Vanadium oxides supported on hydroxyapatite for the activation of *n*-pentane and *n*-hexane

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Introduction

Vanadium oxides have been extremely useful as catalytic materials in many studies [1]. Supported vanadium oxide catalysts have become an important class of catalysts because of their numerous applications. These catalysts exhibit excellent activity and selectivity for a variety of oxidation reactions including the selective oxidation of *n*-butane and *n*-pentane to maleic anhydride(MA) [2], conversion of *o*-xylene to phthalic anhydride (PA) [3], and the oxidative dehydrogenation of the lower alkanes [4]. Heat- conducive ceramic supports, e.g., β-SiC, Si_3N_4 and BN showed significant gains in MA production [5] compared to conventional supports like alumina, silica and titania [6]. Mesoporous aluminosilicates, more specifically, MCM-41 was used as support because of the hexagonal arrangement of its uniformely sized mesopores, thermal stability and large surface areas [7]. Here we report the use of barium, strontium and cobalt substituted hydroxyapatite as supports for the oxidation of *n*-pentane and *n*-hexane. Hydroxyapatites are bifunctional compounds with acidic or basic properties and they have the general formula $[M_{10-x}(HPO_4)_x(PO_4)_{6-x}(OH)_{2-x}, 0 \leq x \leq 1]$. For $x = 1$, we have the stoichiometric with M/P = 1.67.

Materials and Methods

The Ba, Sr and Co hydroxyapatites were prepared by co-precipitation. The vanadium phosphorus oxide (VPO) was prepared in the organic medium [1] Weight percentages, in the range 2.5-15%, were loaded on the hydroxyapatite supports by wet impregnation. The materials were characterized by powder X-ray diffraction (XRD) with a Philips PW 1830 diffractometer and infra-red (IR) spectra were recorded using a Nicolet Impact 420 spectrometer. The BET surface area was obtained by means of dinitrogen physisorption at 77 K using the Micromeritics ASAP 2000 instrument. The concentrations of Ba, Sr, Co, V and P were determined by ICP-OES. Oxidation runs were carried out with a continuous, fixed bed tubular stainless steel reactor. The product stream was analysed by Gas Chromatograph equipped with a FID module and GC-MS using capillary columns. The carbon oxides and light organic compounds were monitored by a TCD Gas Chromatograph.

Results and Discussion

The surface areas of the Ba, Sr and Co hydroxyapatites were 27, 31 and 26 m^2/ g respectively. Table 1 summarises the surface areas together with the surface and bulk compositions of the most efficient catalysts. There is a decrease in the surface area of the materials with an increase in VPO content. This could be attributed to the clogging of the narrow pores of the support with the active component making it inaccessible to nitrogen molecules. The XRD patterns of the hydroxyapatite and the hydroxyapatite- supported catalysts confirmed the presence of phases belonging to hydroxyapatite The patterns for supported catalysts showed the presence of $(VO)_2P_2O_7$ peaks at 2θ angles of $18.6°$, $23.1°$, $28.5°$, $29.9°$, $33.7°$ and $36.9°$ whereas a mixture of the $VOHPO_4 \cdot \frac{1}{2}H_2O$ and $VOPO_4 \cdot 2H_2O$ phases displayed peaks at 2θ angles of $13.2°$, $20.3°$, $21.6°$, $28.9°$, $29.9°$, $41.1°$, $46.3°$, $59.5°$ and $63.8°$.

Table 1. BET surface area, surface and bulk composition

Catalyst	Surface Area (m^2/g)	M/P	P/V (bulk)	P/V(surface)
VBa-HAp2	14	1.83	1.77	0.94
VSr-HAp2	17	1.86	1.82	1.02
VCo-HAp2	16	1.91	1.88	1.12

For the partial oxidation of *n*-pentane, the composition of the product stream depended on the VPO loadings and temperature and to a lesser extent on the Gas Hourly Space Velocity (GHSV). A marginal difference in the activity of Ba-HAp, Sr-HAp and Co-HAp as supports for VPO was observed. There was a significant increase in the activity in terms of conversion of *n*-pentane, but a slight decrease in the formation of MA and PA with an increase in the VPO loadings on all the supports. This could be attributed to the non- crystalline nature of the catalyst surface due to clustering of the VPO at higher loadings leading to a decrease in V^{IV} sites. Lower yields of MA and PA at higher VPO loadings could also be the result of an increase in the total metal content of the catalyst. VPO loadings of 5.0 and 7.5 wt % at temperatures of $320°C$ and $360°C$ with GHSVs of 1900 h^{-1} and 2300 h^{-1} gave good conversions. The major products obtained were phthalic anhydride, maleic anhydride, carbon oxides (carbon monoxide and carbon dioxide), benzoic acid, furan, 2H-pyran-2-one and acetic acid. The selectivities towards maleic anhydride and phthalic anhydride were at its maximum of 52, 51, 54% and 22, 19, 24 % for VBa-HAp2, VSr-HAp2 and VCo-HAp2 (5 wt % VPO loadings) respectively when the P/V ratio was ~ 1 at $360°C$ with a GHSV of 2300 h^{-1}. For *n*-hexane oxidation, there was minimal formation of the anhydrides. The major products obtained were benzoic acid, carbon oxides, benzene and acetic acid.

Significance

Maleic and phthalic anhydrides are important monomers used in the manufacture of synthetic fibers, plastics, paints and adhesives. In this study, optimum yields of up to 55 % maleic anhydride and 24 % phthalic anhydride were obtained during the selective oxidation of *n*- pentane which is a significant increase when compared to the performance of the silica and titania- based catalysts [6].

References

1 G.J. Hutchings, C.J. Kiely, M.T. Sananés-Schulz, A. Burrows, J.-C. Volta, *Catal. Today* 40, 273 (1998).
2 J.M.C. Bueno, G.K. Bethke, M.C. Kung, H.H. Kung, *Catal. Today* 43, 101 (1998).
3 C.R. Dias, M.F. Portela, G.C. Bond, *J. Catal.* 157, 344 (1995).
4 F. Cavani, F. Trifirò, *Catal. Today* 24, 307 (1995).
5 M.J. Ledoux, C. Crouzet, C. Pham-Huu, V. Turines, K. Kourtakis, P.L. Mills, J.J. Lerou, *J. Catal.* 203, 495 (2001).
6 R.A. Overbeek, A.R.C.J. Pekelharing, A.J. van Dillen, J.W. Geus, *Appl. Catal. A: Gen.* 135, 231 (1996).
7 W. Nie, X. Wang, W. Ji, Q. Yan, Y. Chen, C.T. Au, *Catal. Lett.* 76, 201 (2001).