

## Effect of Transition Metal Cation on Multicomponent Bismuth Phosphate Catalyst in Propylene Ammoxidation

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The study on the multiphase catalysts has been attracted by a large number of investigators. One reason for this is that great differences are generally observed in catalytic properties between the multiphase and single-phase type catalysts. The improvement of catalytic performances for a mixture of phases with respect to each phase component has been explained by synergy effect.<sup>1-4</sup> Especially the synergism has been accounted for an effect of the divalent- or trivalent-metal molybdates in the case of multicomponent bismuth molybdate catalysts.<sup>5</sup> The unique role of unadsorbed oxygen and lattice oxygen in selective oxidation on transition metal molybdates has been reviewed by Bielanski and Haber.<sup>6</sup>

In this work, we report on the catalytic behaviors of multicomponent bismuth phosphate (MBP) catalysts that are mainly consisted of the bismuth phosphate and the metal molybdate, where metal ion is  $Mn^{2+}$ ,  $Cr^{3+}$ ,  $Co^{2+}$ , or  $Cu^{2+}$ . In order to understand the catalytic behaviors in the propylene ammoxidation over MBP, that is, Bi-P-Mo-M-Ni-O system, a systematic investigation on the oxygen adsorptive properties has been carried out. The methods of X-ray diffraction, oxygen chemisorption, and IR spectroscopy are used to characterize the catalyst system.

### Experimental Section

**Preparation of MBP.** The catalysts were a series of  $BiPMoM_{0.3}Ni_{0.8}O_y/7\%SiO_2$  with  $M = Mn^{2+}$ ,  $Cr^{3+}$ ,  $Co^{2+}$ , or  $Cu^{2+}$ , which were prepared by the slurry technique with several nitrates. Solution A was prepared by dissolving a mixture of  $Bi(NO_3)_3 \cdot 5H_2O$ , metal cation(M) nitrate and  $Ni(NO_3)_2 \cdot 6H_2O$  in 10%  $HNO_3$ . Solution B was prepared in such a manner that  $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ ,  $H_3PO_4$  and silica sol were dissolved in water by heating. Then, solutions A and B were mixed. After evaporating the solvent by heating on hot plate, the residue was dried in the oven, calcined, and pulverized. The catalyst prepared from the above method represents the following system: Bi-P-Mo-M-Ni-O/X% $SiO_2$ .

**Characterization.** X-ray powder diffraction pattern of the MBP prepared was obtained by Rigaku 2155D6 instrument using monochromatic radiation. It was operated at 35 kV and 15 mA. The experimental conditions correspond to a conventional step width of 0.016 degree and scan speed of 5 degree/min. Oxygen chemisorption on the MBP was performed and measured at 583 K and 723 K in a Micromeritics

ASAP-2010 instrument. The MBP sample was deoxygenated by the evacuation at 583 K following the supply of He gas (super-pure, 99.999%) before the measurement. IR spectra were recorded using the KBr disk method on a MIDAC FT-IR spectroscopy.

**Catalytic reactions.** The catalytic ammoxidation of propylene was performed in a stainless steel tube as a fixed bed flow reactor with a centered thermocouple. All experiments were carried out at 723 K in atmospheric pressure. The feed was a mixture of propylene, ammonia, oxygen, and nitrogen with the molar ratio of 1/1/2.2/9.8, respectively. The analysis of reactants and products was carried out by on-lined gas chromatography (CHROMPACK CP9001).

### Results and Discussion

**Characterization.** The XRD profiles indicate that  $BiP-MoM_{0.3}Ni_{0.8}O_y/7\%SiO_2$  consists mainly of  $BiPO_4$ ,  $NiMoO_4$ , and metal ion molybdate phases. However, of these phases, the phase of metal ion molybdate could not be apparently detected in the MBP. Therefore, it was prepared  $(BiP)_{0.1}MoM_{0.3}Ni_{0.8}O_y/7\%SiO_2$ , which contains the more amount of M than Bi and P. It was detected the phase of the metal ion molybdate in  $(BiP)_{0.1}MoM_{0.3}Ni_{0.8}O_y/7\%SiO_2$ . Accordingly, the metal molybdate phase in  $BiPMoM_{0.3}Ni_{0.8}O_y/7\%SiO_2$  would not be well detected due to excess bismuth phosphate phase having the good crystallinity.

We have measured the amount of oxygen chemisorbed on the MBP with the variation of the metal ion added at two different temperatures, 723 K and 583 K. As shown in Table 1,

**Table 1.** Ionization potential and electronegativity for the transition metal cation(M) and chemisorption of oxygen in  $BiPMoM_{0.3}Ni_{0.8}O_y/7\%SiO_2$

Cation	Ionization Potential <sup>a</sup> (eV)	Electronegativity (Pauling's Scale)	Oxygen Chemisorbed (cm <sup>3</sup> /g STP)	
			at 723 K	at 583 K
$Co^{2+}$	33.5	1.88	0.150	0.021
$Mn^{2+}$	33.7	1.55	≤ 0.0	0.020
$Cu^{2+}$	36.8	2.00	0.160	0.004
$Cr^{3+}$	49.1	-	0.040	0.002
$Cr^{2+}$	31.0	1.66	-	-

<sup>a</sup> Ionization Potential for  $M^{n+} \rightarrow M^{(n+1)+}$

it seems like that there is no regular relationship between the ionization potential of the metal cation and the amount of oxygen chemisorbed on the MBP at 723 K. However, the amount of oxygen chemisorbed decreases with increasing of the ionization potential of the metal cation of the MBP at 583 K. The amount of oxygen chemisorbed on the MBP at 723 K, the temperature at which the propylene ammoxidation on the MBP occurs, increases in the order of  $\text{Mn}^{2+} < \text{Cr}^{3+} < \text{Co}^{2+} < \text{Cu}^{2+}$ . On the other hand, it is clearly visible that the amount of oxygen adsorbed on the surface of the series of the oxysalts is dependent on the ionization potential of the cation of the salt.<sup>6</sup> Bielanski and Haber<sup>6</sup> have reported that the highest surface volume of oxygen adsorbed at 583 K is observed in the case of molybdates of  $\text{Co}^{2+}$  and  $\text{Mn}^{2+}$ , which are characterized by the lowest values of the ionization potential.

In spite of that, the tendency of oxygen chemisorption on the MBP at 723 K observed in this work seems not to be related to that of the ionization potential. However, it is related with rather the electronegativity than the ionization potential of the metal cation. That is, the increase of the electronegativity of the metal cation added induces the increase of oxygen chemisorption. The sequence of the electronegativity of the metal cations<sup>7</sup> is similar to that of oxygen chemisorption at 723 K. This feature would be account for the influence of bismuth phosphate phase of the MBP on the catalytic reaction. The electronegativity of  $\text{Cr}^{3+}$  could be estimated from the value of  $\text{Cr}^{2+}$  in the Table 1.

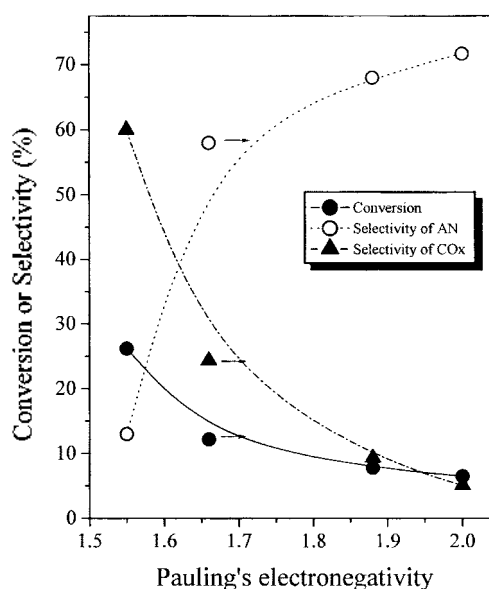
Recently, Delmon, B., *et al.* proposed that the bismuth phosphate is one of the best oxygen donors as oxygen species,  $\text{O}^{2-}$ , dissociated of  $\text{O}_2$ , in comparison with several metal molybdates.<sup>8-10</sup> In this point of view, it is quite reasonable that the bismuth phosphate phase in the MBP plays an important role as an oxygen donor and the metal molybdate phase as an oxygen acceptor in the catalytic ammoxidation of propylene. The acidity of  $\text{Mo}^{6+}$  in the molybdate ( $\text{MoO}_4^{2-}$ ) as the electron acceptor would be increased by the increase of electronegativity of the metal cation bonded within anionic groups. Thus, it would be promoted the chemisorption of oxygen species such as  $\text{O}^{2-}$  dissociated of  $\text{O}_2$  by bismuth phosphate. The  $\text{O}^{2-}$  chemisorbed on the metal molybdate replaces the lattice oxygen used in the reaction.<sup>11</sup>

By such a process described above, the bismuth phosphate and the metal molybdate phases of the MBP would supply active oxygen species to promote the propylene ammoxidation. This is supported by the results shown in Table 1. The amount of oxygen chemisorbed on the MBP is rather much higher at 723 K than at 583 K. Furthermore, the amount of oxygen chemisorbed as the adsorptive ability decreases with increasing of the ionization potential of the cationic metal of the MBP at 583 K, the temperature at which the catalytic ammoxidation of propylene does not work. In the case of  $\text{Mn}^{2+}$  at 723 K, it appears a small negative value of oxygen chemisorption, indicating the possibility of the release of the lattice oxygen.<sup>5</sup> However the value of the oxygen chemisorption might be nil. It would mean that the oxygen species,  $\text{O}^{2-}$  dissociated of  $\text{O}_2$ <sup>8-10</sup> by the bismuth phosphate phase is

chemisorbed at the reaction temperature (723 K) for the propylene ammoxidation followed by the replacement of the lattice oxygen used in the reactions.

The effect of the electronegativity of the metal ion added on the MBP could also be detected by IR spectra of Mo-O bond present in the molybdates. The stretching vibrations of Mo-O of the molybdates assigned are obtained to be 960, 962, 963, and 966 in  $\text{cm}^{-1}$  for  $\text{Mn}^{2+}$ ,  $\text{Cr}^{3+}$ ,  $\text{Co}^{2+}$ , and  $\text{Cu}^{2+}$  as the added metal ion, respectively. The frequencies are agreed well with those given in the literature.<sup>12-14</sup> Even though there is small shift of the stretching vibration of Mo-O with the variation of the metal ions added, the increasing sequence of the stretching vibration of Mo-O,  $\text{Mn}^{2+} < \text{Cr}^{3+} < \text{Co}^{2+} < \text{Cu}^{2+}$ , is parallel to those of the electronegativity and oxygen chemisorption of the MBP of added metal ions.

**Catalytic behaviors.** The correlation between the catalytic behaviors of molybdates and the presence of Mo-O bond will be related to a mechanism of the catalytic ammoxidation of propylene over the MBP. Figure 1 shows the catalytic behavior of the MBP for the propylene ammoxidation. It is noted that the catalytic behavior of the metal ion is well fitted to the curve in the Figure 1, applying the estimated value of electronegativity of  $\text{Cr}^{3+}$  from the value of  $\text{Cr}^{2+}$ . The selectivity of acrylonitrile (AN) due to the selective oxidation pathway increases with the increase of the electronegativity of metal ion added. On the other hand, the selectivity of  $\text{CO}_x$  due to the deep oxidation pathway decreases with it. Therefore, the more deep oxidation pathway could be induced in the reaction of the MBP with  $\text{Mn}^{2+}$ , which is characterized by the lowest value of the electronegativity, than that with  $\text{Cu}^{2+}$  since the former has relatively



**Figure 1.** Dependency of catalytic behavior on electronegativity of M in  $\text{BiPMoM}_{0.3}\text{Ni}_{0.8}\text{O}_y/7\%\text{SiO}_2$  catalysts for the propylene ammoxidation [ $\text{M} = \text{Mn}^{2+}$ ,  $\text{Cr}^{3+}$ ,  $\text{Co}^{2+}$ ,  $\text{Cu}^{2+}$ ]. Reaction conditions: reactants: propylene/ammonia/oxygen/nitrogen = 1/1/2.2/9.8, reaction temperature: 723 K (AN = Acrylonitrile,  $\text{CO}_x = \text{CO} + \text{CO}_2$ ). \*Pauling's scale of  $\text{Cr}^{2+}$  was used instead of  $\text{Cr}^{3+}$  because of its unavailability in reference 7.

less the adsorbed species ( $O^{2-}$ ). As a result, the reaction pathway can be transformed by the electronegativity of the metal ion. However, the increase of electronegativity causes the decrease of the conversion. It would be supposed that both low electronegativity of the metal ion and low capacity of oxygen chemisorption cause simultaneously the decomposition of propylene on the catalyst as a result of the deficiency of lattice oxygen. The bond energy of Mo-O would be responsible for the reaction pathway in oxidation reactions.

In conclusion, the adsorptivity of oxygen on the MBP for the propylene ammoxidation is related more to the electronegativity rather than to the ionization potential of the metal ion added. The electronegativity of the metal ion would affect the chemisorption of oxygen species dissociated of  $O_2$  by bismuth phosphate phase, adjusting the acidity of  $Mo^{6+}$  in  $MoO_4^{2-}$ . The increasing sequences of the stretching vibration of Mo-O and the ability of oxygen chemisorption of the MBP with the variation of added metal ion is parallel to that of electronegativity of the metal ions. The reaction pathway for the catalytic ammoxidation of propylene over the MBP seems to be transformed by the magnitude of bond energy of Mo-O varied by the electronegativity of the metal ion. Relationship between Mo-O bond energy and the reaction pathway in the MBP will be further investigated.

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