Effect of microwave and conventional oven drying methods in the synthesis of vanadium phosphorus oxide catalysts via sesquihydrate route.

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Abstract: A series of vanadyl pyrophosphate (VPOs) catalysts were prepared via sesquihydrate route. Microwave drying process employed at Stage 1 and/or Stage 2 during the synthesis was compared with the oven dried VPOs catalyst. Catalysts dried using microwave exhibited a well-crystallized $(VO)_2P_2O_7$ phase and higher amount of O^{2-}-V^{5+} species as compared to catalyst dried by oven. BET surface area analysis revealed that catalysts with microwave dried process employed at stage 2 yielded highest specific surface area. Microwave dried catalysts could enhance the conversion of *n*-butane to maleic anhydride with lower by-product formation.

Keywords: vanadyl pyrophosphate, sesquihydrate, microwave drying.

1. Introduction

Vanadyl pyrophosphate catalysts have been studied extensively for selective oxidation of n-butane to maleic anhydride [1]. The use of highly active catalysts makes it possible to increase selectivity and conversion of benzene to maleic anhydride. The catalytic properties of the $(VO)_2P_2O_7$ depends on the method by which the precursor is prepared [2]. The influence of microwave heating on solid catalyst systems has been studied intensively in recent years and there have been numerous reports indicating the increase in the rate of chemical reactions and product selectivity when microwave radiation is used during catalyst preparation step [3]. Microwave irradiation is believed to offer substantial benefits in the synthesis of heterogeneous catalysts by increasing the catalyst activity. The other substantial advantages offered by microwave heating are (i) significant reduction in catalyst synthesis costs due to shorter processing time and (ii) improved catalytic properties of synthesized catalysts [4]. In this paper, the physico-chemical properties, reactivity and catalytic performances of bulk VPOs catalysts, prepared via vanadyl hydrogen phosphate sesquihydrate precursor using reflux technique and microwave drying method will be investigated.

2. Experimental (or Theoretical)

The synthesis of sesquihydrate precursor has been divided into a two-step procedure, which involving vanadyl phosphate dihydrate, $VOPO_4{\cdot}2H_2O$ as an intermediate before obtaining the precursor. Microwave and oven drying process were introduced in both stages alternatively. The activated catalysts were denoted as VPOs-MM (catalyst dried by microwave irradiation at both stages), VPOs-MO (catalyst dried via microwave at Stage 1 and oven-dried at Stage 2), VPOs-OM (catalyst prepared via oven drying at Stage 1 and microwave drying at Stage 2), and VPOs-OO (catalyst dried using conventional oven at both stages).

3. Results and discussion

XRD patterns showed that catalysts dried by microwave irradiation at Stage 1 (VPOS-MM and VPOs-MO) would promote the formation of V^{5+} phases in the catalysts. As for the catalysts which oven drying method was employed in Stage 1 (VPOs-OM and VPOs-OO), the reflection plane of (2 0 4) was found to be more intense as compared to the microwave drying counterparts. According to Rownagni et al. (2009) [5] the microwave assisted prepared catalysts displayed a thin rosette-type structure with uniform crystal size and the smaller platelets observed in these catalysts resulted in higher surface area and hence improved catalyst performance, as observed in Figure 2. The specific surface area of VPOs catalysts are as follows; 18 m2g-1 for VPOs-MM, 12 m2g-1 for VPOs-MO, 21 m2g-1 for VPOs-OM, and 15 m2g-1 for VPOs-OO. Previously, Rownaghi et al., (2009) [5] had reported that catalyst prepared via VPD method and microwave drying process on both stages exhibited larger specific surface area than catalysts undergone conventional drying. This is in agreement with catalysts prepared via VPS method as well, where catalyst dried by microwave on both stages (VPOs-MM) has larger specific surface area as compared to conventional drying catalyst (VPOs-OO). The amount of oxygen associated to V^{4+} ($O-V^{4+}$) (Figure 3) was found to increase by 33 % to 46 %, when the catalysts were dried by microwave irradiation in either Stage 1 (VPOs-MO), stage 2 (VPOs-OM) or both stages (VPOs-MM). Higher total amount of H_2 consumption from microwave drying catalyst suggested that microwave irradiation is capable of producing highly active and selective VPOs catalysts. As showed in Table 1, catalysts prepared via microwave irradiation (VPOs-OM, VPOs-MO, VPOs-MM) showed an increment in both activity and selectivity as compared to catalyst produced via conventional oven heating method in both stages (VPOs-OO). Table 1 showed the Although the conversion of *n*-butane to maleic anyhydride of VPOs-MO is not the highest among the catalysts, but when plotted against the specific surface area of the catalysts (TON), it showed the highest rate of conversion of *n*-butane, which might due to the mobility of oxygen associated with V^{4+} phase at lower specific surface area.

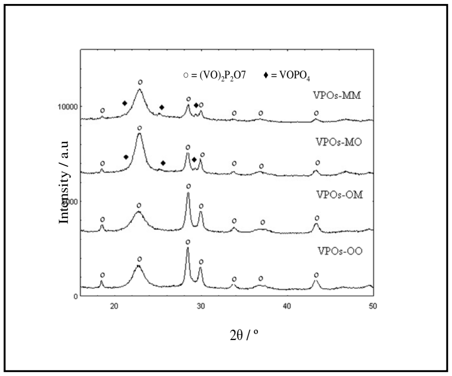


Figure 1. XRD Profiles for VPOs Catalysts.

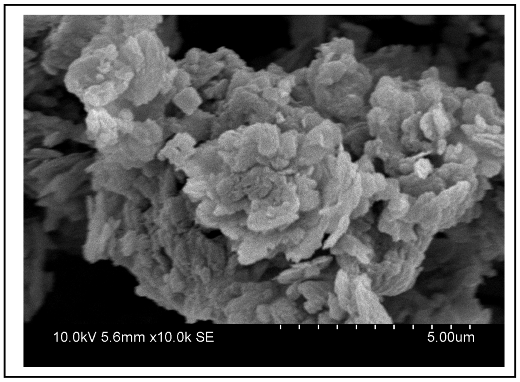


Figure 2. SEM Image of VPOs-MM Catalyst

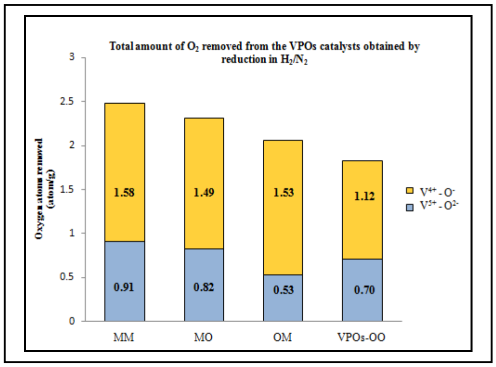
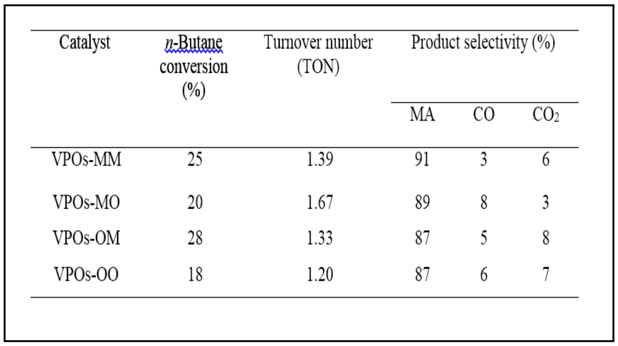


Figure 3. Data chart of TPR in H_2/N_2



Catalyst	*n*-Butane conversion (%)	Turnover number (TON)	Product selectivity (%)		
			MA	CO	CO_2
VPOs-MM	25	1.39	91	3	6
VPOs-MO	20	1.67	89	8	3
VPOs-OM	28	1.33	87	5	8
VPOs-OO	18	1.20	87	6	7

Table 1. Catalytic performances

4. Conclusions

Catalysts treated with microwave irradiation exhibited good crystalline with characteristics peaks of vanadyl pyrophosphate phase and their surface morphologies were found to be in plate-like crystals with folded edges. The use of microwave drying method was observed to induce higher specific surface area and a significant change of morphology of the catalysts.

References

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