Synthesis of vanadium phosphorus oxides enhanced by deep eutectic solvents and its application in selective oxidation of *n*-butane to maleic anhydride

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Abstract:

In the present work, the deep eutectic solvents (DES) was used as additives during the synthesis of vanadium phosphorus oxides (VPO) catalyst to improve its catalytic performance in the selective oxidation of *n*-butane to maleic anhydride (MA). Results showed that the DES worked as a crystal face inductive agent of VPO due to its coordination ability, which facilitated the formation of the active phase $(VO)_2P_2O_7$ and enhanced its crystallinity. This compound exhibited a much higher activity and selectivity than that of VPO obtained without DES additive.

Keywords: vanadium phosphorus oxide (VPO), deep eutectic solvents (DESs), maleic anhydride (MA), selective oxidation, *n*-butane oxidation.

1. Introduction

Although vanadium phosphorus oxides (VPO) have been commercialized as the most effective catalysts for the selective oxidation of n-butane to maleic anhydride (MA), low selectivity towards MA remains a serious problem. Therefore, it is strongly desirable to develop new and functional forms of VPO that can offer improvement to this oxidation process. So far, significant efforts have been devoted to enhance the performance of VPO. The previous reported work mainly focused on improving the performance by the addition of metal promoters, like Bi, Co, Mo, Au, et. al.[1] But metal promoters might cause many problems, like increasing costs, generat NO_x, et. al.

Deep eutectic solvents (DES) is obtained by complexion of quaternary ammonium salts with hydrogen bond donors such as acids, amines, et. al. DESs are designable, low cost, biodegradable and nontoxic, therefore are widely used in various fields, especially, in the field of materials synthesis.[2] it was reported that DES can modulate the crystal nucleation and growth mechanisms by passivating particular crystal faces and dictating growth along preferred crystallographic direction. [3]However, the work on its enhancement on synthesis of VPO is few studied.

Here, we employed choline chloride/ oxalic acid (ChCl/oa) DES as an additive during the synthesis of VPO to improve its catalytic performance in selective oxidation of n-butane to MA. The role it played during this process was investigated in details. It was found that DES worked as a crystal face inductive agent to induce the formation of active face, resulting in good catalytic performance. This findings provide a novel, green, efficient method for catalysts reinforcement.

2. Experimental

ChCl/oa was obtained by thermal treatment（at 80℃） the mixture of H-bond donor (oxalic acid dehydrate) and H-bonding acceptor (choline chloride) with magnetic stirring at the optimized molar ratio (1:1)until a homogenous liquid was formed.

The VPO catalysts were prepared by organic synthesis method. V_2O_5 was in a mixture of isobutyl alcohol and benzyl alcohol. A certain quality of DES was added to this system. The suspension was stirred under reflux at 408K for 3 h. Then a proper amount of 85% phosphoric acid was added. The solution was maintained under reflux at 408K for 16 h and obtained the precursors $VOHPO_4 \cdot 0.5H_2O$. The $VOHPO_4 \cdot 0.5H_2O$ are designated DES-x, x representing the additional amount (g) of DES. The activation of catalysts and its catalytic tests were carried out in a fixed-bed reactor. The temperature was raised to 430 ^oC and kept for 12 h and the active phase $(VO)_2P_2O_7$ was obtained. Then the n-butane selective oxidation was carried out under 420 ^oC.

3. Results and discussion

Figure 1 shows the XRD patterns of $VOHPO_4 \cdot 0.5H_2O$ (a) and $(VO)_2P_2O_7$ (b). $VOHPO_4 \cdot 0.5H_2O$ gave higher intensity of (001) plane, which is transformed topotactically similar to (200) plane of $(VO)_2P_2O_7$ and is believed to be responsible for the catalytic activity in n-butane oxidation. The addition of DES gave rise to enhanced $I_{(200)}/I_{(013)}$ ratio, indicating the presence of more vanandyl group on the surface of the catalyst due to the exposure of (200) plane.

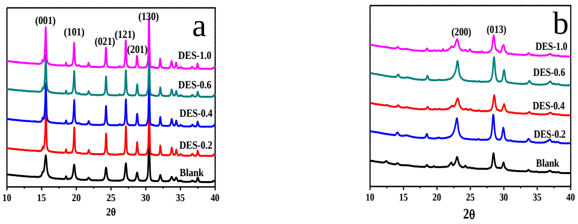

Figure 1. XRD patterns of $VOHPO_4$ 0.5H_2O（a） and $(VO)_2P_2O_7$（b）

VPO without DES possess a thin plate-like morphology (Figure2 a). A much thicker and more orderly morphology were observed in DES-VPO (Figure2 c). The latter consisted of thick laminated structure with different growth orientation, suggesting that the crystal growth of $VOHPO_4 \cdot 0.5H_2O$ have been changed. Meanwhile, SAED suggesting that DES-VPO (Figure2 d) preferred the exposure of (001) crystal face compared with blank sample (Figure 2 b), which is in accordance with the XRD results.

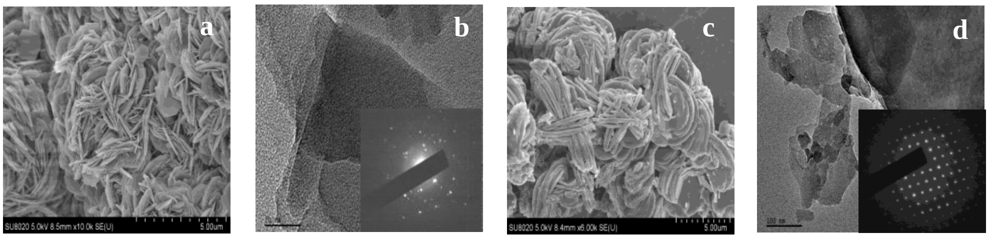

Figure 2. SEM and TEM images of VPO (a and b) and VPO-DES(c and d)

Here we proposed the function of DES during synthesis of VPO as shown in Figure 3 (a). This compound exhibited higher activity and selectivity to MA (61% selectivity at 95% conversion), 11% higher in *n*-butane conversion, 7% higher in MA selectivity than VPO obtained without DES addition.

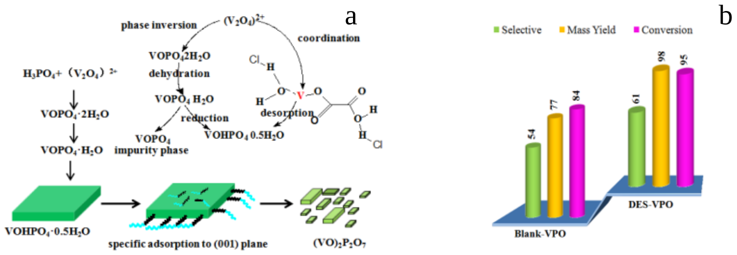

Figure 3. (a) Proposed function of DES during the synthesis of VPO and (b) catalytic performance in selective oxidation of n-butane

4. Conclusions

DES is a promoting effective additives during the synthesis of VPO for improving its catalytic performance in selective oxidation of *n*-butane to maleic anhydride. It was found that the DES worked as a crystal face inductive agent of VPO due to its coordination ability, facilitated the formation of the active phase $(VO)_2P_2O_7$ and monocrystal was obtained as characterized by TEM and SAED. Furthermore, its carytallity of DES-VPO was enhanced, suggested for the XRD results of improvement of the $I_{(200)}/I_{(013)}$ ratio of $(VO)_2P_2O_7$. All these were assumed to contribute to the good catalytic performance.

References

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