Hydration of ethene over W–P mixed metal oxide catalysts

Takashi Ushikubo *, Mitsuhiko Kurashige, Teruyo Koyanagi, Hiroto Ito and Yoshihisa Watanabe

Mitsubishi Chemical Corporation, Yokkaichi Plant, 1 Toho-cho, Yokkaichi, 510-8530, Japan

Received 2 May 2000; accepted 17 July 2000

W–P mixed metal oxide catalysts are active and selective for the gas-phase hydration of ethene to ethanol. The activity and selectivity of this catalytic reaction depend on the W/P atomic ratio. However, ethene conversion slightly decreases at higher $W/(W+P)$ atomic ratio. The selectivity for ethanol increases with the W/P atomic ratio and reaches the highest value (92%) at $W_{0.81}P_{0.19}O_x$. The $W_{0.81}P_{0.19}O_x$ catalyst is less active than the conventional H_3PO_4/SiO_2 catalyst, but the activity is maintained for a long time without the supply of any catalyst components. The reaction temperature does not affect substantially the rate of ethene hydration over the $W_{0.81}P_{0.19}O_x$ catalyst. The H_2O/ethene molar ratio of 0.4 is the most appropriate for both reaction rate and selectivity. The active species of W–P mixed metal oxide are amorphous. But there is Keggin structure of W–P oxide species ($PW_{12}O_{40}^{3-}$) in the presence of steam. And the species are the active sites for the hydration of ethene, confirmed by *in situ* Raman spectroscopy.

Keywords: ethene, ethanol, hydration, W–P oxide catalyst, Raman spectroscopy

1. Introduction

Ethanol is one of the most versatile oxygen-containing organic chemicals because of its unique combination of properties as a solvent, a germicide, an antifreeze, a fuel and especially as a chemical intermediate for other organic chemicals. Industrial ethanol can be produced synthetically from ethene, or by the fermentation of sugar, starch or cellulose.

At present, the vapor-phase hydration of ethene is carried out by using catalysts based on phosphoric acid supported on silica. In this method, although the selectivity for ethanol is very high, continuous elusion of acid components from the catalysts readily occurs under the reaction conditions and causes a rapid deactivation of the catalyst. The acid components from the waste water need to be recovered due to environmental concerns. Furthermore, the conversion of ethene is very small due to equilibrium restrictions, especially at higher temperatures. Therefore, noble catalysts, especially stable under the reaction conditions and active at lower temperatures, are typically employed for the hydration of ethene.

There have been many papers and patents concerning new catalysts of the hydration of ethene to ethanol as well as the improvement of catalyst carriers for phosphoric acid [1–7]. Many acidic metal oxides, such as TiO_2–SiO_2 and zirconium tungstate and copper(II) fluoborate, alkali metal or ammonium sulfate catalysts and heteropolyacids, such as phosphotungstic acid and phosphomolybdic acid have been demonstrated for the hydration of ethene.

In this paper, we wish to report that unsupported W–P mixed metal oxide catalysts are active and selective for the gas-phase hydration of ethene at moderate temperatures. The activity and selectivity depend on the W/P atomic ratio, with $W_{0.81}P_{0.19}O_x$ showing the highest selectivity for ethanol. The catalyst has a long catalyst life without the need to supply any catalyst components. The active species are amorphous. But there is Keggin structure of W–P mixed metal oxide species ($PW_{12}O_{40}^{3-}$) in the presence of steam, that is confirmed by Raman spectroscopy. And the surface species are active sites for the gas-phase hydration of ethene.

2. Experimental

2.1. Catalyst preparation

The W–P mixed metal oxide catalysts with different W/P atomic ratio were prepared as follows: ammonium dodecatungstic acid pentahydrate was dissolved in warm deionized water. Phosphoric acid was sequentially added. The obtained slurry was evaporated to dryness at 358 K and dried at 393 K for 15 h. The dried product was crushed, calcined in a flowing air stream at 973 K for 3 h, and the resulting powder was molded into tablet form. The W/P atomic ratio was controlled by the amounts of dodecatungstic acid and phosphoric acid added to the aqueous solution. Specific surface area of the W–P mixed metal oxides, that was measured by using a Carlo–Erba Sorptomatic 1800 (BET apparatus), was less than 1 $m^2\,g^{-1}$.

$H_3PW_{12}O_{40}/SiO_2$, $H_3PMo_{12}O_{40}/SiO_2$ and H_3PO_4/SiO_2 catalysts were prepared by the impregnation of silica (the reference silica of the Catalysis Society of Japan, JRC-SIO-1, specific surface area 166 $m^2\,g^{-1}$) with an aqueous solution containing 70 wt% of $H_3PW_{12}O_{40}$, $H_3PMo_{12}O_{40}$ and H_3PO_4, respectively.

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* Present address: Mitsubishi Chemical Corporation, Mizushima Plant, 3-10 Ushiodori, Kurashiki, 712-8054, Japan.

2.2. Catalytic activity testing

Hydration of ethene was carried out under 0.6 MPa in an ordinary flow-type fixed-bed reactor. Typical reaction conditions were: GHSV $= 900\ \mathrm{h}^{-1}$, catalyst amount 10 cm^3, temperature 450–530 K, feed gas molar ratio H_2O/ethene $= 0.2$–1.0. The reaction effluent was introduced directly to a gas chromatography system (Okura Riken GC10S, column porous poymer Gasukuropak 54) and analyzed. Reported conversions and selectivities are based on ethene.

2.3. Catalyst characterization

XRD measurements were carried out by using a Philips PW1700 with Cu Kα source. The Raman spectrometer system consisted of a Triplemate spectrometer (Spex, model 1877) coupled to an optical multi-channel analyzer (Princeton Applied Research model 1463) equipped with an intensified photodiode array detector (cooled to 238 K). The Raman spectra from the catalysts were generated with the 514.5 nm line of an Ar^+ laser utilizing about 10 mW of radiant power. *In situ* Raman experiments over the catalysts were performed at various temperatures between 298 and 623 K and different compositions of the gases with a total flow rate of 100 $\mathrm{cm}^3\,\mathrm{min}^{-1}$. The composition of the reaction gas was calculated on the basis of the saturated water vapor pressure and the flow rate of each mixed gas, i.e., $C_2H_4/H_2O/He = 5/2/93$ or 10/2/88 mol%.

3. Result and discussion

The catalytic activities of the W–P oxide catalysts for the vapor-phase hydration of ethene are compared with those of other catalysts in table 1. The $H_3PW_{12}O_{40}/SiO_2$ catalyst shows the highest activity, but its selectivity for ethanol is the lowest. The selectivity for ethyl ether, that is the product of intermolecular dehydration of ethanol, is high over the $H_3PW_{12}O_{40}/SiO_2$ catalyst. In the current commercial process, ethyl ether is recycled to the reactor together with unreacted ethene in order to hydrolyze it to ethene. So, the more ethyl ether produced, the poorer is the process efficiency. In addition to ethyl ether, a considerable amount of hydrocarbons, such as butane, butenes, hexane and hexenes, are produced over the $H_3PW_{12}O_{40}/SiO_2$ and the $H_3PMo_{12}O_{40}/SiO_2$ catalysts. Because these heteropolyacid compounds are highly acidic, ethene easily polymerizes to C_4 and C_6 hydrocarbons. On the other hand, the H_3PO_4/SiO_2 catalyst shows the highest selectivity for ethanol with moderate hydration activity. The W–P oxide catalysts are less active than the H_3PO_4/SiO_2 catalyst because the specific surface area of W–P oxide catalysts is less than 1% of silica-supported acid catalysts.

The activity and selectivity of the W–P mixed metal oxide catalysts depend on the W/P atomic ratio, as shown in figure 1. Although ethene conversion slightly decreases at higher W/(W+P) atomic ratio, the selectivity for ethanol increases and reaches the highest value at $W_{0.81}P_{0.19}O_x$. Over the W–P oxide catalysts with lower W/(W + P) atomic ratio, the selectivity for acetaldehyde is high. For example,

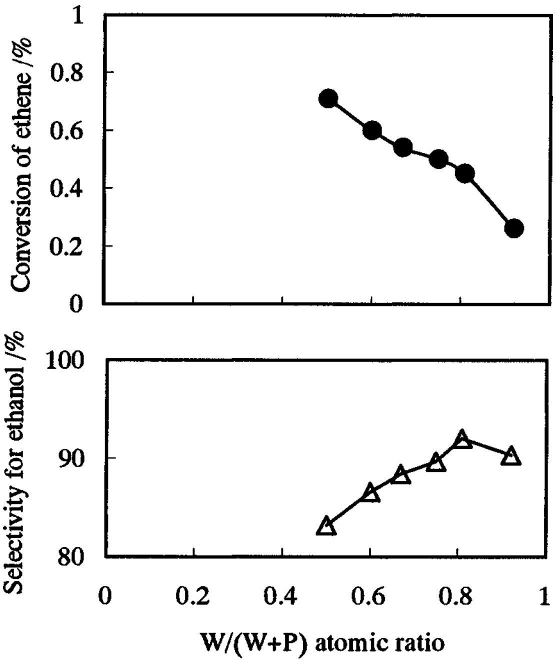

Figure 1. Effect of W/(W + P) atomic ratio of W–P mixed metal oxide catalysts on the activity and the selectivity of the hydration of ethene. Reaction conditions: temperature 473 K, pressure 0.6 MPa, SV $= 900\ \mathrm{h}^{-1}$, catalyst amount 10 cm^3, feed gas ratio $H_2O/C_2H_4 = 0.4$ mol mol^{-1}.

Table 1
Catalytic activities of W–P mixed metal oxides for the hydration of ethene, compared with those of other solid acid catalysts.[a]

Catalyst	Conv. ethene (%)	Selectivity (%) C_2H_5OH	$(C_2H_5)_2O$	CH_3CHO	Hydrocarbons
$W_{0.5}P_{0.5}O_x$	0.71	83.2	9.8	4.3	1.5
$W_{0.81}P_{0.19}O_x$	0.45	92.0	7.7	0.1	0
$W_{0.92}P_{0.08}O_x$	0.26	90.3	6.5	1.0	1.0
$H_3PW_{12}O_{40}$ 52.1 wt%/SiO_2	4.99	60.1	25.1	6.5	8.2
$H_3PMo_{12}O_{40}$ 47.5 wt%/SiO_2	1.46	72.3	7.3	15.6	4.7
H_3PO_4 55.9 wt%/SiO_2	1.21	95.7	4.2	0	0

[a] Reaction conditions: temperature 473 K, pressure 0.6 MPa, SV $= 900\ \mathrm{h}^{-1}$, catalyst amount 10 cm^3, feed gas ratio $H_2O/C_2H_4 = 0.4$ mol mol^{-1}.

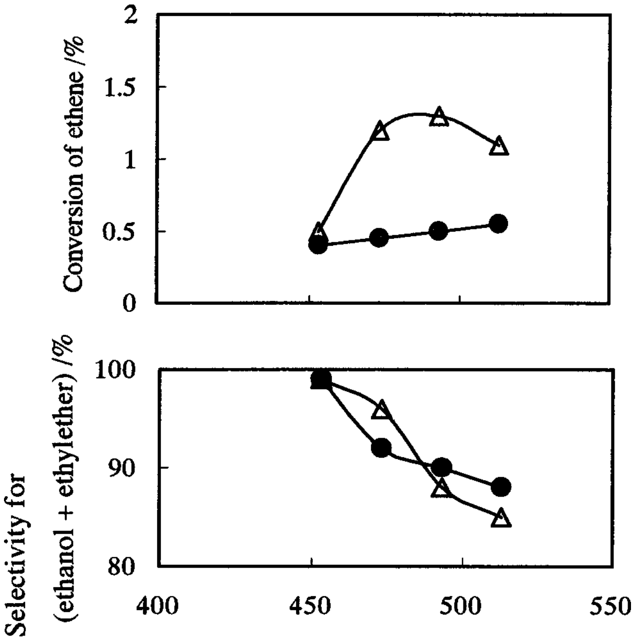

Figure 2. Effect of reaction temperature on ethene conversion and ethanol selectivity of the hydration of ethene over $W_{0.81}P_{0.19}O_x$ catalyst (●), compared with H_3PO_4/SiO_2 catalyst (△). Reaction conditions: pressure 0.6 MPa, SV = 900 h^{-1}, catalyst amount 10 cm^3, feed gas ratio H_2O/C_2H_4 = 0.4 mol mol^{-1}.

over the $W_{0.5}P_{0.5}O_y$ catalyst the selectivity is 4.3%, that is forty times of that over the $W_{0.81}P_{0.19}O_x$ catalyst. Oxidative dehydration sites apparently are present on the W–P oxide catalysts with lower W/(W + P) atomic ratio.

Reaction temperature does not affect substantially the rate of ethene hydration over the $W_{0.81}P_{0.19}O_x$ catalyst, as shown in figure 2. On the other hand, ethene conversion reaches its highest value at 493 K over the H_3PO_4/SiO_2 catalyst. The conversion decreases significantly due to the equilibrium at higher temperature. Although the effect of reaction temperature on the hydration rate is different among the catalysts, the effect on ethanol selectivity is similar over the $W_{0.81}P_{0.19}O_x$ and the H_3PO_4/SiO_2 catalysts. At higher temperature than 490 K, however, the $W_{0.81}P_{0.19}O_x$ catalyst exhibits a higher ethanol selectivity than the H_3PO_4/SiO_2 catalyst.

Figure 3 shows the effect of H_2O/ethene molar ratio on the hydration of ethene over the $W_{0.81}P_{0.19}O_x$ and the H_3PO_4/SiO_2 catalysts. The ratio of 0.4 is the most appropriate for both reaction rate and selectivity over these two catalysts. At the lower H_2O/ethene molar ratio, considerable amounts of hydrocarbons form in addition to ethyl ether. The activity of the $W_{0.81}P_{0.19}O_x$ catalyst is maintained for more than 1500 h under the optimized reaction conditions without the supply of any catalyst components. On the other hand, the activity of the H_3PO_4/SiO_2 catalyst decreases significantly without the supply of phosphoric acid. That will be reported elsewhere.

Catalyst characterizations were undertaken in order to determine the structure of active sites of W–P mixed metal oxide catalysts. However, XRD only provides information about WO_3 crystals and no characteristic phase information is given for the $W_{0.81}P_{0.19}O_x$ catalyst. This suggests that the active W–P–O phase is amorphous. Consequently, Raman spectroscopy characterization was undertaken in order to obtain information about the amorphous phase.

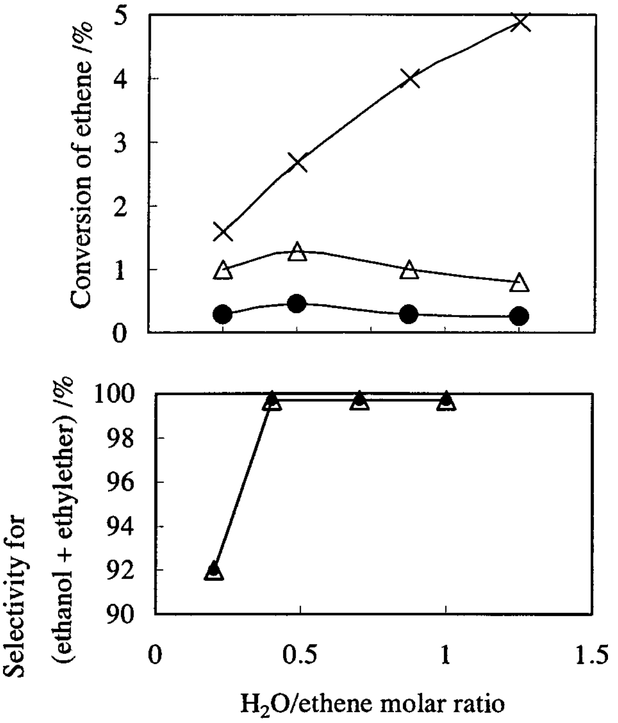

Figure 3. Effect of H_2O/ethene molar ratio on ethene conversion and ethanol selectivity of the hydration of ethene over $W_{0.81}P_{0.19}O_x$ catalyst (●), compared with H_3PO_4/SiO_2 catalyst (△) and the equilibrium conversion (×). Reaction conditions: temperature 473 K, pressure 0.6 MPa, SV = 900 h^{-1}, catalyst amount 10 cm^3.

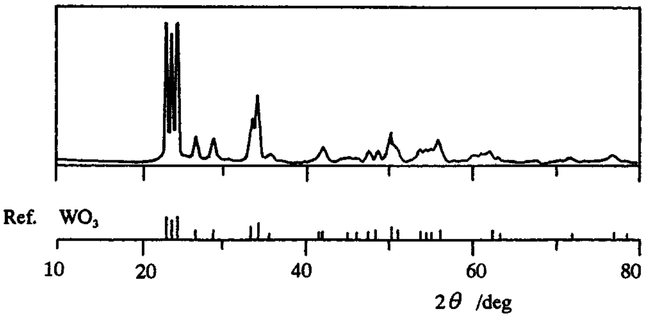

Figure 4. X-ray diffraction pattern of $W_{0.81}P_{0.19}O_x$ catalyst.

The ambient Raman spectrum of $W_{0.81}P_{0.19}O_x$, collected in the 100–1200 cm^{-1} region, is compared with those of WO_3 and $H_3PW_{12}O_{40}$ in figure 5. The Raman spectrum of $W_{0.81}P_{0.19}O_x$ indicates that the sample contains WO_3 crystallites (WO_3 characteristic Raman features at ~812(vs), ~720(s), ~620(w), ~332(m), ~280(s), ~250(w), ~193(m) and ~142(s) cm^{-1}). In addition, broad and weak Raman bands were also observed in the 900–1050 cm^{-1} region, as shown in figure 6. These vibrations are not present on the pure WO_3 crystallites. The vibra-

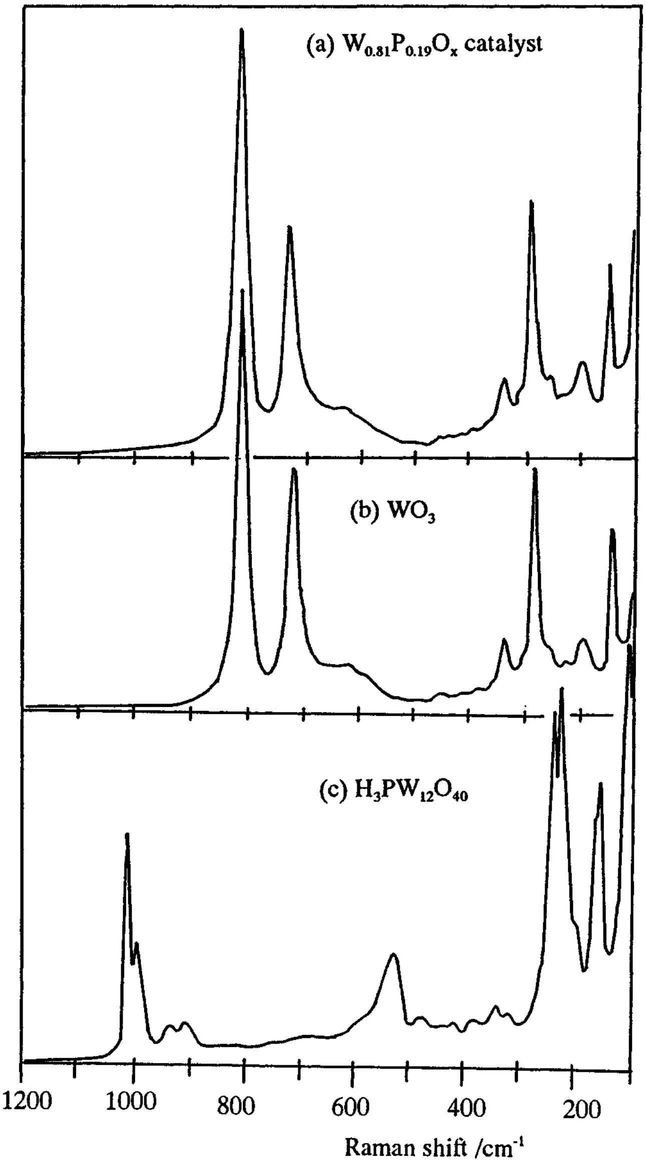

Figure 5. Raman spectra of (a) $W_{0.81}P_{0.19}O_x$ catalyst, (b) WO_3 and (c) $H_3PW_{12}O_{40}$.

tions of the species in the hydrated samples are similar to polytungstate-Y vibrations which has Raman features at ~955(s), ~880(w), ~830(w), ~650(w), ~360(w) and ~300(w) cm^{-1} [8]. The additional Raman band appearing at ~1010 cm^{-1} in the hydrated sample is similar to the $PW_{12}O_{40}^{3-}$ structure, that is known as the Keggin structure. The $PW_{12}O_{40}^{3-}$ structure possesses Raman features at ~1013(vs), ~993(m), ~935(w), ~905(w), ~526(m), ~239(vs), ~222(vs) and ~152(s) cm^{-1}, as shown in figure 5(c). Moreover, $PW_{11}O_{39}^{n-}$ heteropolyanion, a "defect" Keggin structure, also exhibits similar Raman features as $PW_{12}O_{40}^{3-}$ [9]. Unfortunately, the corresponding Raman bands below 900 cm^{-1} cannot be observed due to the strong Raman scattering of WO_3 crystallites in this vibrational region. Although the $W_{0.81}P_{0.19}O_x$ catalyst was heat-treated at 973 K, both WO_3 and a Keggin phase coexist. Figure 6 shows Raman spectra of $W_{0.81}P_{0.19}O_x$ catalyst under hydration and dehydration conditions. The Raman spectra drastically change in the presence/absence of H_2O vapor. There is a distinct peak at 991–997 cm^{-1} in the presence of H_2O. The Raman spectra of the supported $PW_{12}O_{40}^{3-}/PW_{11}O_{39}^{7-}$ units with Keggin structure can be changed upon the presence/absence of water molecules, because the $PW_{12}O_{40}^{3-}/PW_{11}O_{39}^{7-}$ structure are joined together by water molecules in order to generate the secondary structure. Hence, the peak of 991–997 cm^{-1} seems to be assignable to $PW_{12}O_{40}^{3-}$. The dehydrated species can be re-hydrated in the presence of water molecules. The water effect determined is present on the surface due to the reversibility of the structure upon the hydration/dehydration procedures. The hydration/dehydration procedures do not perturb the bulk WO_3 crystalline structure.

During the ethene hydration reaction, *in situ* Raman studies revealed a decrease of Raman intensity of the 991–997 cm^{-1} band with increasing reaction temperature from 523 to 623 K, as shown in figure 7. The surface $PW_{12}O_{40}^{3-}$ species are consumed or reduced under the presence of ethene molecules. Simple tungsten oxide (WO_3) and silica-supported amorphous tungsten oxide (WO_3/SiO_2), prepared by an incipient-wetness impregnation method with an aqueous solution of ammonium metatungstate, were inactive for the hydration of ethene. The above Raman experiments strongly suggest that the surface $PW_{12}O_{40}^{3-}$ species are the active site for the ethene hydration reaction. More detailed characterization concerning the active species and the reaction mechanism will be reported elsewhere.

4. Conclusion

W–P mixed metal oxide catalysts are active and selective for the gas-phase hydration of ethene to ethanol. The activity and selectivity depend on the W/P atomic ratio. $W_{0.81}P_{0.19}O_x$ shows the highest selectivity for ethanol. The following key points emerge from this study:

(1) Although ethene conversion slightly decreases at higher W/(W + P) atomic ratio, the selectivity for ethanol increases and reaches the highest value (92%) at $W_{0.81}P_{0.19}O_x$.

(2) Although highly acidic $H_3PW_{12}O_{40}/SiO_2$ and $H_3PMo_{12}O_{40}/SiO_2$ catalysts are very active for the hydration, the selectivity for ethanol is poor in order to co-produce ethyl ether and hydrocarbons. H_3PO_4/SiO_2 catalyst shows the highest selectivity for ethanol with the moderate hydration activity. $W_{0.81}P_{0.19}O_x$ catalyst is less active than these supported acid catalysts, but the activity maintains for a long time without the supply of catalyst component.

(3) Reaction temperature does not affect substantially the rate of ethene hydration over the $W_{0.81}P_{0.19}O_x$ catalyst. A H_2O/ethene molar ratio of 0.4 is the most appropriate for both reaction rate and selectivity.

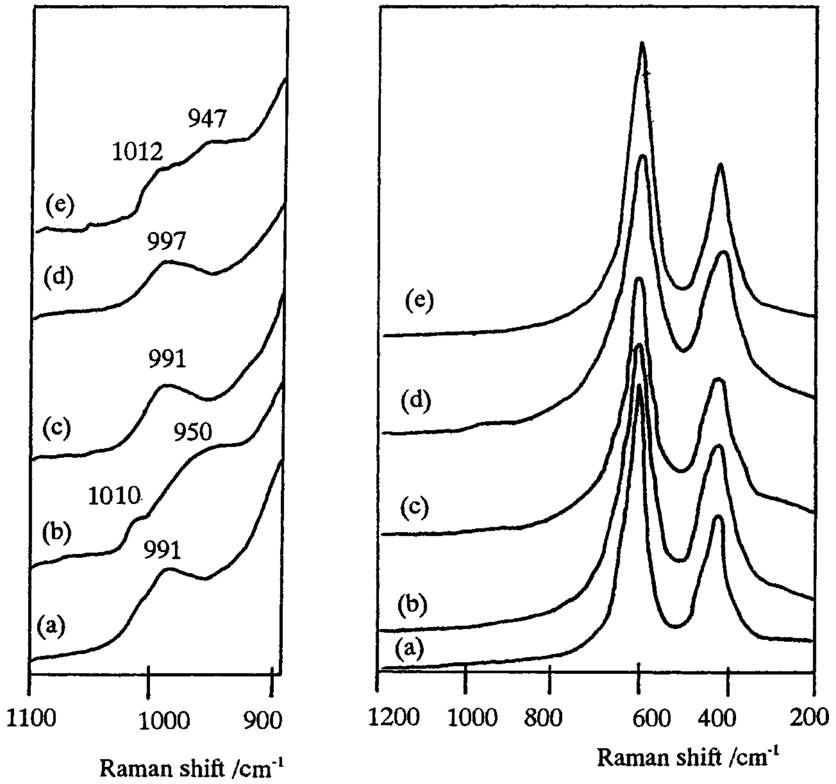

Figure 6. Raman spectra of $W_{0.81}P_{0.19}O_x$ catalyst under hydration and dehydration conditions: (a) He, 298 K (without any treatment); (b) He, 523 K; (c) H_2O/He, 523 K; (d) H_2O/He, 623 K; and (e) He, 523 K.

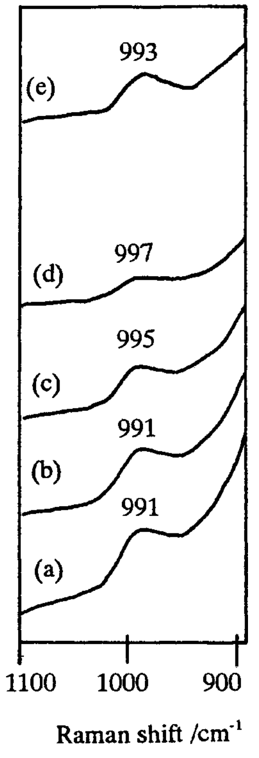

Figure 7. Raman spectra of $W_{0.81}P_{0.19}O_x$ catalyst under hydration conditions: (a) He, 298 K (without any treatment); (b) H_2O/He, 523 K; (c) C_2H_4/H_2O/He, 523 K; (d) C_2H_4/H_2O/He, 623 K; and (e) He, 523 K.

(4) The active species of W–P mixed metal oxide are amorphous. But there is Keggin structure of W–P oxide species ($PW_{12}O_{40}^{3-}$) in the presence of steam. And the species seem to be the active sites for the hydration of ethene, which was confirmed by *in situ* Raman spectroscopy.

Acknowledgement

Professors Jih-Mirn Jehng and Israel Wachs are greatly acknowledged for the Raman spectra. We wish to thank MITI and the Japan Alcohol Association for their support and approval to the presentation of this paper.

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