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Involvement of active sites of promoted vanadyl pyrophosphate in selective oxidation of propane

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Abstract

Involvement of active sites in the selective oxidation of propane was investigated using $(VO)_2P_2O_7$ catalysts promoted by Sb, Ti, Zr, Hf, Cu, and Ce. Based on X-ray diffraction patterns, infrared spectra, and Raman spectra, the formation of a $(VO)_2P_2O_7$ phase was confirmed for all of the promoted catalysts; no other phases were detected. After the addition of Sb, Ti, and Zr, the selectivity to acrylic acid increased, whereas Cu-, Ce-, and Hf-promoted catalysts showed lower selectivity than pure $(VO)_2P_2O_7$. The effect of promoters on the activity and selectivity for the propane oxidation was investigated on the basis of the nature of surface active sites. The surface $V{=}O$ species, evaluated by the nitric oxide–ammonia rectangular pulse technique, decreased with the addition of the promoters. A proportional correlation between the number of surface $V{=}O$ species and reaction rate of propane clarified that the surface $V{=}O$ species is the controlling factor for the catalytic activity of propane oxidation. In the case of Sb-, Ti-, and Zr-promoted catalysts, the selectivity to acrylic acid increased significantly. The selectivity was compared with the number and strength of Brønsted and Lewis acid sites estimated from dimethylpyridine temperature-programmed desorption. A good correlation was observed between the selectivity to acrylic acid and the surface concentration of Lewis acid sites. It was experimentally demonstrated that Lewis acid sites represent the key factor in selective oxidation.

Keywords: Selective oxidation of propane; Vanadyl pyrophosphate; Effect of promoters; Solid Lewis acid; Surface $V{=}O$ species

1. Introduction

Selective oxidation of lower alkane by molecular oxygen is of great interest in the catalysis research [1]. In particular, the selective oxidation of propane to acrylic acid using molecular oxygen as an oxidant is currently attracting much industrial and scientific attention [2–21]. Various catalysts have been reported to be active and selective for propane oxidation; these can be classified as (a) Mo-based mixed-oxide catalysts, such as Mo–V–Nb–Te mixed oxide, [2–9], Bi–Mo-based oxides [10,11], and Ag–Mo–P mixed oxide [12]; (b) heteropoly acid-based catalysts [13–16]; and (c) vanadyl phosphate-based catalysts [17–21]. Among these series of catalysts, Mo–V–Te–Nb mixed oxide is currently the most widely investigated, and a voluminous literature is available in both patents and scientific papers.

As for the Mo–V-based mixed-oxide catalysts, most of the reports to date have focused on the roles of the various components and the formation of a specific crystal phase. It is generally accepted that the catalytic performance of Mo–V–Te–Nb mixed oxide depends strongly on the crystal phase [22–27]. Tsuji and Koyasu identified an orthorhombic phase (phase i) and hexagonal phase (phase k) and noted that the former demonstrates higher catalytic performance in the selective oxidation of propane [22]. Katou et al. prepared a new orthorhombic Mo–V–O catalyst by hydrothermal synthesis and clarified the role of each element in Mo–V–Te–Nb oxide catalysts [25].

Although the effect of the bulk structure on catalytic performance has been well investigated, few papers have reported the roles of catalyst surface and surface functional species. Although the redox activity of the surface sites and the importance of Lewis acid sites have been pointed out, the roles of these sites have not been well investigated experimentally. The relationship between surface structure and catalytic performance

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should clarify the essential factors for the design of selective oxidation catalysts.

The objective of this study is to clarify the involvements in the surface functional species on the selective oxidation of propane. Promoted $(VO)_2P_2O_7$ catalysts were investigated as model catalysts, because the active bulk phase for the selective oxidation of alkane is already known to be $(VO)_2P_2O_7$ [28,29]. Furthermore, it has already been proposed that the surface V=O species on $(VO)_2P_2O_7$ is responsible for oxidation of n-butane [30–33] and that the surface V=O species can be measured by the nitric oxide ammonia rectangular pulse (NARP) technique [32–34]. For the measurement of surface acid sites, we previously reported that dimethylpyridine temperature-programmed desorption (DMP-TPD) is applicable for measuring Brønsted and Lewis acid sites on metal oxide catalysts [35]. In this report, the involvements of these functional groups in the oxidation of propane are investigated.based on the measurement of surface V=O species, Brønsted acid sites, and Lewis acid sites on a series of promoted $(VO)_2P_2O_7$.

2. Experimental

2.1. Catalyst preparation

Pure and promoted $(VO)_2P_2O_7$ catalysts were prepared from an aqueous media as reported previously [32–34]. 85% H_3PO_4 (0.24 mol) and $NH_2OH{\cdot}HCl$ were dissolved in 200 ml of distilled water and stirred at 353 K. Then V_2O_5 (0.1 mol) was slowly added into the solution and evaporated at 423 K. After drying at 403 K for 12 h, the $VOHPO_4{\cdot}0.5H_2O$ thus obtained was boiled in distilled water for 10 min. As for pure $(VO)_2P_2O_7$ (abbreviated as VP hereinafter), the $VOHPO_4{\cdot}0.5H_2O$ was calcined at 823 K in flowing N_2 for 2.5 h. The promoted $(VO)_2P_2O_7$ catalysts were prepared by impregnating an aqueous solution containing additive elements $VOHPO_4{\cdot}0.5H_2O$ by the incipient wetness method. $Sb(CH_3COO)_3$, $Ti(C_2H_5O)_4$, $ZrOCl_2{\cdot}8H_2O$, $HfOCl_2{\cdot}8H_2O$, $Cu(CH_3COO)_2{\cdot}H_2O$, and $Ce(CH_3COO)_3{\cdot}H_2O$ were used as sources of additives. The atomic ratio of additive metal was $M(\text{additive})/V = 0.05$. The promoted $VOHPO_4{\cdot}0.5H_2O$ was calcined at 823 K in flowing N_2 for 2.5 h. The catalyst names were abbreviated with VP (for the promoter element), as shown in Table 1.

2.2. Characterizations

X-ray diffraction (XRD) analysis was done with a Rigaku RINT-1200 diffractometer with Cu$K\alpha$ radiation. Raman spectra were achieved on powders at room temperature using a JASCO NRS-100 spectrometer. The exciting line of a semiconductor laser source at 532 nm was focused using a 100× objective. The spectral resolution was about 3 cm^{-1}. Infrared (IR) spectra were measured with a JASCO FT/IR-300 equipped with a diffuse reflectance unit. As for the spectra of catalyst bulk, the samples were diluted with KBr, and the spectra were measured using a triglycine sulfate detector with the resolution of 4 cm^{-1}. IR spectra of adsorbed pyridine were measured using a JASCO FT/IR-620 equipped with a diffuse reflectance unit connected to a flow system [35]. After calcination at 823 K for 2 h in flowing dry He, pyridine was saturated in the flowing He and adsorbed on the sample at room temperature. After purging in flowing dry He at room temperature for 4 h, an absorption spectrum was measured with 100× accumulation and resolution of 2 cm^{-1} using a mercury cadmium telluride detector.

Dimethylpyridine temperature-programmed desorption (DMP-TPD) was performed as reported previously [35]. Both 2,6-dimethylpyridine (2,6-DMP) and 3,5-dimethylpyridine (3,5-DMP) were used as probe molecules. 100 mg of a sample was placed in a U-shaped tubular cell and preheated at 673 K for 2 h in a dehydrated helium flow of 150 $cm^3\,min^{-1}$. After cooling to 523 K, the sample was exposed to a stream of the probe molecule diluted in helium for 30 min. Then the sample was left in flowing helium at 523 K for 120 min to purge any excess and/or weakly held probe molecules. Finally, the TPD measurement was performed from 523 to 1073 K at a heating rate of 5 $K\,min^{-1}$. The desorbed probe was detected with a flame ionization detector (FID).

NARP measurements were carried out as reported previously [32,33]. After oxidation of catalyst (0.1 g) in flowing oxygen at 773 K for 30 min, the sample was cooled to a predetermined temperature (450–600 K). Then NO–NH_3 mixture ($NO/NH_3 = 1/4$) gas was injected as a rectangular pulse with a width of 60 s. The number of surface V=O species was determined according to the analysis of produced nitrogen profile as described previously [32,36].

Table 1
Surface area and amount of active sites on pure and promoted $(VO)_2P_2O_7$ catalysts

Catalyst	Surface area ($m^2\,g^{-1}$)	Surface V=O species		Amount of acid sites		
		(10^{-6} mol g^{-1})	(10^{-6} mol m^{-2})	Total (10^{-6} mol m^{-2})	Brønsted acid (10^{-6} mol m^{-2})	Lewis acid (10^{-6} mol m^{-2})
VP	9.3	59.5	6.4	0.60	0.35	0.25
VP–Sb	12.1	47.2	3.9	0.62	0.08	0.54
VP–Ti	17.6	84.5	4.8	0.63	0.28	0.35
VP–Zr	18.7	71.1	3.8	0.72	0.34	0.37
VP–Hf	25.2	95.8	3.8	0.36	0.15	0.21
VP–Cu	12.6	52.9	4.2	0.34	0.17	0.17
VP–Ce	45.6	104.9	2.3	0.27	0.15	0.13