

Improvement of the performances of supported $(\text{NH}_4)_3\text{HPMo}_{11}\text{VO}_{40}$ catalysts for isobutane selective oxidation

Fangli JING^a, Sébastien PAUL^{a,b,*}, Élisabeth BORDES-RICHARD^a

^a Univ. Lille Nord de France, Unité de Catalyse et de Chimie du Solide, UCCS (UMR CNRS 8181), Cité Scientifique, F-59650, Villeneuve d'Ascq, France

^b Ecole Centrale de Lille, F-59655 Villeneuve d'Ascq, France

* sebastien.paul@ec-lille.fr

Introduction

Bulk $\text{H}_4\text{PMo}_{11}\text{VO}_{40}$ Keggin-type heteropolyacid (HPA) and its salts (like NH_4^+ and Cs^+) have been proved to be effective catalysts of the selective oxidation of isobutane into methacrolein (MAC) and methacrylic acid (MAA) [1]. Here supported $(\text{NH}_4)_3\text{HPMo}_{11}\text{VO}_{40}$ (APMV) catalysts were prepared varying the support type and the catalytic performances for isobutane oxidation were studied.

Experimental

$\text{Cs}_3\text{PMo}_{12}\text{O}_{40}$ (CPM) and SiO_2 (CARiACT® - Q-15, Fuji Silysia) were selected as supports. Supported catalysts containing 40 wt% of APMV active phase were prepared using a co-precipitation and a 2-step impregnation techniques. They are denoted as APMV/CPM and APMV/ SiO_2 respectively. The freshly prepared samples were calcined under static air at 350 °C for 3 h to obtain the catalysts. Bulk APMV was also synthesized by a co-precipitation method for comparison. D8 Advance (Bruker AXS) was employed for *in situ* XRD analysis. The catalytic tests were performed in a fixed-bed reactor in which 570 mg catalyst was loaded at 340 °C and atmospheric pressure, with a total flowrate of 7.13 mL/min STP with the following feed molar ratios for isobutane/ O_2 / H_2O /He: 27/13.5/10/49.5.

Results/Discussion

The catalytic performances obtained using the different catalysts are listed in Table 1. It is clear that the catalytic activity is significantly improved over the supported catalysts compared to that of the APMV bulk sample. As far as the products distribution is concerned, APMV/ SiO_2 is much more selective to acetic acid (AA) than the other two samples, which suggested a strong interaction of the reactants and/or of the APMV active phase with the support. The selectivity to MAA is improved considerably over APMV/CPM and the activity is also the highest.

Table 1. Catalytic performances for the selective oxidation of isobutane over different samples

Catalyst	Conversion, %		Selectivity, %				$Y_{\text{MAC+MAA}}$, %
	O_2	Isobutane	MAC	AA	MAA	CO_x	
APMV	10.7	2.5	20.4	5.9	34.3	35.8	1.4
APMV/ SiO_2	51.8	11.3	14.7	27.5	12.7	42.9	3.1
APMV/CPM	61.6	15.3	10.0	14.1	42.0	30.7	8.0

The changes in products distribution were probably caused by modifications of the active phase on the surface of the support. Actually, in ethane and propane oxidation over Mo-V-O mixed-metal oxides acetic acid was obtained as a main product or by-product [2, 3]. *In situ* XRD experiments (Figure 1) showed that APMV/CPM sample displayed a much better stability of the structure than APMV/ SiO_2 . On the later, a partial decomposition of the active phase may occur under the reaction conditions which could be the reason for the decrease in selectivity of the desired products.

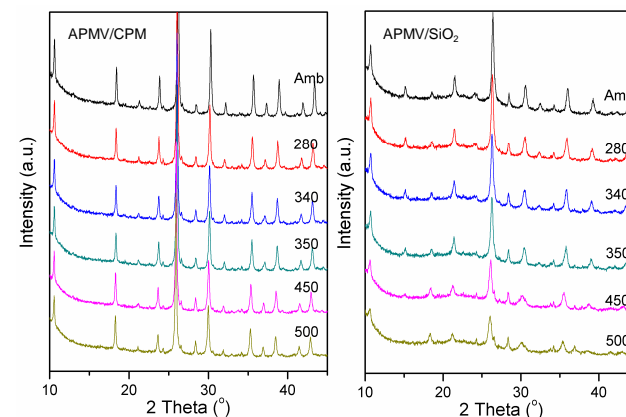


Figure 1. *In situ* XRD patterns of the supported catalysts

References

1. S. Paul, V. Le Courtois, D. Vanhove, *Ind. Eng. Chem. Res.* **36**, 3391 (1997).
2. W. Ueda, K. Oshihara, *Appl. Catal. A: Gen.* **200**, 135 (2000).
3. M. M. Lin, *Appl. Catal. A: Gen.* **207**, 1 (2001).