TABLE I

| Catalyst | Ethanes (%) $d_0$ | $d_1$ | $d_2$ | $d_3$ | $d_4$ | $d_5$ | $d_6$ | Conversion (%) |
|---|---|---|---|---|---|---|---|---|
| 1 | 14.7 | 30.1 | 29.5 | 12.7 | 7.4 | 3.7 | 1.8 | 19 |
| 2 | 17.1 | 23.8 | 37.2 | 12.3 | 5.3 | 2.9 | 1.3 | 25 |
| 3 | 17.2 | 21.8 | 40.3 | 12.2 | 5.2 | 2.2 | 1.1 | 22 |
| 4 | 21.3 | 23.3 | 35.3 | 11.5 | 4.4 | 2.5 | 1.7 | 16 |

metal to support occurs to promote ethylene hyrdogenation on the support then a difference would be expected in the data from Pt–$SiO_2$ mixed with $SiO_2$ or $Al_2O_3$. The absence of this difference, mirrored by the less sensitive ethane distributions, plainly indicates that the reaction takes place only on the metal and is in disagreement with the proposal of Sinfelt and Lucchesi (*1*) concerning hydrogen spillover and reaction on the support. Furthermore, although it was not the object of this work to obtain detailed kinetic data, the estimated initial rates of reaction for catalysts 2–4 when related to unit Pt weight (assuming similar Pt dispersions on $SiO_2$ and $Al_2O_3$) are the same to within 20%. The value for catalyst 1 which is very different from the others is still only about half these. Since all catalysts were subjected to oxygen cleaning treatment at 300°C before runs these observations are in complete agreement with the more detailed kinetic data obtained by Schlatter and Boudart on this system (*2*).

## References


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# Defect Control in Oxidation Catalysts

Active sites on heterogeneous catalysts have long been suspected to be intimately related to surface defects. However, the control and characterization of such defects is very difficult. We have introduced lattice defects into the bulk structure of scheelite-type catalysts and find that catalytic activity correlates well with total defect concentration. Thus, it appears that we are also controlling surface defects.

The scheelite-structure catalysts for this study were all single-phase, crystalline materials. The scheelite structure[1] (*1*) has the ideal formula $AMO_4$ and exists for many molybdates and tungstates, e.g., $Ca^{2+}W^{6+}O_4$ and $Pb^{2+}Mo^{6+}O_4$. Substitution on the A site is possible giving scheelite compounds of the type $A^{1+}_{0.5}A^{3+}_{0.5}MO_4$, e.g., $Li_{0.5}La_{0.5}MoO_4$ and $Na_{0.5}Bi_{0.5}WO_4$. We find that defects can be introduced according to the formulas $A^{2+}_{1-3x}A^{3+}_{2x}\square_xMO_4$ or $A^{1+}_{0.5-3x}Bi_{0.5+x}\square_{2x}MO_4$

[1] A description of the scheelite structure and many examples of compounds with this structure may be found in Ref. (*1*).

where □ represents a vacant lattice site which would normally be occupied by an A cation.

The catalysts were prepared by solid state reactions between intimate mixtures of appropriate quantities of oxides at 600 to 800°C, e.g., $7PbO + Bi_2O_3 + 10MoO_3 \rightarrow 10Pb_{0.7}Bi_{0.2}\square_{0.1}MoO_4$. X-Ray powder patterns of the products showed only one crystalline phase. Since this crystalline phase completely accounts for the reactants, there is little possibility of an amorphous phase also being present. Density measurements show that the defect introduced is indeed a cation vacancy and not, for example, an oxygen interstitial.

The type of substitution we are performing would not be expected to greatly affect the electronic component of electrical conductivity, but it might well contribute an ionic component. In fact, we find that both $PbMoO_4$ and $Pb_{0.88}Bi_{0.08}\square_{0.04}MoO_4$ are electrically insulating with room temperature resistivities greater than $10^9$ ohm cm.

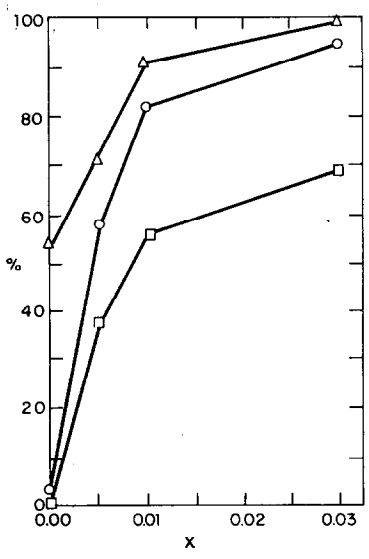


FIG. 1. Percentage consumption of $NH_3$ (△) and propylene (○) with the percentage conversion of propylene (□) to acrylonitrile vs defect concentration in the system $Pb_{1-3x}Bi_{2x}\square_xMoO_4$ Thirty cm³ of ⅛-in. pellets in ½-in. i.d. U-tube reactor with feeds of 4.0% $C_3H_6$, 4.8% $NH_3$, 47.7% air, 43.5% $N_2$ at 440°C, a contact time of 6.0 sec, and a pressure of zero psig.

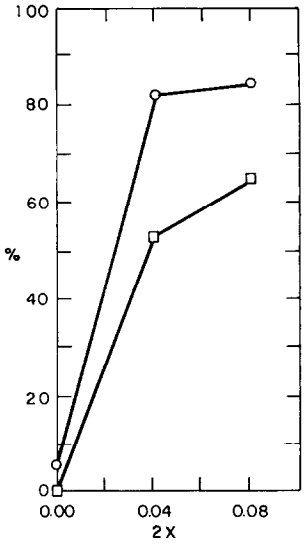


FIG. 2. Percentage consumption of propylene (○) and the percentage conversion of propylene (□) to acrolein vs defect concentration in the system $Na_{0.5-3x}Bi_{0.5+x}\square_{2x}MoO_4$. Fifteen cubic centimeters of ⅛-in. pellets in ⅜-in. i.d. U-tube reactor with feeds of 5.0% $C_3H_6$, 10.0% $O_2$, 85.0% $N_2$ at 450°C, a contact time of 4.0 sec, and a pressure of zero psig.

The tetragonal unit cell dimensions of the scheelite phases can either decrease or increase with increasing vacancy concentration. For $PhMoO_4$, $a = 5.436$ Å and $c = 12.109$ Å, while for $Pb_{0.7}Bi_{0.2}\square_{0.1}MoO_4$, $a = 5.388$ Å and $c = 12.018$ Å. For $Li_{0.5}Bi_{0.5}MoO_4$, $a = 5.221$ Å and $c = 11.469$ Å, while for $Li_{0.26}Bi_{0.58}\square_{0.16}MoO_4$, $a = 5.242$ Å and $c = 11.627$ Å. These differences are consistent with relative ionic sizes since $Bi^{3+}$ is smaller than $Pb^{2+}$ but larger than $Li^+$.

The defect phases prepared were found to be active and selective catalysts for many oxidation reactions such as methanol to formaldehyde, ethylene glycol to glyoxal, propylene to acrolein, and butene to butadiene. Our primary focus, however, has been the ammoxidation of propylene to acrylonitrile. The relationship between catalytic activity for propylene ammoxidation and defect concentration is shown for the $Pb_{1-3x}Bi_{2x}\square MoO_4$ system in Fig. 1; a similar correlation for propylene oxidation over the $Na^+_{0.5-3x}Bi_{0.5+x}\square_{2x}MoO_4$ sys-

tem is shown in Fig. 2. Reaction conditions are summarized in the captions. The activity is insignificant when cation vacancies are not present ($x = 0$) but increases with increasing defect concentration for both systems despite the very different $Bi^{3+}$ concentrations in the two systems. However, the presence of at least some $Bi^{3+}$ appears necessary for good selectivity.

We have studied the catalytic properties of more than thirty scheelite-structure phases represented by the formula $A_{1-x}\square_xMo_4$ where M = Mo, W, and/or V, and A may include Li, Na, K, Ag, Ca, Sr, Ba, Cd, Pb, Bi and/or a rare earth in quantities appropriate to achieve charge balance for normal oxidation states. Without exception we find that catalytic activity increases with increasing defect concentration. Detailed kinetic and adsorption studies are in progress.

The defects which have been introduced to the bulk in these phases must surely manifest themselves in some manner at the surface. Thus, by controlling the type and concentration of defects in the bulk, one can hope to also control the surface defects. If the surface defects are active sites for catalysis, then their concentration will correlate with activity and their type should affect selectivity. We feel that this is the most plausible explanation of our results.

## Reference

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