

## Catalytic Oxidation of Propene over Zirconium Phosphates

In recent years, attention has been focused on practical applications of the  $\alpha$ -zirconium phosphates (1-5). This is mainly due to the discovery that this compound has a structure with zeolite type cages (6), and behaves as a cation exchanger (7-9). However, only a few investigations (2-5) have examined the use of the zirconium phosphates as catalysts for chemical reactions. Since amorphous metal phosphates have been found to show a catalytic activity for certain reactions (10, 11) and transition metal cations can be exchanged for hydrogen into the zirconium phosphates, it is of interest to evaluate the performance of the various zirconium phosphates in catalytic reactions.

$\alpha$ -Zirconium phosphate,  $Zr(HPO_4)_2 \cdot H_2O$ , hereafter referred to as  $\alpha$ - $ZrH_2P$ , has a layered structure with an interlayer spacing of 0.756 nm (6, 12). Exchange of metal ions does not readily occur with  $\alpha$ - $ZrH_2P$ , probably because the hydrated metal ions are too large to pass through the narrow passageways into the internal cavities (13). Recently, however, a quantitative uptake of transition metal ions was found to proceed by using acetate solutions of  $M^{2+}$  ions (14). Albertsson *et al.* (15) suggested that an acetate ion behaves as a base and causes an increase in the spacing of the passageways of the metal ions. In the present work, the catalytic activities of the zirconium phosphates substituted with Mn(II), Co(II), Ni(II), Cu(II), and Zn(II) ions for the oxidation of propene were studied.

$\alpha$ - $ZrH_2P$  was prepared by the method of Hasegawa and Tomita (9), which was a modified method of that reported by Clearfield and Stynes (16). The gelatinous zirconium phosphates were suspended in 6.7 M phosphoric acid and refluxed for 120 hr at 343 K. After refluxing, the solution was allowed to stand for an additional 24 hr and

the crystals obtained were filtered. They were washed with 2% phosphoric acid and then with distilled water until free from phosphate ions, and dried at 323 K in air. TGA and DTA curves and the X-ray powder diffraction pattern for this compound were identical with the data previously reported (17, 18). The ion-exchange of  $\alpha$ - $ZrH_2P$  was performed by refluxing in 0.2 N solutions of the corresponding metal acetates (14). The TGA, DTA, and X-ray patterns (Fig. 1) for these materials were also in good agreement with those by Allulli *et al.* (19) and Clearfield *et al.* (7). The extents of exchange of the metal ions were determined to be 85, 78, 42, 100, and 43 for Mn(II), Co(II), Ni(II), Cu(II), and Zn(II) ions, respectively, by conventional analytical procedures. These catalysts are designated as  $ZrMeP$ , where Me indicates the metal ion substituted. Mixtures of  $C_3H_6$  (10 vol%),  $O_2$  (20 vol%), and  $N_2$  (70 vol%) were passed through a tubular reactor loaded with 1 g of catalyst. The total flow rate was set at 30  $cm^3/min$ .

Over some types of  $ZrMeP$  the oxidation of propene proceeded above ca. 573 K. The reaction products,  $CH_3CHO$ ,  $CH_2CHCHO$ , CO,  $CO_2$  and  $H_2O$  were detected by gas chromatography. A trace of  $C_2H_4$  was also formed above 673 K, but no other hydrocarbon was detected. A steady-state reaction was achieved for reaction times greater than about 30 min. The results at 673 K are summarized in Table 1. At this temperature  $\alpha$ - $ZrH_2P$  exhibited negligibly small catalytic activity for the reaction, while the respective  $ZrMeP$  catalysts were more or less active for the oxidation. This indicates that the exchange of the transition metal ions into the zirconium phosphate caused an appearance of catalytic performance for oxidation reactions. From plots of the logarithm of reaction rates versus reciprocal

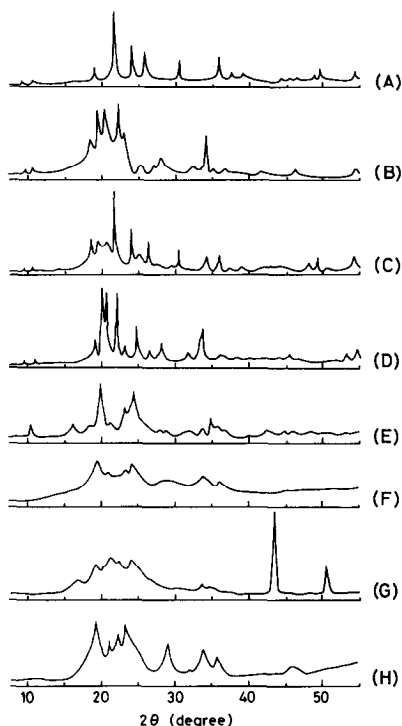


FIG. 1. X-Ray powder patterns of crystalline zirconium phosphate before (A-E) and after (F-H) the use in the oxidation of propene at 673 K for 2 hr: ZrMnP (A), ZrCoP (B, F), ZrNiP (C), ZrCuP (D, G), ZrZnP (E, H). These patterns were obtained with Ni filtered copper X-rays.

absolute temperatures, the apparent activation energies for the oxidation of propene were evaluated and listed in Table 1. The value for  $\alpha$ -ZrH<sub>2</sub>P was much larger than those of the ZrMeP samples, suggesting that the introduction of the transition metal

ions was useful for lowering of the activation energy. A compensation law between the apparent activation energies and frequency factors was confirmed to apply in the present results.

The X-ray powder patterns demonstrated that  $\alpha$ -ZrH<sub>2</sub>P changed to zirconium pyrophosphate upon the use in the reaction at 673 K. This is slightly surprising in view of the fact that  $\alpha$ -ZrH<sub>2</sub>P transforms in air to  $\eta$ -ZrH<sub>2</sub>P at 523 K and subsequently to the pyrophosphate at 873–923 K (17). Although no further reference is made with respect to this phenomenon, it is obvious that the particular experimental circumstance for the sample affects the phase transition. On the other hand, after the use as a catalyst at 673 K, ZrCuP (that is, ZrCu(PO<sub>4</sub>)<sub>2</sub> · 4H<sub>2</sub>O) changed into the phase G (that is, ZrCu(PO<sub>4</sub>)<sub>2</sub>) defined by Clearfield and Pack (7). This phase change is reasonable because the same phase transition occurs at ca. 523 K in air (7). In the case of the other phosphates, the variations of the X-ray powder diffraction patterns (Fig. 1) were similarly observed, though no data have been available for the comparison with the present results. Consequently, the active phase of each sample for the reaction is likely to be the corresponding dehydrated phase.

The order of catalytic activities of metals or metal oxides is often discussed by referring to thermodynamic parameters such as the heats of formation of the corresponding

TABLE I  
Catalytic Activities of Various Zirconium Phosphates in the Oxidation of Propene at 673 K

Catalyst	Conversion of propene (%)	Selectivity to (%)				Activation energy (kcal/mol)
		CH <sub>3</sub> CHO	CH <sub>2</sub> CHCHO	CO	CO <sub>2</sub>	
ZrH <sub>2</sub> P	0.24	Trace	0	54.2	45.8	61.1
ZrMnP	1.93	28.5	0	50.2	21.2	33.2
ZrCoP	5.46	10.3	7.7	35.9	46.2	21.7
ZrNiP	6.19	3.9	3.9	30.7	61.6	19.7
ZrCuP	10.75	5.6	7.0	54.6	32.9	17.7
ZrZnP	2.66	10.5	0	5.3	84.2	28.5

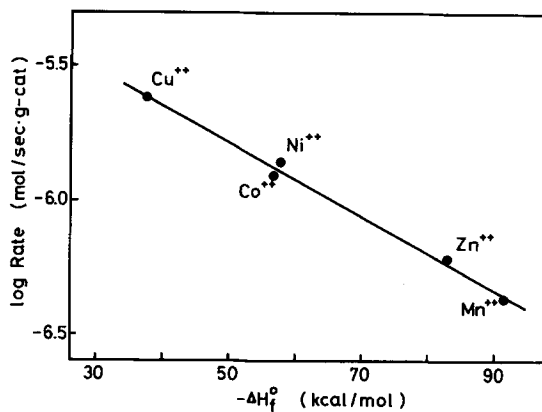


FIG. 2. Correlation between the rates of propene oxidation at 673 K over various zirconium phosphates and the heats of formation ( $-\Delta H_f^0$ ) of the corresponding oxides per g-atom of oxygen.

oxides; for example, Morooka and Ozaki (20) obtained a good correlation between the catalytic activities for propene oxidation and the heats of formation of the oxides. This indicates that the latter can be used as a parameter for the strength of metal-oxygen bonds. In Fig. 2, thus, the rates of propene oxidation which were calculated from Table 1 are plotted against the heats of formation ( $-\Delta H_f^0$ ) of the corresponding oxides per g-atom of oxygen. Clearly a fairly good correlation is recog-

nized. This suggests that the introduced metal ions act as the sites activating the oxygen species and the reactivities of the oxygen species depend on the strength of the metal-oxygen bonds. The low catalytic activity of  $\alpha$ -ZrH<sub>2</sub>P sample would result from a lack of active sites for oxygen.

As shown in Table 1, the catalytic activity of ZrCuP was higher than those of the others, so that its activity was examined in more detail. The results were plotted in Fig. 3 as a function of reaction temperature. The extent of conversion of propene increased with increasing temperature, but the increase in temperature from 723 to 773 K resulted in only a little increment of the conversion level. Furthermore, the distribution of the products varied extremely between 723 and 773 K, and the rate of CO formation increased at 773 K. These phenomena would be combined with a phase change. In the X-ray powder pattern of the catalyst after the experimental run of Fig. 3, each diffraction line was lowered in strength and broadened, compared with that of the phase G. This is consistent with the fact that the condensation of phosphate groups to form amorphous pyrophosphate begins at 773 K (7). It is clear that the difference between the product distributions at 723 and 773 K was caused by the change of the catalyst phases, though the mechanism cannot be clear yet.

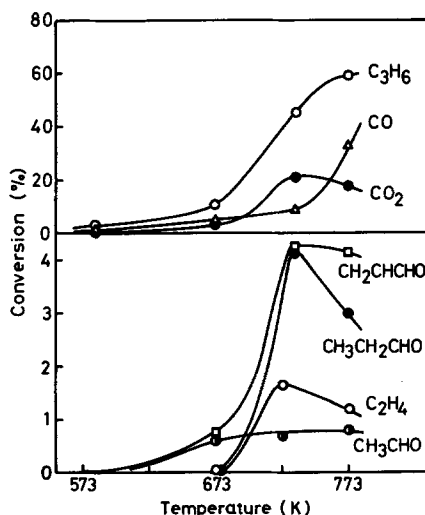


FIG. 3. Oxidation of propene over a copper-substituted zirconium phosphate catalyst. The extent of conversion was calculated on the basis of the propene.

Finally, the influence of water on the reaction over ZrCuP was investigated at 673 K. Upon addition of water (40 vol%) the degree of conversion of propene reduced to 3.9%, whereas the selectivities for CH<sub>3</sub>CHO and CH<sub>2</sub>CHCHO increased to 30.1 and 15.1%, respectively. These values are much greater than those given in Table 1. It is concluded that water addition is effective in obtaining partially oxidized compounds.

On the basis of the experimental evidence presented here, it follows that metal ion-substituted  $\alpha$ -zirconium phosphates act as catalysts for oxidation reactions whose activities are comparable with those of the corresponding metal oxides. The catalytic activity of the sample depends on its phase and the presence of water.

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