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An Interpretation of the Action of Bismuth Molybdates in Ammoxidation of Propylene

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The experimental data of Aykan [*J. Catal.* **12**, 281 (1968)] which reveal a maximum in acrylonitrile yield in ammoxidation of propylene from a m $Bi_2O_3 \cdot n$ MoO_3 catalyst at an m, n value of 1, 2 are reinterpreted in terms of oxidation of Bi^{3+} with a consequent increase in the concentration of Mo^{5+}. The relationship between the m/n ratio and Mo^{5+} concentration behaves in a manner exactly parallel to the experiental data of Aykan.

The ammoxidation of propylene to produce acrylonitrile, as well as other nondesirable products, is a complex catalytic reaction network. Of the catalysts which favor a reasonable yield of acrylonitrile, the catalyst system Bi–Mo has received attention in the literature. Specifically, Aykan (*1*) has published data of interest insofar as he has revealed a maximum in yield of acrylonitrile for a Bi/Mo atomic ratio of unity. For the catalytic formulation m $Bi_2O_3 \cdot nMoO_3$ the optimum m, n values are, therefore, $m = 1$, $n = 2$. Significantly while pure Bi oxide grants zero yield, a small but finite yield is reported by Aykan for the pure Mo oxide. These observations suggest that selective ammoxidation to acrylonitrile is a function of a specific oxidation state of Mo and, so, the maximum yield is a function of a redox process involving oxidation of Bi^{3+} to Bi^{4+} with consequent reduction of Mo^{6+} to Mo^{5+}. Let us consider the equilibrium reactions:

$$\begin{aligned} Bi^{3+} &\rightleftarrows B^{4+} + e, \\ e + Mo^{6+} &\rightleftarrows Mo^{5+}, \end{aligned} \tag{1}$$

yielding

$$[Mo^{5+}][Bi^{4+}] = K[Bi^{3+}][Mo^{6+}]. \tag{2}$$

The total $[Mo^{5+}]$ is equal to $[Bi^{4+}]$ plus thermally produced Mo^{5+} or $[Mo^{5+}]_0$. The charge balance equation yields:

$$[Mo^{5+}] = [Mo^{5+}]_0 + [Bi^{4+}]. \tag{3}$$

Now $$[Bi^{4+}] = \frac{2m}{2m+n} \tag{4}$$

and $$[Mo^{6+}] = \frac{n}{2m+n}.$$

Substituting Eqs. (3) and (4) into Eq. (2) there results upon solving for $[Mo^{5+}]$

$$[Mo^{5+}] = \frac{[Mo^{5+}]_0}{2} \times \left\{1 + \left[1 + \frac{8Km \cdot n}{(2m+n)^2[Mo^{5+}]_0{}^2}\right]^{1/2}\right\} \tag{5}$$

which for small concentrations of thermal $[Mo^{5+}]_0$, reduces to

$$[Mo^{5+}] = \frac{(2Kmn)^{1/2}}{2m+n} \tag{6}$$

Let $Z = [\mathrm{Mo}]/[\mathrm{Bi}] = n/2m$, then

$$[\mathrm{Mo}^{5+}] = \mathrm{K}^{1/2}\left(\frac{Z^{1/2}}{1 + Z}\right) \tag{7}$$

We note that $[\mathrm{Mo}^{5+}]$ is a maximum at $Z = 1$ or for

$$\mathrm{Bi_2O_3} \cdot 2,\mathrm{MoO_3},$$

the composition at which Aykan observed a maximum in the yield of acrylonitrile.

It should be noted that the lower oxidation states of Mo do not give yields which would conform with Aykan data. Thus for instance, assumption that Mo^{4+} rather than Mo^{5+} is an important component of a catalytic site, would result in a maximum in Aykan curve corresponding to $m = 1$ $n = 1$. Therefore, it would appear that the yield of acrylonitrile is proportional to Mo^{5+} concentration in the Bi–Mo system, the small but nevertheless finite yield of acrylonitrile observed by Aykan for pure $\mathrm{MoO_3}$ can be attributed to the concentration of Mo^{5+}, herein, designated as thermally produced $[\mathrm{Mo}^{5+}]_0$. This model further suggests that reaction of ammoxidation of propylene involves electron exchange between adsorbed propylene molecule and Mo^{5+}.

As K in Eq. (7) must be temperature sensitive, yield of acrylonitrile will, of course, be temperature sensitive insofar as the equilibrium in favor of Mo^{5+} can be altered thereby.

Finally, chemical promotion by other easily oxidized ions of the Bi–Mo system to favorably affect the Mo^{5+} concentration can be anticipated should the thesis herein presented prove to be correct.

ACKNOWLEDGMENT

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REFERENCE

1. AYKAN, K., *J. Catal.* **12**, 281 (1968).