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Effects of Organic Compounds Used in Preparing V/Ti Binary Phosphate Catalysts

INTRODUCTION

A V_2O_5–TiO_2–H_3PO_4 ternary system prepared by adding a dilute orthophosphoric acid [H_3PO_4] to a mixture of fine powders of V_2O_5 and TiO_2, followed by evaporation to dryness and calcination, has been claimed to be effective as a catalyst for a vapor-phase reaction of methanol and methyl acetate in the presence of gaseous oxygen to form methyl acrylate (*1*).

In addition to basic oxides, metal phosphates have been claimed to be effective as catalysts for a vapor-phase aldol condensation of formaldehyde [HCHO] with acetic acid and propionic acid to form acrylic acid and methacrylic acid, respectively (*2*). Lately vanadium phosphate catalysts consisting of vanadium pyrophosphate [$(VO)_2P_2O_7$] prepared from an organic solvent have been claimed to be more effective than any other metal phosphate catalyst (*3*). The performance of these $(VO)_2P_2O_7$ catalysts has been studied in more detail (*4*, *5*).

Recently, it has been found that the combination of $(VO)_2P_2O_7$ with titanium pyrophosphate [TiP_2O_7] brings about an enhanced catalytic performance in the aldol condensation (*6*, *7*).

In this study, we investigated the effects of the organic compounds used in preparing V/Ti binary phosphate catalysts on their physical and chemical properties as well as on their catalytic performance for the aldol condensation.

EXPERIMENTAL

Preparation of Catalysts

Unless otherwise indicated, the catalysts were prepared by the following procedures. First, a paste-like titanium hydroxide gel was prepared as follows. The required quantity (usually about 20 ml) of $TiCl_4$ was added dropwise to about 500 ml of chilled water. The solution was diluted with about 5 liters of water and then a dilute ammonia solution was added to precipitate the hydroxide. The obtained precipitate was washed about 10 times with water by decantation, and then it was filtered.

Portions (9.7 g) of NH_4VO_3 were added to about 50 ml of an organic compound, e.g., ethylene glycol. The mixture was warmed slowly and oxalic acid was added to the mixture in amounts sufficient to dissolve the NH_4VO_3 completely. A clear blue solution of VO^{2+} was obtained. Required quantities of the titanium hydroxide gel and 85% H_3PO_4 were mixed with stirring. A white sticky syrup was obtained. Thereafter, the sticky syrup was mixed with the blue solution of VO^{2+}. Excess water was then evaporated off with vigorous stirring by means of hot air current, yielding a light blue cake. The obtained cake was evaporated again in an oven by gradually raising the temperature from 50 to 200°C for 6 h. The resulting solid was first calcined at 300°C for 6 h in a stream of air; then it was broken up and sieved to an 8- to 20-mesh size. Finally, it was calcined again at 450°C for 6 h in a stream of air.

Characterization of Catalysts

The surface areas of the catalysts were measured by the BET method using nitrogen as adsorbate at −196°C.

X-ray diffractograms for the sample catalysts were recorded with the aid of a Rigaku X-ray diffractometer using Cu*K*α radiation.

The average oxidation numbers of va-

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nadium ions in the catalysts were determined by the redox titration method described previously (*8*, *9*).

Procedures of the Vapor-Phase Aldol Condensation

The reaction of acetic acid and HCHO was carried out with a continuous-flow system. The reactor was made of a steel tube, 50 cm long and 1.8 cm i.d., mounted vertically and immersed in a lead bath. Nitrogen was fed in from the top of the reactor with a fixed rate of 140 ml (at 20°C)/min as the carrier or the diluent, and a mixture of trioxane [$(HCHO)_3$] and acetic acid was introduced into a preheating section of the reactor by means of an injection syringe pump. The feed rate was $CH_3COOH/HCHO/N_2$ = 36.8/17.5/350 mmol/h. The amount of catalyst used was 2.2 g and the space velocity [SV] was about 3100 h^{-1}, unless otherwise indicated. The activity data were taken after 30 min of run. The other procedures were the same as those described in the previous studies (*4*–*7*). The yield was defined as 100 · (moles of product)/(moles of HCHO fed in).

RESULTS

Effect of Organic Compounds

The catalysts used in this study were V/Ti binary phosphate with a V/Ti/P atomic ratio of 1/2/5.5; the amount of phosphorus was in slight excess with respect to stoichiometric $(VO)_2P_2O_7$–$4TiP_2O_7$ (V/Ti/P = 1/2/5.0). They were prepared according to the procedures described under Experimental and using 50-g portions of different organic compounds as the solvents to dissolve the vanadyl oxalate.

Mono-alcohols and carboxylic acids such as ethanol, 2-propanol, isobutyl alcohol, acetic acid, and propionic acid were found to be undesirable as the solvents, because vanadyl oxalate is insoluble in these solvents. Further, at the boiling points of methanol and tetrahydrofuran, vanadyl oxalate was not formed by the reaction of NH_4VO_3 with oxalic acid.

As an index of the catalytic performance in the aldol condensation of HCHO with acetic acid, one-pass yield of acrylic acid was measured for each catalyst under the conditions described under Experimental, i.e., at 320°C and SV = 3100 h^{-1}. The results are listed in Table 1, together with the specific surface area and the average oxidation numbers of vanadium ions in both the fresh and the used catalysts.

It was found that a good performance is obtained with the catalysts prepared using a diol or hydroxy carboxylic acid (oxy-acid) and that water, formic acid, and glyoxal, as well as above-cited mono-alcohols, carboxylic acids, and tetrahydrofuran, are not effective.

As may be seen in Table 1, the yield of acrylic acid is related to the specific surface area of catalyst. The average oxidation number of vanadium ions in the used catalysts remains at 3.8 to 4.0, irrespective of the kind of solvent used. The X-ray diffraction patterns indicated that all of the catalysts are amorphous. Therefore, these data show no information about the effect on the textural property of catalyst.

Effect of the Amount of Ethylene Glycol Used

In order to ascertain the effect of the amount of an organic compound used in preparing the catalysts, a series of V/Ti/P atomic ratio = 1/2/5.0 catalysts were prepared according to the procedures described under Experimental, while the amount of ethylene glycol used was changed. That is, 9.7-g portions of NH_4VO_3 were dissolved with the aid of oxalic acid in about 50-ml portions of aqueous solutions containing different amounts of ethylene glycol.

The yield of acrylic acid obtained under the conditions described under Experimental, the specific surface area, and the average oxidation numbers of vanadium ions were determined for each catalyst. The results are listed in Table 2.

The yield of acrylic acid increases

TABLE 1

Effect of Organic Compound Used in Preparing V/Ti/P Catalysts

Organic compound[a]	Acrylic acid yield (mol%)	Surface area (m^2/g)	AV[b]	
			Fresh	Used
Ethylene glycol	64	80.8	4.64	3.80
1,2-Propanediol	66	76.3	4.62	3.90
1,3-Propanediol	66	77.6	4.62	3.97
2,3-Butadeniol	63	73.6	4.65	3.85
1,3-Butanediol	63	76.3	4.56	3.80
1,4-Butanediol	66	75.0	4.65	4.00
1,5-Pentanediol	63	78.6	4.61	3.85
1,6-Hexanediol	63	60.0	4.70	4.00
Glycolic acid	60	62.1	4.28	3.95
Lactic acid	66	70.0	4.44	3.90
Citric acid + water	54	43.2	4.87	3.99
Glyoxal	36	22.7	4.28	3.95
Formic acid	22	11.7	4.00	3.97
Ethanol + water	12	2.7	3.80	3.70
Water	3.5	0.9	4.21	4.02
Water	3.0	1.1	4.04	4.02

[a] Fifty milliliters of organic compound was used for 9.7 g of NH_4VO_3.

[b] Average oxidation numbers of vanadium ions in the fresh and used catalysts.

markedly with an increase in the amount of ethylene glycol used. The average oxidation number varies scarcely with the change in the amount of ethylene glycol.

Effect of the Modification of Preparation Procedures

Several V/Ti/P = 1/2/5.0 catalysts were prepared according to the following procedures which are different from those described under Experimental. NH_4VO_3 (9.7 g) was dissolved with the aid of oxalic acid at 80 to 90°C in 50 ml of ethylene glycol. To this solution the required quantity of the paste-like titanium hydroxide was added and the mixture was vigorously stirred. Thereafter, the required quantity of 85% H_3PO_4 was added. The other procedures were the same as those described under Experimental.

It was found that the catalysts prepared according to the above-mentioned procedures were almost the same as those prepared by the procedures described under Experimental, in their catalytic performance, surface area, and average oxidation number of vanadium ions.

Catalysts Prepared by Another Method

Several V/Ti/P catalysts were prepared according to the procedures described by

TABLE 2

Effect of the Amount of Ethylene Glycol Used

Ethylene glycol[a] (ml)	Acrylic acid yield (mol%)	Surface area (m^2/g)	AV[b]	
			Fresh	Used
0	3.5	0.9	4.21	4.02
0	3.0	1.1	4.04	4.02
2	11.0	8.8	4.55	4.05
7	40.0	35.0	4.66	4.00
10	50.0	46.0	4.75	3.88
15	54.0	70.0	4.85	3.95
20	56.0	83.0	4.78	3.80
30	61.0	94.0	4.80	3.79

[a] Amount of ethylene glycol used for 9.7 g of NH_4VO_3.

[b] Average oxidation number of vanadium ions in the fresh and used catalyst.

TABLE 3

Performances and Properties of the V/Ti/P Catalysts Prepared from V_2O_5, TiO_2, and H_3PO_4[a]

Catalyst (atomic ratio)	Acrylic acid yield (mol%)	Surface area (m^2/g)	AV[b]	
			Fresh	Used
V/Ti/P (1/1.14/1.38)	24.0	6.0	4.87	4.63
V/Ti/P (1/0.8/1.38)	18.0	5.7	4.95	4.76
V/Ti/P (1/0.85/2.3)	6.0	1.7	4.90	4.60
V/Ti/P (1/2/5.5)	6.0	0.6	4.88	4.19
V/P (1/1.1)[c]	15.4	3.0	4.63	4.48
V/P (1/1.1)[d]	36.0	23.0	4.18	3.80

[a] According to Ref. (*1*).

[b] Average oxidation number of vanadium ions in the fresh and used catalysts.

[c] Prepared in an aqueous medium (*10*).

[d] Prepared in an isobutanol medium (*10*).

Fernholz and Wunder (*1*). That is, the required quantity of dilute H_3PO_4 was added to a mixture of fine powders of V_2O_5 and TiO_2. After a while, the mixture solidified. The obtained solid was evaporated in an oven at 200°C for 6 h and it was calcined at 300°C for 6 h in a stream of air. Thereafter, it was broken up and sieved to an 8- to 20-mesh size. Finally it was calcined again at 450°C for 6 h in a stream of air.

The performance in the aldol condensation and the properties of these catalysts are listed in Table 3. For comparative purposes, the results obtained from V/P catalysts prepared in an aqueous and isobutyl alcohol medium (*10*) are also shown in Table 3.

It is clear that the catalysts prepared from V_2O_5, TiO_2, and H_3PO_4 are markedly less active than those prepared by the procedures described under Experimental. This may be ascribed in part to their low surface area and the higher oxidation number of vanadium ions in the catalysts used.

DISCUSSION

The X-ray diffraction analysis showed that all of the V/Ti/P catalysts prepared in this study are amorphous. Therefore, it is hard to discuss the effect of organic compounds used on the textural property.

As may be seen in Table 1, the average oxidation number of vanadium ions in the used catalysts is scarcely affected by the difference in the organic compounds used. This suggests that the chemical properties of a catalyst are not changed by the difference in the solvent used. This leads us to consider that the advantage of the use of an organic compound such as diol and hydroxy carboxylic acid, in preparing a catalyst, consists in the possibility of obtaining a large surface area, much as in the case of V/P catalysts, which exhibit an excellent performance in the oxidation of butane to maleic anhydride (*11*, *12*).

However, isobutyl alcohol, 2-propanol, and tetrahydrofuran which have been claimed to be effective in preparing a V/P catalyst with a large surface area are not desirable in preparing the V/Ti/P catalysts. This leads us to assume that the function of the diols and hydroxy carboxylic acids is not the same as that of isobutylic alcohol, 2-propanol, and tetrahydrofuran.

Organic compounds with multifunctional groups such as diols and hydroxy carboxylic acid are able to form complexes with metal ions and to act as combining agents of metal ions. They have been used in the field of ceramics (*13–15*). This technique is called chemical mixing or the alkoxide method and is applied to the field of catalyst preparation, too.

V_2O_5–TiO_2 (*16*) and TiO_2–ZrO_2–V_2O_5 (*17*) prepared by the alkoxide method were found to be effective as catalysts. Moreover, ethylene glycol has been used in preparing various supported-metal catalysts (*18*) and La_2O_3–Cu–SiO_2 catalyst (*19*). Recently, the effects of various kinds of diols used in preparing SiO_2-supported metals (*20*) and SiO_2–Al_2O_3 (*21*) on their catalytic properties have been studied. However, the role of the diol is not yet clear.

Ethylene glycol (*22*) and hydroxy carboxylic acids, such as lactic acid, citric acid, malic acid, and tartaric acid (*8*, *9*), have been used as reducing agents in preparing V/P catalysts. On the other hand, in preparing mixed metal oxides, various hydroxy carboxylic acids were used about 20 years ago as agents forming complexes with metal ions (*23*). Moreover, it has been reported that the mixed oxides thus obtained are amorphous and highly homogeneous (*24*). Since systematic studies are lacking, however, the role of hydroxy carboxylic acids is not yet clear.

It may be concluded from the present study that diols and hydroxy carboxylic acids play a role in the complexation of vanadium and titanium ions. This results in the formation of a very homogeneous mixture of two phosphates, and fine pore structures are formed when these high-boiling-point compounds are evaporated off at a relatively high temperature.

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MAMORU AI

Research Laboratory of Resources Utilization,
Tokyo Institute of Technology,
4259 Nagatsuta, Midori-ku, Yokohama 227, Japan

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