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An Investigation of the Role of Bismuth and Defect Cation Vacancies in Selective Oxidation and Ammoxidation Catalysis[1]

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The roles of bismuth and cation vacancy defects in the selective ammoxidation of propylene to acrylonitrile were investigated. Based on kinetic and spectroscopic studies of several scheelite molybdate catalysts, it is concluded that bismuth, and not cation vacancies, is responsible for the formation of the allylic intermediate from propylene. Cation vacancies generate molybdenyl-type functionalities in the vicinity of the defects which are responsible for the insertion of oxygen or nitrogen into the allylic intermediate in the selective oxidation or ammoxidation of propylene, respectively.

INTRODUCTION

Several types of defects have been suggested to play important roles in determining the catalytic behavior of metal oxides in the selective oxidation and ammoxidation of olefins. Their exact mechanistic role in the catalytic cycle was however, not well understood. For example, it has been reported (*1*) that cation vacancies are responsible for the rate-controlling α-hydrogen abstraction from olefins during catalytic oxidation and ammoxidation over scheelite molybdate catalysts. Subsequently (*2, 3*), several researchers have proposed that cation vacancies have a similar function in other types of metal oxide catalysts. Recent mechanistic studies (*4*) on bismuth-containing oxide catalysts, however, lend substantial credence to the realization that bismuth (specifically surface lattice oxygen bound to bismuth) is responsible for the formation of the allylic intermediate via α-H abstraction.

In order to resolve this question we have reexamined the catalytic behavior and the solid state structural aspects of some doped scheelite molybdate catalyst systems wherein the bismuth and cation vacancies in a $PbMoO_4$ host have been independently varied in a systematic manner.

EXPERIMENTAL

Four series of unsupported catalysts were prepared by coprecipitation: $Pb_{0.88}La_{0.08-x}Bi_x\square_{0.04}MoO_4$ with $0 \leq x \leq 0.08$, $Pb_{0.84+x}Bi_{0.08}\square_xNa_{0.08-2x}MoO_4$, $Pb_{0.84-3x}Bi_{0.08}Na_{0.08}La_{2x}\square_xMoO_4$ and $Pb_{1-3x}La_{2x}\square_xMoO_4$ with $0 \leq x \leq 0.04$ where $\square$ represents a vacant cation site in the $PbMoO_4$ structure. After drying, the catalysts were heat-treated at 290, 425, and 500°C for 3, 3, and 16 h, respectively.

Propylene ammoxidation experiments were conducted at 430°C using 2.5 g of catalyst in a fixed bed, plug flow U-tube ($\frac{3}{8}$ in. diameter) stainless-steel microreactor and a gaseous feed mixture consisting of propylene/ammonia/air/water = 1/1.2/10.5/4.0 with a contact time of 3.0 s. Propylene conversion in all cases was less than 60%.

RESULTS AND DISCUSSION

The catalytic behavior of the $Pb_{0.88}La_{0.08-x}Bi_x\square_{0.04}MoO_4$, $Pb_{0.84+x}Bi_{0.08}\square_xNa_{0.08-2x}MoO_4$, $Pb_{0.84-3x}Bi_{0.08}Na_{0.08}La_{2x}\square_xMoO_4$, and $Pb_{1-3x}La_{2x}\square_xMoO_4$ solid

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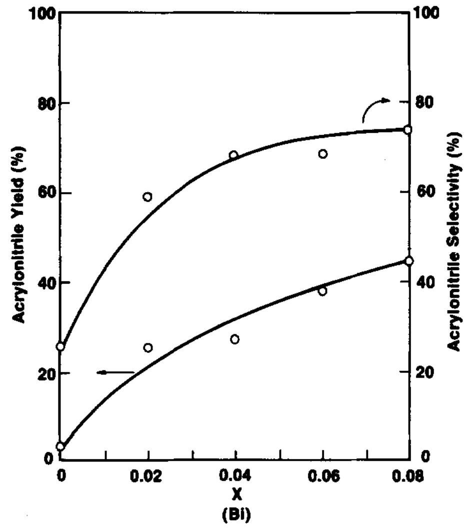

FIG. 1. Catalytic activity and selectivity for propylene ammoxidation for the $Pb_{0.88}La_{0.08-x}Bi_x\Box_{0.04}MoO_4$ system as a function of bismuth content.

solutions in the ammoxidation of propylene at 430°C is summarized in Figs. 1, 2, 3, and 4, respectively. Powder X-ray diffraction showed all these materials to be single phase over the entire composition range studied. For the $Pb_{0.88}La_{0.08-x}Bi_x\Box_{0.04}MoO_4$ system where the bismuth level is varied with constant cation vacancy concentration, both the catalytic activity and selectivity to acrylonitrile increase with increasing bismuth content (Fig. 1). The incease is greatest with the initial addition of bismuth to the solid. For systems in which the cation vacancy level is varied with a constant bismuth level, only the catalytic activity increases with increasing vacancy concentra-

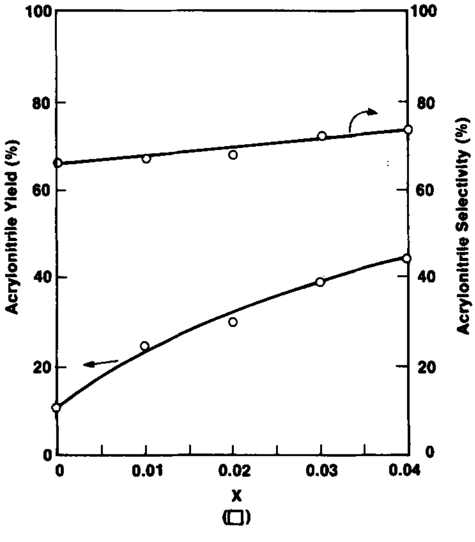

FIG. 2. Catalytic activity and selectivity for propylene ammoxidation for the $Pb_{0.84+x}Bi_{0.08}\Box_xNa_{0.08-2x}MoO_4$ system as a function of cation vacancy concentration.

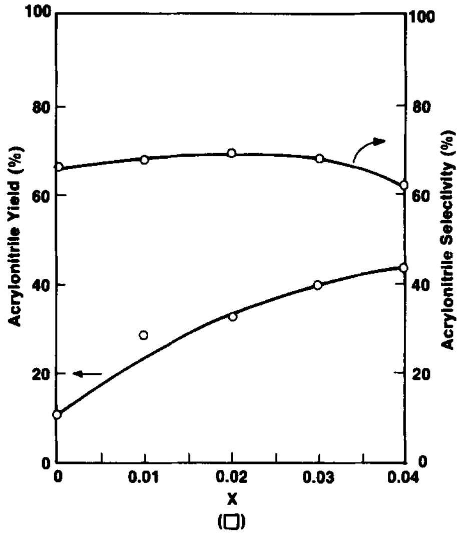

FIG. 3. Catalytic activity and selectivity for propylene ammoxidation for the $Pb_{0.84-3x}Bi_{0.08}Na_{0.08}La_{2x}\Box_xMoO_4$ system as a function of cation vacancy concentration.

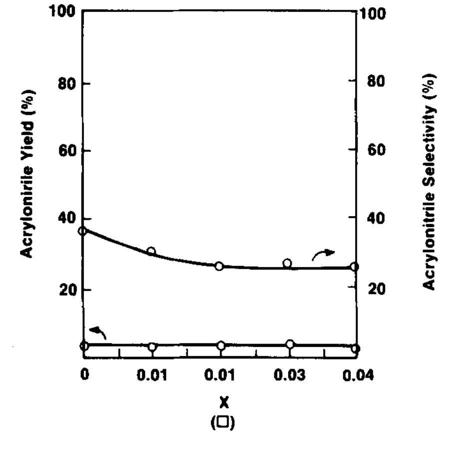

FIG. 4. Catalytic activity and selectivity for propylene ammoxidation for the $Pb_{1-3x}La_{2x}\Box_xMoO_4$ system as a function of cation vacancy concentration.

tion (Figs. 2 and 3). The selectivity to acrylonitrile, however, changes only slightly as the cation vacancy level is increased. The selectivity remains high for all catalysts containing bismuth, irrespective of the cation vacancy content. Figure 4 shows that the catalytic activity and selectivity of the bismuth-free $Pb_{1-3x}La_{2x}\square_xMoO_4$ system are substantially less than for the bismuth-containing catalysts. Substitution of La^{3+} for Pb^{2+} has no effect on the acrylonitrile yield and results in a decrease in selectivity in the absence of bismuth.

From an examination of the catalytic behavior of the $Pb_{1-3x}Bi_{2x}\square_xMoO_4$ system, where both cation vacancy and bismuth levels are varied simultaneously, Sleight (*1*) concluded that cation vacancies are responsible for the formation of the allylic intermediate by hydrogen abstraction from the olefin. However, if a cation vacancy is necessary for α-hydrogen abstraction, and bismuth is responsible only for catalyst reoxidation and high oxygen mobility as suggested by Sleight (*1*), the $Pb_{0.88}Bi_{0.08}Na_{0.08}MoO_4$ catalyst would be expected to be active but not selective. In addition, the bismuth-free $Pb_{1-3x}La_{2x}\square_xMoO_4$ catalysts would be expected to show increasing selectivity with increasing cation vacancy content. This however is not the case. Since only the bismuth-containing molybdate systems are selective, it is apparent that bismuth and not cation vacancies are necessary for α-H abstraction and the formation of the allylic intermediate from propylene.

It is clear that the overall activity of the bismuth-containing $PbMoO_4$ catalyst increases with increasing cation vacancy content. The role of the cation vacancy in the mechanism of selective olefin oxidation and ammoxidation can be discerned from the vibrational spectra of these catalysts. Examination of the Raman and infrared spectra of the $Pb_{0.84+x}Bi_{0.08}\square_xNa_{0.08-2x}MoO_4$ system, shown in Figs. 5 and 6, clearly reveals the formation of higher order Mo–O bonds in the $PbMoO_4$ lattice when cation vacan-

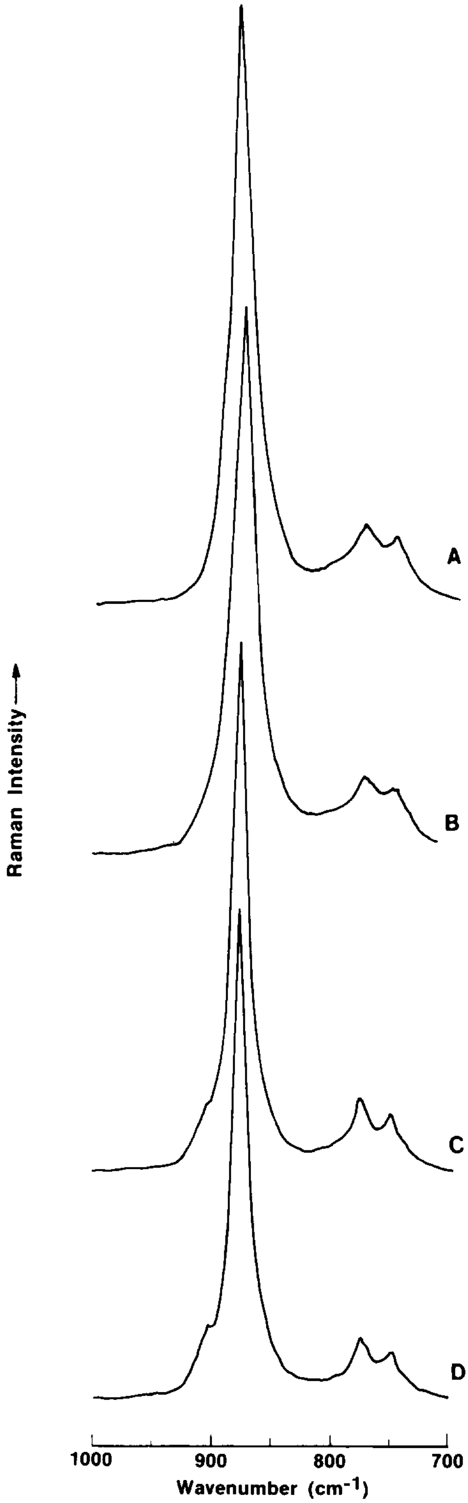

FIG. 5. Raman spectra of the $Pb_{0.84+x}Bi_{0.08}\square_xNa_{0.08-2x}MoO_4$ system: (A) $x = 0$; (B) $x = 0.02$; (C) $x = 0.03$; (D) $x = 0.04$.

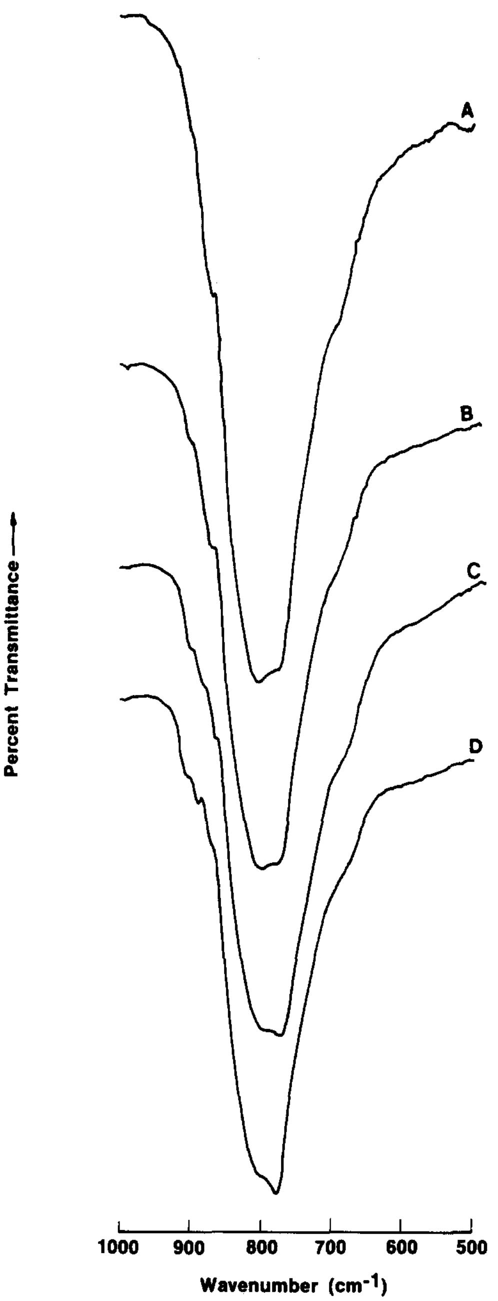

FIG. 6. Infrared spectra of the $Pb_{0.84+x}Bi_{0.08}\square_x Na_{0.08-2x}MoO_4$ system: (A) $x = 0$; (B) $x = 0.02$; (C) $x = 0.03$; (D) $x = 0.04$.

cies are introduced in the structure. This is evidenced by the appearance of a high-frequency band at about 893 cm^{-1} in the Raman and bands at 902 and 889 cm^{-1} in the infrared. Examination of the vibrational spectra of the other systems shows that the appearance of these high-frequency bands is only a direct function of the cation vacancy concentration.

Justification for the assignment of the new high-frequency band to a local mode involving higher order Mo–O bonds is derived from an examination of the vibrational spectra and crystal structure of Pb MoO_4. Lead molybdate has the ideal ABO_4 scheelite structure (space group $I_{4_1/a} - C_{4h}{}^6$) (*5*) in which all Mo atoms are tetrahedrally coordinated by oxygen at a distance of 1.772 Å. In addition, all of the oxygens bridge the Pb and Mo cations. There are no terminally bound oxygens in the structure. This is manifested in the Raman spectrum of pure $PbMoO_4$ which shows the highest Mo–O stretching frequency (the symmetric $\nu_1(A_g)$ mode) at 869 cm^{-1} (*6*) whereas the stretching frequencies associated with terminal Mo=O moieties in MoO_3 (*7*) and $Bi_2(MoO_4)_3$ (*3*) appear at 997 and 955 cm^{-1}, respectively. In order to estimate vibrational frequencies in lead molybdates containing defect cation vacancies, a molecular cluster calculation (*8*) was performed for both MoO_4 tetrahedra (C_{4h} symmetry) and the postulated MoO_4 cluster in which the bond order of one of the Mo–O bonds is increased (C_{3v} symmetry). The valence force field calculation was performed by first determining a set of force constants from the observed modes of MoO_4 tetrahedra in $PbMoO_4$. For purposes of comparison, the shortest Mo–O bond (1.68 Å) in $Bi_2(MoO_4)_3$ (*9*), which has a calculated bond order of 1.98 (*10*), was used to represent a higher order Mo–O bond in the defect lead molybdate. Using the general relationship between force constants and bond order given by Gordy (*11*), the modes of this new local cluster were calculated. The result of increasing the bond order of one of the Mo–O bonds is the emergence of a mode at 916 cm^{-1}. This indicates that the Mo–O bonds located next to the cation vacancies have bond orders greater than one but probably less than that of the molybdenyl groups in $Bi_2(MoO_4)_3$. In addition, it should be noted that the appearance of the high-frequency band in both the Raman and infrared spectra is consistent with the proposed model since the A_1 mode in the C_{3v} point group is both Raman and infrared active.

Thus, our results support the general mechanistic scheme for bismuth molybdenum oxide catalysts (*4*) in which the important role of bismuth in the selective oxidation and ammoxidation of olefins is the formation of the allylic intermediate by the abstraction of an α-hydrogen from propylene. Defect cation vacancies in a scheelite $PbMoO_4$ structure are not directly involved in this rate-determining hydrogen abstracting step. Instead, these defects generate higher order Mo–O centers in the structure making lattice oxygen available for the partial oxidation reaction. These molybdenyl-type functionalities are the centers for olefin chemisorption and selective oxygen, or in the presence of ammonia selective nitrogen insertion into the allylic intermediate (*4*). Cation vacancies also improve lattice oxygen diffusion and thereby further enhance catalytic activity by facilitating the replenishment of oxygen ions in the redox cycle of the catalyst and by maintaining the oxygen insertion centers in an optimum high oxidation state.

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