic since under the same conditions the selectivity toward acetone is 4% whereas that toward propylene is 94%. Now, both catalysts give almost the same results in the ammoxidation ($NH_3 + O_2$) of propylene at 460°C: 80% selectivity toward acrylonitrile for Sb–Sn–O and 75% for Bi–Mo–O. The selectivity toward acetonitrile is almost the same (2.5–3%) for both catalysts, whereas a Beckmann rearrangement of *cis*-allyl oxime, favored on Bi–Mo–O (more acidic) catalyst, should enhance the formation of acetonitrile. The similarity in the yield of the reaction products on both catalysts would be in favor of the same type of mechanism (*8*).

Finally, the interaction between NO and propylene (*2*, *3*) or isobutylene (*10*) on catalysts of the type NiO/Al_2O_3 and $NiO/SiO_2–Al_2O_3$, giving mainly acrylo- or methacrylonitrile, cannot be explained by the mechanisms given by Menon (*1*). If NO was not dissociated but simply added to the allyl intermediate (the product of this interaction being then isomerized into allyl oxime) the NiO would be reduced by propylene with the formation of an allyl radical and would not be reoxidized, whereas the kinetic results clearly show that a reduction–oxidation mechanism is operating. This dissociation of NO on NiO-based catalyst is moreover demonstrated by the quantitative synthesis of ammonia from the NO–H_2 mixture and the absence of the synthesis of ammonia from the N_2–H_2 mixture, under the same conditions (*3*).

Concerning the formation of side products it was observed that the formation of acetonitrile is decreased on a more acidic catalyst ($NiO/SiO_2–Al_2O_3$) by comparison with that on a less acidic catalyst (NiO/Al_2O_3) (*3*). A Beckmann rearrangement of the *cis*-allyl oxime, favored by acids, should enhance the yield of acetonitrile on $NiO/SiO_2–Al_2O_3$ catalyst, whereas the reverse behavior is observed. On both catalysts acetonitrile is directly produced from acrylonitrile (as a feed) and NO (or without NO) through oxidation of the C_3 nitrile into C_2 nitrile by lattice oxygen (of NiO), without the possibility of *trans*-allyl oxime intermediate formation from the acrylonitrile.

The last two side products, formaldehyde and hydrocyanic acid, were never detected on NiO-based catalysts. Formaldehyde should be formed (*1*) in an amount comparable to that of acetonitrile, and hydrocyanic acid should be formed in an amount comparable to that of acetaldehyde (detected in our case). Therefore the *cis*-allyl oxime, with or without a Beckmann rearrangement, cannot be an intermediate on NiO-based catalysts.

REFERENCES

1. Menon, P. G., *J. Catal.* **58**, 314 (1979).
2. Zidan, F., Pajonk, G., Germain, J. E., and Teichner, S. J., *J. Catal.* **52**, 133 (1978).
3. Zidan, F., Pajonk, G., Germain, J. E., and Teichner, S. J., *Bull. Soc. Chim. Fr.*, 603, 1011, 1021 (1977).
4. Trifiro, F., and Pasquon, J., *J. Catal.* **10**, 86 (1968).
5. Dixon, J. K., and Longfield, J. E., *in* "Catalysis" (P. H. Emmett, Ed.), Vol. 7, p. 281. Reinhold, New York, 1960.
6. Germain, J. E., and Perez, R., *Bull. Soc. Chim. Fr.*, 739 (1975).
7. Crozat, M., and Germain, J. E., *Bull. Soc. Chim. Fr.*, 3526 (1972).
8. Voge, H. H., and Adams, C. R., Adv. in Catalysis, *17*, 151 (1967).

9a. Cathala, M., Thesis, Lyon, 1971.

9b. Perrard, A., Thesis, Lyon, 1976.

10. Zidan, F., Pajonk, G., Germain, J. E., and Teichner, S. J., *Bull. Soc. Chim. Fr.*, 366 (1978).

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