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Selective Catalytic Oxidation of O-xylene to Phthalic Anhydride over VPO/HZSM-5: An Optimization Study

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ABSTRACT

Selective gas-phase oxidation of o-xylene to phthalic anhydride over VPO/HZSM-5 catalysts was investigated. The catalysts with various P/V ratio were facilely synthesized by impregnation method. The prepared catalysts were characterized by several techniques such as SEM, TPD-NH_3, H_2-TPR, FT-IR, BET and XRD. The effects of P/V ratio (1.6–2.4), reaction temperature (350–450 ◦C), Ox/O_2 ratio (0.15–0.60) and gas hourly space velocity (G.H.S.V) of O_2/N_2 (600–1200 h^{-1}) on yield of PA were studied by Box–Behnken design. The influence of independent factors and their quadratic interactions were examined by means of the Analysis of Variance (ANOVA). Present results indicate that P/V ratio has a different effect on the conversion and selectivity of PA. The catalyst with P/V ratio = 2.0, Ox/O_2 ratio = 0.37, G.H.S.V of 770 h^{-1} and reaction temperature of 370 ◦C produced maximum yield of PA (80.7 %). The analysis revealed that the predicted results agree well with the experimental data (P/V ratio = 2.0, Ox/O_2 ratio = 0.38, G.H.S.V of the carrier gas = 900 h^{-1} and reaction temperature of 400 ◦C with 74.3% yield).

Keywords: VPO/HZSM-5 catalyst; phthalic anhydride; selective oxidation; o-xylene

1. Introduction

Vanadium oxide-based catalysts is commonly used for several important industrial reactions, including in the oxidation of n-butane (VPO) and of benzene (supported V-MoO) to maleic anhydride, production of phthalic anhydride from o-xylene oxidation, in the reduction of NO_X with ammonia and production of sulphuric acid by oxidation of SO. Growing annual production of phthalic anhydride (5.5 million tons in 2015) is indicative of importance of its applications in the manufacture of polyester resins, phthalate plasticizers, phthalocyanine dyes and numerous fine chemicals.

The industrial reaction process was carried out in range of 380-400°C, near atmospheric pressure to give maximum conversion of o-xylene (100%) and good selectivity to phthalic anhydride (70-75%). Recently, the main object of several investigations demonstrated that V_2O_5 can be highly dispersed on the surface of anatase obtaining an active and selective V/Ti/O catalyst. The formation of polymerized and isolated vanadia species on the surface and its strong interaction with the support have important influences on reaction performance and improve long life in the o-xylene oxidation.

At present work, a novel VPO/HZSM-5 catalyst (P/V molar ratio from 1.6 to 2.4) at constant total weight percentage of V and P atoms = 20% was prepared by impregnation method. The effect of the preparation condition (or independent factors), such as P/V ratio supported on HZSM-5 (A) and operation conditions, such as reaction temperature (B), OX/O_2 molar ratio (C) and Gas hourly space velocity (G.H.S.V) (D) on the performance and activity of the catalyst were investigated. Response surface methodology (RSM) was used in order to optimize the selective oxidation reaction along with desirable PA selectivity. The interaction between reaction parameters (factors) and o-xylene conversion were evaluated to find the optimum conditions for achievement the highest yield of PA. Powder X-ray diffraction (XRD), Scanning electron microscopy (SEM) and temperature-programmed desorption of NH_3 (TPD-NH_3) were employed to characterize the texture and structure of the catalysts.

2. Experimental

Materials and method

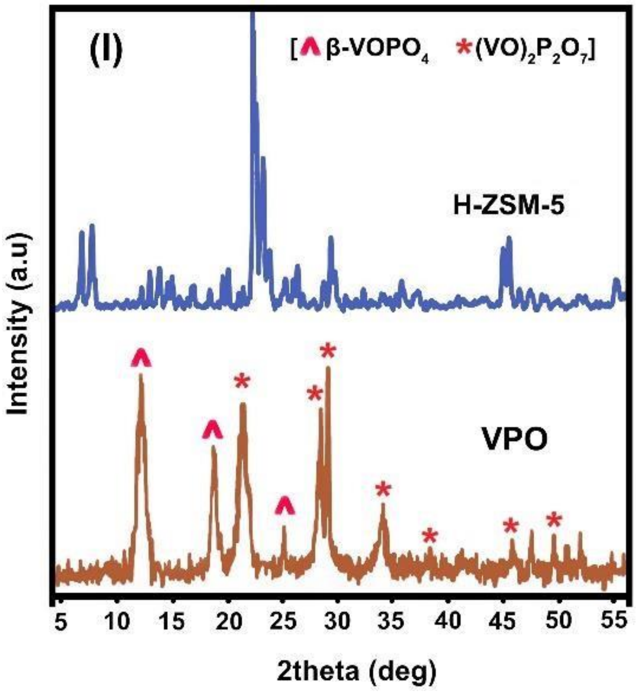
The VPO-2.0 catalyst (unsupported) was synthesized according to a literature procedure through an organic route using isobutyl alcohol and benzyl alcohol as reducing agents. A mixture of V_2O_5 (4.85 g), 2-butanol (99%, 30 mL) and benzyl alcohol (anhydrous, 99.8%, 20 mL) was refluxed at 150°C for 3 h. The color of the solution changed from yellow-orange to black-green. Then, 7.30 mL of phosphoric acid (85%) was added to obtain the P/V molar ratio of 2. The resulting solution was then heated again to 120ºC and maintained under reflux with constant stirring for 5 h. After, the suspension was filtered and turquoise blue solid ($VOHPO_4.0.5H_2O$) was washed with iso butanol and acetone, respectively, then further dried in air at 130°C for 24 h. VPO-x /HZSM-5 catalysts with x ranged from 1.6 to 2.4 were prepared by the impregnation method. In a typical experiment, 1.185 gram of V_2O_5 (0.0066 mol) was dissolved in a mixture of 2-butanol (99%) and benzyl alcohol (anhydrous, 99.8%) and then refluxed at 150 °C for 3 h, required amount of phosphoric acid (1.78 ml, 85%) was drop-wise added to obtain P/V = 2. Then, a given amount of H-ZSM-5 (9.15 gr) was impregnated with the impregnation liquid for another 5 h of refluxing under vigorous stirring to make VPO-2.0/ HZSM-5 sample. VPO-x / HZSM-5 samples with P/V= 1.6, 1.8, 2.2 and 2.4 molar ratio were also prepared according to previous section. The total weight percentage of V and P atoms was 15%. Finally, the gel was removed by filtration, washed thoroughly with water and dried at 130 ºC overnight. Both unsupported and supported precursors were calcined in a programmable muffle furnace at 800°C for 2 h in air flow with heating rate of $2^{\circ}C.min^{-1}$ to produce pure vanadium phosphorus oxide (VPO or $(VO)_2P_2O_7$) and VPO/HZSM-5 powders. The surface area of prepared VPO-2.0 (with P/V=2.0 molar ratio) was 28.5 m^2/gr.

3. Results and discussion

The X-ray diffraction patterns of the HZSM-5 and synthesized samples, VPO-2.0 and VPO/ HZSM-5 with various P/V molar ratio from 1.6 to 2.4 molar ratio are presented in Fig. 1 (I, II). As before mentioned, all of samples were calcined in air flow at 800 °C for 2

h. According to PDF No. 44-0003, The HZSM-5 characteristic peaks appear at 2θ value of 7.87, 8.81, 23.09, 23.86, 24.34, 29.20 and 29.88.

Besides, the diffractogram of synthesized VPO-2.0 is also presented in Fig.1 and the peaks observed at 2θ = 22.8, 28.3, 29.2, 33.6, 37.7, 46.2 and 49.5° indicates the presence (VO)2P2O7 (JCPDS: 41-698), while the peaks appeared at 2θ = 12.1, 19.3, 25.2° confirm the presence of β-VOPO4 (JCPDS: 27-948), respectively. Fig.2 depicted the selective oxidation reaction in the presence of VPO/ HZSM-5 catalysts. The specific surface area (SBET), pore volume and pore diameter for HZSM-5, pure VPO-2.0 and VPO/HZSM-5 catalysts of this study are tabulated in Table 1. As compared with the pure VPO-2.0, Using of HZSM-5, not only enhanced specific surface area of the supported samples but also improved the dispersion of active phase significantly. It is apparent that, by increasing of P/V molar ratio, BET surface areas are gradually decreased from 352 m^2 g^{-1} with micro-pore volume of 0.13 cm^3/g to 292 m^2 g^{-1} with micro-pore volume of 0.10 cm^3/g.



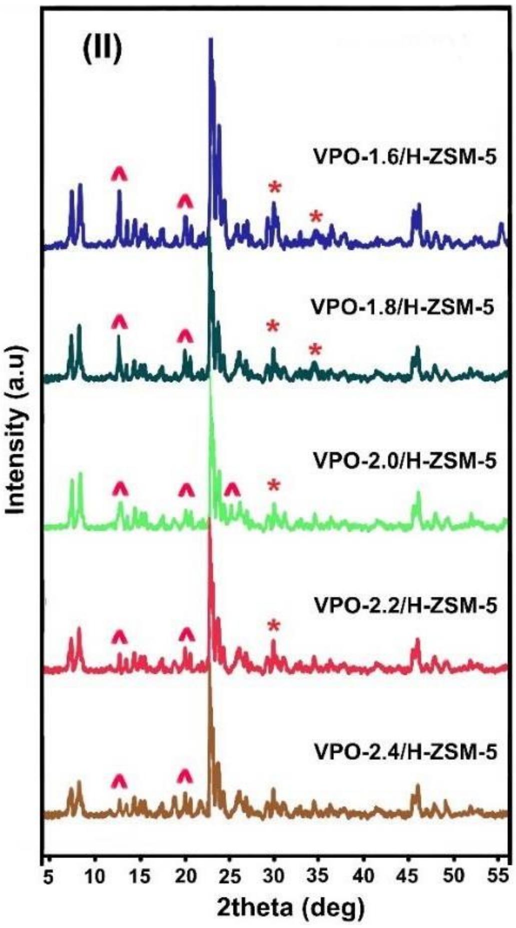


Fig.1: The chemical reaction for selective oxidation of o-xylene to PA

From results of Table 1, could be related to interaction between support and unreacted phosphoric acid, which are causing to decrease specific surface area and micro-pore volume probably by blocking the pores. In order to gain a better understanding of the interaction effects of variables on conversion and selectivity, 3D surface plot for the measured responses were formed based on the model equations (Eq. 1- 2).

VPO-X/HZSM-5 Catalysts	**BETsa (m^2/g)[a]**	**Mv (cm^3/g)[b]**	**Apd(Å)[c]**	**Tad (μmol/g)[d]**
HZSM-5	380	0.138	22. 6	438.5
VPO-2.0	28.5	0.047	48. 1	1860.4
1.6	352	0.130	22. 9	825.2
1.8	338	0.125	23. 7	972.6
2.0	323	0.121	26. 3	1005.5
2.2	310	0.112	29. 2	987.3
2.4	292	0.100	34. 6	821.7

a surface area **b** Micropore volume **c** Average pore diameter **d** Totalammonia desorption

Table1. Results of BET surface area, pore size distribution measurements, acidic properties various VPO/HZSM-5 catalysts.

The results of surface response 3-D plots of OX conversion and PA selectivity as a function of two independent variables: (a, e) P/V molar ratio on the HZSM-5 and OX/O2 ratio; (b, f) G.H.S.V and P/V molar ratio; (c, g) OX/O2 ratio and temperature, (d, h) G.H.S.V and temperature are shown in Fig. 3(a)–(h), respectively.

Independent variables	**Range and level**		
	-1	0	1
P/V molar ratio, A	1.6	2	2.4
Temperature (◦C), B	350	400	450
o-xylene/ O_2 molar ratio, C	0.15	0.30	0.60
G.H.S.V(h-1), D	600	900	1200

Table 2. Experimental range and levels for Box-Behnkendesign

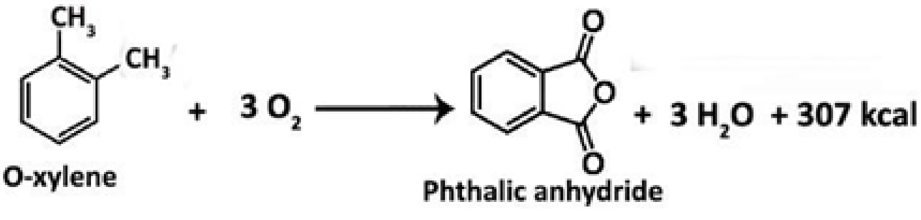


Fig.2. The chemical reaction for selective oxidation of o-xylene to PA

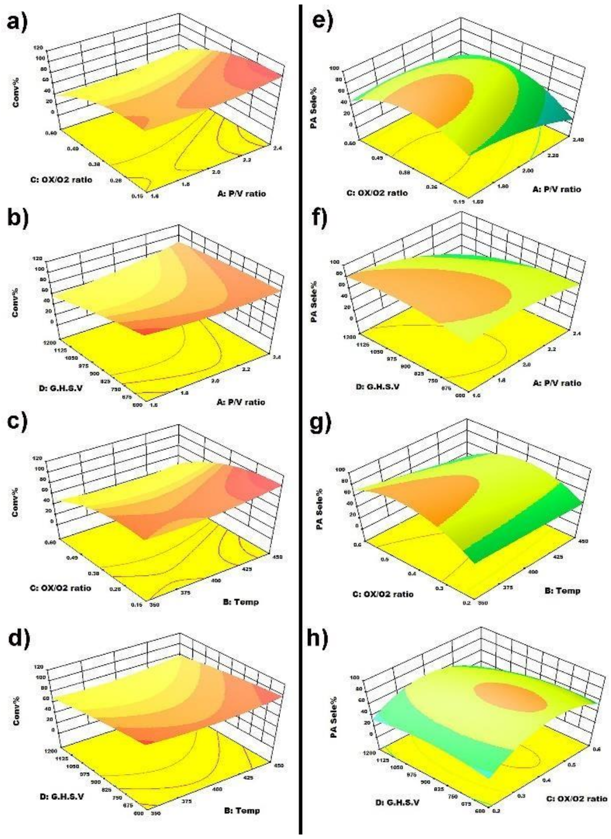


Fig.3. surface plots describing the response surface for:(Left: OX conversion, Right: PA selectivity)

(1) OX Conv(%) = $82.0+6.45A+2.91B-25.22C-11.51D+0.08AB+0.57AC+8.93AD-3.70BC+1.87BD-6.92CD+5.11A^2+6.30B^2-16.67C^2-2.15D^2$

(2) PA Sele(%) = $81.24-15.97A-10.04B+4.48C-6.14D-14.35AB+9.52AC-11.68AD-6.88BC-6.75BD-5.75CD-10.86A^2-0.45B^2-31.93C^2-10.52D^2$

4. Conclusions

A response surface model, based on the Box-Benkhen technique, was developed to describe the conversion of o-xylene, PA selectivity and yield. Temperature programmed desorption of ammonia (NH3-TPD) showed that the amount of strong acid sites decreased by increasing of P/V ratio while number of total acid sites significantly increased. X-ray diffraction patterns and temperature programmed reduction (H2-TPR) showed that the catalysts with high P/V ratio (VPO- 2.2/HZSM-5 and VPO-2.4/HZSM-5) have more amounts of reducible V^{5+} species, which is mainly because of highly dispersed β-VOPO4 and γ-VOPO4 species. Also, we found that the catalytic activity and product distributions depend on reaction temperature, B/B+L ratio and V^{5+}/V^{4+} ratio. The obtained results from ANOVA showed that the most significant factor affecting the conversion of OX and PA selectivity were P/V molar ratio and OX/O2 molar ratio, respectively. Coefficient of determination (R^2) value of 0.9955 and 0.9864 obtained from Eqs. (1) and (2) shown that quadratic polynomial regression model could properly interpret the experimental data. Thus, weak-medium strength acid sites efficiently promoted the oxidation reaction. With P/V ratio = 2.0, Ox/O2 ratio = 0.37, G.H.S.V of 770 h^{-1} and reaction temperature of 370 ◦C, we could achieve the highest yield of PA (80.7%). Also, to show the validity of this prediction, we run the experiment at this condition and gained 79.3% for the yield of PA. These studies confirm that the predicted values are fully compatible with the experimental values.

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