Direct Oxidative Transformation of Glycerol into Acrylic Acid over Phosphoric Acid-added W–V–Nb Complex Metal Oxide Catalysts

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The addition of phosphoric acid to W–Nb–O catalyst active for glycerol transformation to acrolein and to W–V–Nb–O catalyst active for direct transformation of glycerol to acrylic acid appreciably improved their catalytic performance. The phosphoric acid-added W–Nb–O catalyst gave acrolein yield of 81.8%, and the phosphoric acid-added W–V–Nb–O catalyst gave acrylic acid yield of 59.2% in the direct glycerol transformation. The improvement of the catalytic performance seems due to the increases of the acid amount and the Brønsted acidity.

Glycerol is a main by-product in biodiesel production by transesterification of plant oils or animal fat with methanol and has been produced heavily at a relatively low price.[1] Because of this situation, transformation of glycerol into other desirable chemicals by various catalytic reactions has been attempted by many researchers.[2] Dehydration of glycerol to acrolein is one of the most valuable reactions, since acrolein is an important intermediate for chemical and agricultural industries. Various solid acid catalysts have been reported for the dehydration of glycerol.[3] We have reported that layer-structured W–Nb–O catalysts synthesized via hydrothermal method gave acrolein in high yield (75%) in gas-phase glycerol dehydration.[4] Direct oxidative transformation of glycerol to acrylic acid is also a very important reaction.[5] Achievement of this reaction is, however, challenging because not only improvement of selectivity for both dehydration of glycerol and selective oxidation of acrolein but also tuning of optimum catalytic functions for each reaction are required to achieve higher acrylic acid yield. Nevertheless, we have recently found that modification of the W–Nb–O catalyst with vanadium turned out to be an efficient catalyst for the direct transformation of glycerol to acrylic acid[6] but the yield of acrylic acid was as low as 45%.

Very recently we found that the addition of phosphoric acid to the W–Nb–O catalyst and the W–V–Nb–O catalysts had pronounced effects on the transformation of glycerol to acrolein and the direct transformation to acrylic acid, respectively. The achieved single pass yield of acrylic acid was about 60% and is currently the highest amongst the reported results. This paper reports the effects of phosphoric acid addition to the W–Nb–O catalyst and the W–V–Nb–O catalysts on the selectivity in the glycerol transformation.

The complex metal oxide catalysts of W, V, and Nb (W–V–Nb–O) were prepared by hydrothermal synthesis. $(NH_4)_6$-$[H_2W_{12}O_{40}] \cdot nH_2O$ (W: 2.7 mmol), $VOSO_4 \cdot nH_2O$ (V: 0.6 mmol), and $Nb_2O_5 \cdot nH_2O$ (Nb: 2.0 mmol) were added to 45 mL of ion-exchanged water under stirring. This mixed suspension was put in a stainless steel autoclave with a Teflon liner and heated at 448 K for 72 h. The formed solid was filtered, washed with ion-exchanged water, dried at 353 K, and then calcined at 673 K for 4 h in air. W–Nb–O (W/Nb = 1.35) was similarly prepared.

Phosphoric acid-added catalysts were prepared by impregnation of uncalcined W–Nb–O or W–V–Nb–O with an aqueous solution of phosphoric acid, followed by calcination at 673 K in air. Phosphoric acid-added W–Nb–O and W–V–Nb–O were denoted as H_3PO_4/WNb and H_3PO_4/WVNb, respectively. The content of P was set to be 2.5 wt% of the supports after optimization of P content. XRD analysis confirmed that the layered structure of the W–Nb–O and W–V–Nb–O catalysts was maintained after the phosphoric acid treatment (Figure S1).[7]

Surface area of the catalysts was estimated by BET method where nitrogen physisorption amount was measured at 77 K with a BELSORP max (BEL Japan Inc.). Prior to the measurement, the samples were evacuated at 473 K for 2 h. Powder X-ray diffraction (XRD) pattern of the catalysts was recorded on a RINT2200 (Rigaku) with Cu Kα radiation (tube voltage: 40 kV, tube current: 20 mA). The acid amount of catalysts was measured with NH_3-TPD with a TPD apparatus (BEL Japan Inc.). Prior to the measurement, the samples were pretreated under He flow at 673 K for 2 h. NH_3 was adsorbed on the catalysts at 473 K. Acidity of catalysts was measured by FT-IR spectroscopy (PARAGON 1000, Perkin-Elmer) of adsorbed pyridine with an evacuable furnace cell with CaF_2 windows, containing a self-supporting disk of sample. Pyridine was adsorbed at 373 K, and after evacuation at 523 K for 1 h the adsorption spectrum was recorded. The spectrum of adsorbed pyridine on sample in the presence of water vapor (4.6 Torr) was also recorded.

Transformation of glycerol was carried out in a vertical fixed-bed reactor. The molar percent composition of reaction gas was glycerol/O_2/N_2/H_2O = 5/14/56/25 (mol%). Reaction products and unconverted glycerol in both gas and liquid phases were collected hourly and analyzed with GC. Oxidation of acrolein was carried out in the same reactor as the transformation of glycerol.

The catalytic performance of the W–Nb–O and H_3PO_4/WNb catalysts in the glycerol transformation was first examined, and the results are shown in Table 1. Both the glycerol conversion and the acrolein yield were clearly increased by the phosphoric acid addition, and the H_3PO_4/WNb catalyst gave the acrolein in yield of 81.8% at $W/F = 2.5 \times 10^{-3}$ g_{cat} min mL^{-1}. The improvement can be explained by changes in the surface acidity because of the following results. As shown in Table 2, the number of acid sites per gram largely increased by the addition of phosphoric acid. At the same time, the addition increased the ratio of Brønsted to Lewis acidity. Moreover, it was observed in the FT-IR study that water substantially decreased the intensity of the IR-band ascribed to the adsorption of pyridine on Lewis acid sites and on the other hand increased the intensity of IR-band ascribed to that on Brønsted acid sites. This result indicates that Lewis acid sites are hydrated and change into Brønsted acid sites in the presence of

Table 1. Effect of phosphoric acid addition on catalytic performance of W–Nb–O and W–V–Nb–O

| Catalyst | (W/F) /g_{cat} min mL^{-1} | GLR[a] conv.[b] /% | O$_2$ conv. /% | Yield[c]/% | | | | | | | |
				ACRL	**AA**	ACAL	PRAL	HACT	ACA	CO$_x$	others
W–Nb–O	6.3×10^{-4}	64.3	1.4	32.4	0.1	0.5	0.3	2.5	0.1	0.8	27.6
	2.5×10^{-3}	98.9	6.5	74.5	0.1	2.9	1.0	0.4	0.7	3.8	15.5
H$_3$PO$_4$/WNb	6.3×10^{-4}	72.3	2.6	43.2	0.1	0.4	0.2	2.6	0.1	0.6	25.1
	2.5×10^{-3}	100	5.6	**81.8**	0.3	2.1	0.6	0.5	0.3	2.7	11.7
W–V–Nb–O	6.7×10^{-3}	100	48.6	3.5	46.2	1.4	<0.1	<0.1	12.7	33.8	2.4
H$_3$PO$_4$/WVNb	1.0×10^{-2}	100	45.3	0.5	**59.2**	0.3	<0.1	<0.1	8.2	22.3	9.5

[a]GLR: glycerol. [b]Reaction conditions: set temperature of the furnace, 558 K; composition of reactant gas, glycerol/O$_2$/N$_2$/H$_2$O = 5/14/56/25 (mol %). [c]ACRL: acrolein, AA: acrylic acid, ACAL: acetaldehyde, PRAL: propanal, HACT: hydroxyacetone, ACA: acetic acid.

**Table 2.** Surface area and acid properties of the W–Nb–O and H$_3$PO$_4$/WNb catalysts

Catalyst	Surface area /m^2 g^{-1}	Acid amount /µmol g^{-1}	B/L[a] —	B/L[a] +H$_2$O[b]
W–Nb–O	118	136	0.4	3.6
H$_3$PO$_4$/WNb	91	244	1.5	23.4
W–V–Nb–O	120	129	0.4	3.2
H$_3$PO$_4$/WVNb	97	250	1.7	25.6

[a]Ratio of the integral absorbance (peak area) of the peak at 1540 cm^{-1} (Brønsted) to 1450 cm^{-1} (Lewis). [b]B/L in the presence of water (4.6 Torr).

Figure 1. Effect of contact time on the yields of acrolein and acrylic acid in the glycerol transformation over W–V–Nb–O (acrolein, ○; acrylic acid, ●) and H$_3$PO$_4$/WVNb (acrolein, △; acrylic acid, ▲). Reaction conditions: set temperature of the furnace, 558 K; composition of reactant gas, glycerol/O$_2$/N$_2$/H$_2$O = 5/14/56/25 (mol %).

water. This change more clearly occurs over H$_3$PO$_4$/WNb, and in fact Lewis acidity was hardly observed on H$_3$PO$_4$/WNb in the presence of water vapor. The same effect of the phosphoric acid addition was observed in the case of W–V–Nb–O as shown in Table 2. As a consequence, such high Brønsted acidity of H$_3$PO$_4$/WNb and H$_3$PO$_4$/WVNb should be beneficial for the catalytic reaction, since it is considered that Brønsted acid sites are responsible for the glycerol transformation to acrolein. The observed clear effect of water on the surface acid properties in the case of H$_3$PO$_4$/WNb is interesting, but the actual function of surface H$_3$PO$_4$ is under investigation.

Next, the catalytic performance of the W–V–Nb–O and H$_3$PO$_4$/WVNb catalysts in the direct glycerol transformation to acrylic acid was examined, and the results are also shown in Table 1. Like acrolein formation, addition effect of H$_3$PO$_4$ is also prominent. The attained maximum yield of acrylic acid was 59.2% at $W/F = 1.0 \times 10^{-2}$ g$_{cat}$ min mL^{-1}. The performance of this catalyst was the highest of the catalysts reported for the direct transformation of glycerol to acrylic acid.[5] Of additional importance is that the yield of acrylic acid was kept almost constant during 5 h of the reaction; that is, no deactivation occurs within this reaction period, while appreciable deactivation occurs in the transformation of glycerol to acrolein.

Figure 1 illustrates the yield of acrolein and acrylic acid in the glycerol transformation at various contact times over the W–V–Nb–O and H$_3$PO$_4$/WVNb catalysts. Acrylic acid yield increased with decreasing acrolein yield over both W–V–Nb–O and H$_3$PO$_4$/WVNb, indicating that acrolein formed on acid sites was consecutively oxidized to acrylic acid on V sites. Over the
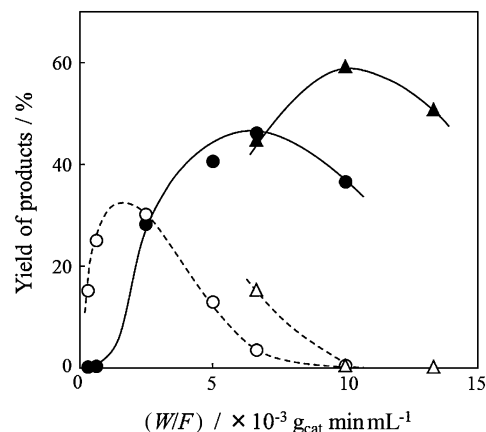
W–V–Nb–O catalyst, acrylic acid yield reached the maximum value (46.2%) when acrolein was mostly consumed at $W/F = 6.7 \times 10^{-3}$ g$_{cat}$ min mL^{-1}. At a contact time above $W/F = 6.7 \times 10^{-3}$ g$_{cat}$ min mL^{-1}, the acrylic acid yield decreased because the sequential oxidation to CO$_x$ started. Over H$_3$PO$_4$/WVNb, on the other hand, 15.3% yield of acrolein was still sustained at $W/F = 6.7 \times 10^{-3}$ g$_{cat}$ min mL^{-1}, and a further increase of the contact time increased the acrylic acid yield. Then the yield of acrylic acid reached 59.2% at $W/F = 1.0 \times 10^{-2}$ g$_{cat}$ min mL^{-1}.

The results shown in Figure 1 evidently indicate the sequential reactions from glycerol to acrylic acid via acrolein and ultimately to CO$_x$. In order to elucidate the role of phosphoric acid in this course of the transformation, we separately conducted acrolein oxidation over W–V–Nb–O and H$_3$PO$_4$/WVNb. Figure 2 shows the conversion of acrolein and the yield of acrylic acid and CO$_x$ in the oxidation of acrolein. The difference of acrolein conversion was little observed between W–V–Nb–O and H$_3$PO$_4$/WVNb, while the maximum acrylic acid yield was improved from 64.4% (581 K) over W–V–Nb–O to 71.7% (577 K) over H$_3$PO$_4$/WVNb. This indicates that
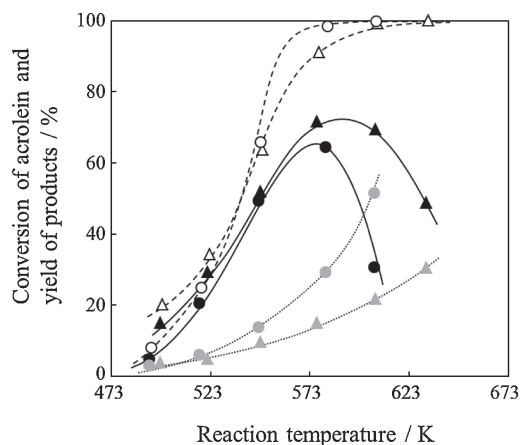
Figure 2. Conversion of acrolein, yield of acrylic acid and CO_x in the acrolein oxidation over W–V–Nb–O (acrolein, ○; acrylic acid, ●; CO_x, ◐) and H_3PO_4/WVNb (acrolein, △; acrylic acid, ▲; CO_x, ▲). Reaction conditions: catalyst weight, 0.2 g; flow rate, 77 mL min^{-1}; composition of reactant gas, acrolein/O_2/N_2/H_2O = 1/15/58/26 (mol %).

phosphoric acid enhances not only the selectivity to acrolein in the glycerol transformation but also the selectivity to acrylic acid in the acrolein oxidation. It should be noted in Figure 2 that over W–V–Nb–O acrylic acid yield decreased drastically at a reaction temperature above 581 K but that this decrease was retarded appreciably over H_3PO_4/WVNb. It is clear that the phosphoric acid can suppress the sequential overoxidation of acrylic acid to CO_x which would inevitably occur on V site of the catalysts.

In summary, the addition of phosphoric acid increased the acid amount and the Brønsted acidity of the W–Nb–O catalyst. In addition to the improvement of the acidity, phosphoric acid interacts with V sites for suppressing the sequential oxidation of acrylic acid to CO_x. As a result, acrylic acid yield in the glycerol transformation increased significantly. The H_3PO_4/WVNb catalyst gave acrylic acid in yield of 59.2% directly from glycerol ($W/F = 1.0 \times 10^{-2}$ g$_{cat}$ min mL^{-1}, reaction temperature 594 K).

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