Novel Preparation of Vanadyl Pyrophosphate for Selective Oxidation of *n*-Butane Utilizing Intercalation and Exfoliation

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Intercalation–exfoliation of $VOPO_4·2H_2O$ crystallites (20 μm in size) in 2-butanol, followed by reduction with 2-butanol, brought about thin layers of precursor, $VOHPO_4·0.5H_2O$, with size of about 2 μm. The obtained vanadyl pyrophosphate (27 $m^2\ g^{-1}$) and the corresponding SiO_2 composite were highly active and selective for selective oxidation of *n*-butane.

Vanadium phosphate catalysts have extensively been studied for selective oxidation of *n*-butane to maleic anhydride (MA), since they are well-characterized crystalline compounds and at the same time they are only effective compounds.[1] Vanadyl pyrophosphate, $(VO)_2P_2O_7$, is a main component of the commercial catalyst for this reaction. Since the yield of maleic anhydride is still not sufficient, it is thus keenly desired to improve the catalyst performance.

There are many reports about the preparation of vanadyl pyrophosphates.[2–5] $VOPO_4·2H_2O$ is a possible starting material. Johnson et al.[2] demonstrated that the precursor $VOHPO_4·0.5H_2O$ was obtained by direct reduction of $VOPO_4·2H_2O$ with alcohol. Hutchings et al.[3] reported that the morphology of the precursor could be controlled by the choice of alcohol to perform the reduction of $VOPO_4·2H_2O$.

On the other hand, $VOPO_4·2H_2O$ has been known to be intercalated by various molecules including alcohol.[6] Intercalation of $VOPO_4·2H_2O$ could be intriguing as a method of preparing new nanostructurally modified catalysts. Benzinger et al.[4] claimed that $VOHPO_4·0.5H_2O$ was intercalated with alkylamines and the resulting compounds catalyzed *n*-butane oxidation, while the selectivity to MA was less than 50%.

Recently "exfoliation" technique has been developed from intercalation for various layered materials like clays,[7] zirconium phosphate,[8] niobates,[9] and titanates,[10] in which exfoliation is a method of delaminating stacked inorganic sheets in a solvent by infinite swelling of their interlayer spaces. We showed that an intercalation compound of $VOPO_4$ with 4-butylaniline was exfoliated in polar solvents.[11] Here we wish to report that a novel vanadyl pyrophosphate prepared through the intercalation, exfoliation, and reduction in 2-butanol exhibited a high catalytic performance.

$VOPO_4·2H_2O$ was prepared according to the literature,[12] and the structure was confirmed by IR and XRD. As Figure 1 shows, the $VOPO_4·2H_2O$ consisted of square platelets with the lateral dimensions of around 20 μm and the thickness of about 1 μm (Figure 1a). $VOPO_4·2H_2O$ (1.0 g) was added to 50 cm^3 of 2-butanol at room temperature, at which $VOPO_4·2H_2O$ remained as the solid state. When the suspension was heated at 323, 343, or 363 K for 1 h, the solution became homogeneous, which is the result of exfoliation via the intercalation of 2-butanol.[11] We have already reported the evidence for the exfoliation of intercalation compounds of $VOPO_4$.[11,13]

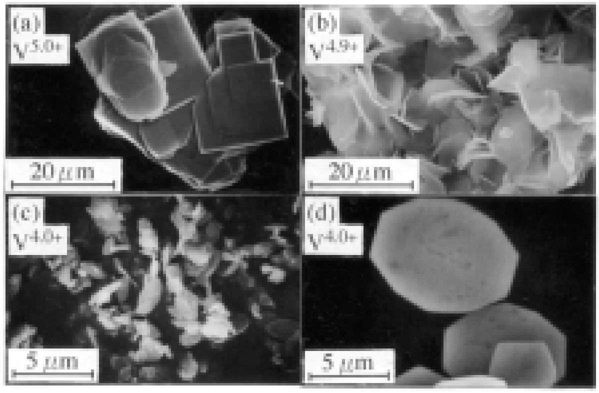

Figure 1. SEM images of (a) $VOPO_4·2H_2O$, (b) the solid recovered from $VOPO_4$-2-butanol exfoliated solution by evaporation, (c) EP(2-Bu), and (d) P(2-Bu). The oxidation numbers of V measured by a redox titration method are indicated on the photographs.

By the evaporation of the resulting 2-butanol homogeneous solution at 333 K, the green powder was recovered. This solid showed a shape like flower petals (Figure 1b), which are greatly different from that of the starting $VOPO_4·2H_2O$ (Figure 1a). From the IR and XRD, the structure of the resulting solid was shown to be the same as that of $VOPO_4·2H_2O$, indicating the conservation of lattice structure during the exfoliation process.

Refluxing the exfoliation solution (378 K) in the presence of small amount of $VOHPO_4·0.5H_2O$ (5 mg) for 20 h produced the precipitates which were confirmed to be the precursor $VOHPO_4·0.5H_2O$. As Figure 1c shows, the precursor consists of smaller thin platelets (~2 μm in length). This precursor is denoted to EP(2-Bu). As a reference, another precursor was separately prepared by direct reduction of $VOPO_4·2H_2O$ with 2-butanol at 423 K using 2.5 g of $VOPO_4·2H_2O$ and 25 cm^3 of 2-butanol. The obtained precursor had a shape of large platelet (8 μm in length) as shown in Figure 1d. This precursor is denoted to P(2-Bu).

Figure 2 shows the dependence of the conversion of *n*-butane on the contact time (W/F; W = catalyst weight (g) and F = flow rate of *n*-butane ($mol·h^{-1}$)) (Figure 2A) and the selectivity as a function of the conversion (Figure 2B). The oxidation of *n*-butane was performed in a flow reactor under an atmospheric pressure at 703 K using a mixture consisting of *n*-butane 1.5 vol%, O_2 17 vol%, and He (balance).[14] The precursor was activated in the reactant gas by heating from room temperature to 703 K at a rate of 5 $K·min^{-1}$. Since the stationary activity and selectivity were obtained at about 100 h after the temperature reached 703 K, the data were collected after at least 100 h of reaction. The products were analyzed with gas chromatographs

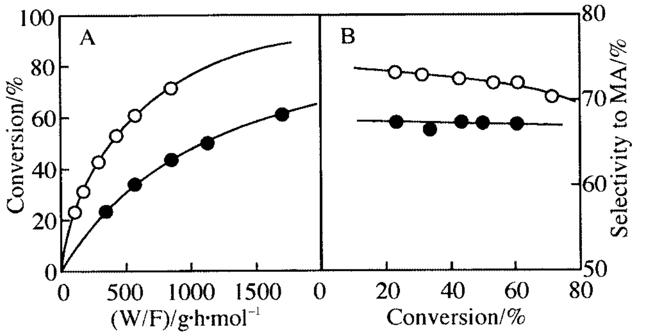

Figure 2. Dependence of conversion of *n*-butane on W/F (A), and selectivity to MA as a function of conversion (B): (○) EC(2-Bu) and (●) C(2-Bu). *n*-Butane 1.5%, O2 17% at 703 K.

(a high speed GC (TCD), Aera Japan M-200, and FID-GC, a Shimazu GC-8A) equipped with MS-5A and porapak QS columns.

It was confirmed by XRD that these precursors were transformed to $(VO)_2P_2O_7$ after the activation process for 100 h. The obtained $(VO)_2P_2O_7$ from EP(2-Bu) and P(2-Bu) are denoted to EC(2-Bu) and C(2-Bu), respectively. Figure 2 demonstrates that EC(2-Bu) was about 3 times more active than the conventional catalyst C(2Bu). Furthermore, it was found that the selectivity to MA reached about 75% over EC(2-Bu) at low conversions. We deduce that the improvement of the selectivity in EC(2-Bu) is due to the suppression of the formation of V^{5+} phase, since V^{5+} phases were less selective.[15] As a matter of fact, the V^{5+} phases were not detected on EC(2-Bu), while α_{II} phase (V^{5+}) was formed on C(2-Bu) after the reaction. As was pointed out by Kiely et al.,[16] the V^{5+} phase tended to be readily formed as the crystallite size of the precursor increased. Since EC(2-Bu) consists of crystallites with the smaller size and thinner layer, V^{5+} phase might be little formed.

One of the advantages of the exfoliation is usability for the preparation of supported or composite catalysts. Here the SiO_2-composite catalysts were prepared from the exfoliated solution and SiO_2 (Aerosil 50, 51 m^2·g^{-1}) by the addition of SiO_2 in the exfoliated solution during the reduction.[17] As Table 1 summerizes, the obtained SiO_2-composites containing 13 wt% or 31 wt% of $(VO)_2P_2O_7$ gave high activities; the activities were about 6 times that of C(2Bu). Furthermore the selectivities to MA were 61 and 63% at about 60%-conversion over 13 wt% and 31 wt%VPO-SiO_2 composites, respectively. The slight decrease in the selectivity by supporting is probably due to interaction between VP species and the support. These selectivities were higher than those reported so far for the supported catalysts.[18–20] These results demonstrate that the present method utilizing intercalation and exfoliation of the layered materials is promising for the preparation of efficient catalysts.

Table 1. Activity and selectivity for selective oxidation of *n*-butane[a]

Catalyst	SA[b] /m^2·g^{-1}	Rate /10^{-4}mol·g^{-1}·h^{-1}	Selectivity[c] /%
EC(2-Bu)	27	30	72
13wt%EC(2-Bu)-SiO2		60[d]	61
31wt%EC(2-Bu)-SiO2		57[d]	63
C(2-Bu)	10	10	67

[a] *n*-Butane 1.5%, O2 17% at 703 K. [b] Surface area measured by BET method. [c] Selectivity to MA at about 60% conversion. [d] 10^{-4}mol·(g of $(VO)_2P_2O_7$)$^{-1}$·h^{-1}.

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