In situ XRD investigations of the $Cs_1H_3PVMo_{11}O_{40}$ heteropolyacid; structural changes occurring during the catalytic methacrolein oxidation reaction

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In situ X-ray diffraction (XRD) investigations of the structural changes of $Cs_1H_3PVMo_{11}O_{40}$ Keggin type heteropolyacid catalysts show that during the methacrolein (MA) to methacrylic acid (MAA) oxidation reaction the crystallites of the HPA disintegrate to small crystallites of about 10 nm in size. When turning the MA supply repeatedly on and off the observed broadening of the diffraction lines appears and disappears in a rather reversible and reproducible way indicating that the disintegration of the crystallites must be attributed to the catalytic interaction between MA and the HPA catalyst. The reported effect shows some similarities to the formation of the so-called quasiliquid phase by the interaction of $H_3PW_{12}O_{40}$ with polar organic molecules like pyridine or methanol. Presented results suggest that under the conditions of the catalytic reaction MA molecules penetrate into the intracrystalline pore system of the HPA and thus the participation of a quasiliquid phase in the catalytic reaction.

Keywords: heteropolyacids, methacrolein, methacrylic acid, *in situ* XRD, structure–activity relationship, effect of vanadium, crystalline site effect, lattice distortions, quasiliquid phase

1. Introduction

Keggin type heteropolyacids (HPAs) are effective catalysts for acid type and various oxidation processes. There are already several commercial processes in which HPA-based catalysts are used, among them the oxidation of methacrolein to methacrylic acid [1,2]. Beside the applications for industrial processes HPAs are suitable materials for fundamental studies. Their chemical composition and thus the catalytic performance can be modified by ion exchange. Furthermore, various elements can be substituted for the components of the heteropoly anion. In oxidation reactions an improvement of catalytic performance is observed when Mo atoms are partially substituted by V atoms [3]. In the MA to MAA oxidation, for example, the selectivity increases from ∼60 to ∼80% when one vanadium atom in the $PMo_{12}O_{40}$ Keggin anion is substituted for molybdenum. This selectivity level was a basic requirement for an economical realization of the commercial MAA production process.

Because of this great economical importance several studies have been performed to the understanding of the benefit effect of vanadium on activity and selectivity and various theories of the role of vanadium have been proposed:

It was postulated that the higher selectivity of vanadium-containing HPA is due to the modification of the electron density distribution of the Keggin anion [4]. It has been shown that under reaction conditions V is released from the initial Keggin structure onto the intracrystalline pore system of the HPA under formation of cationic VO^{2+} species. The enhanced selectivity of vanadium-containing catalysts was related to the stabilization of the catalytically more active and selective cubic structure by the VO^{2+} cations [3,5,6]. A possible further role of V relates to the restructuring process of the Keggin anions for which vanadium was found to be a catalyst. Vanadium would act as a structural rather than an electronic promoter [7].

The studies mentioned above were carried out using the acid form of the HPA which at elevated temperatures often undergoes structural changes similar to those observed during the catalytic interaction. Moreover, the active catalyst consists of several phases which renders data interpretation more difficult.

Therefore, we have carried out *in situ* XRD experiments on the structural changes of the thermally stable cubic $Cs_1H_3PVMo_{11}O_{40}$ HPA salt in the MA to MAA oxidation reaction by simultaneous measurement of the activity and selectivity of the catalyst.

2. Experimental

The catalyst was prepared by acidification of an aqueous solution of ammonium molybdate, ammonium vanadate, phosphoric acid and cesium nitrate with nitric acid. The resulting suspension was evaporated to dryness. The precipitate was calcined at 653 K for 5 h. The product was tabletted, crushed and sieved to a mesh size of 0.2–0.4 mm.

The catalyst was characterized by chemical analysis, by means of XRD analysis, BET surface area and porosimetry measurements by Hg penetration. After the calcination procedure the XRD diagram showed a pure monophasic compound having the cubic Keggin structure. BET surface area was 3.5 m^2/g, the porosity value 0.22 ml/g.

Oxidation of MA was carried out under continuous-flow conditions between temperatures from 593 to 633 K. The *in situ* chamber was a commercial available Paar high-temperature XRD camera which was modified with a special sample holder having a 5 ml catalyst bed volume. The standard feed composition was 1.17 g MA, 1.02 g H_2O, 3.5 l air and 2.82 l N_2/5 g-catalyst h.

XRD patterns were obtained by a Siemens D-5000 theta/theta diffractometer using Cu Kα radiation.

3. Results

At 613 K in H_2O/N_2/air atmosphere the XRD pattern of the catalyst remained unchanged for several days (figure 1(a)) and corresponded to that of the fresh catalyst.

XRD diagrams obtained at 613 K under conditions of the catalytic reaction are shown in figure 1 (b)–(d). Compared with diagram figure 1(a) the most striking feature of XRD

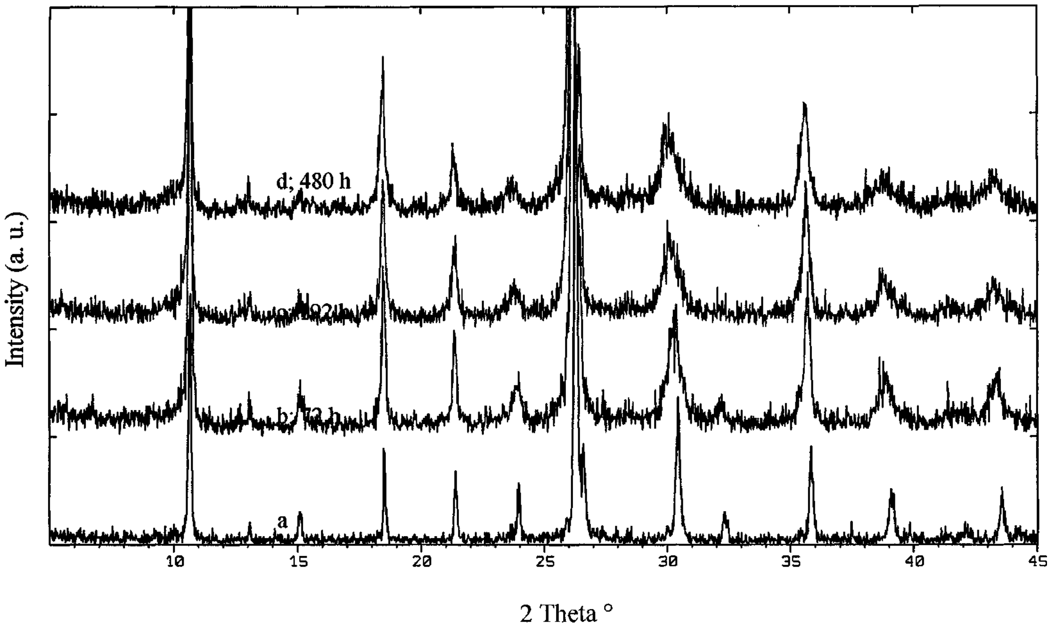

Figure 1. *In situ* X-ray diffraction patterns at 613 K: fresh catalyst (a) in H_2O/N_2/air atmosphere after 2 days and under reaction conditions at the indicated time on stream (b)–(d).

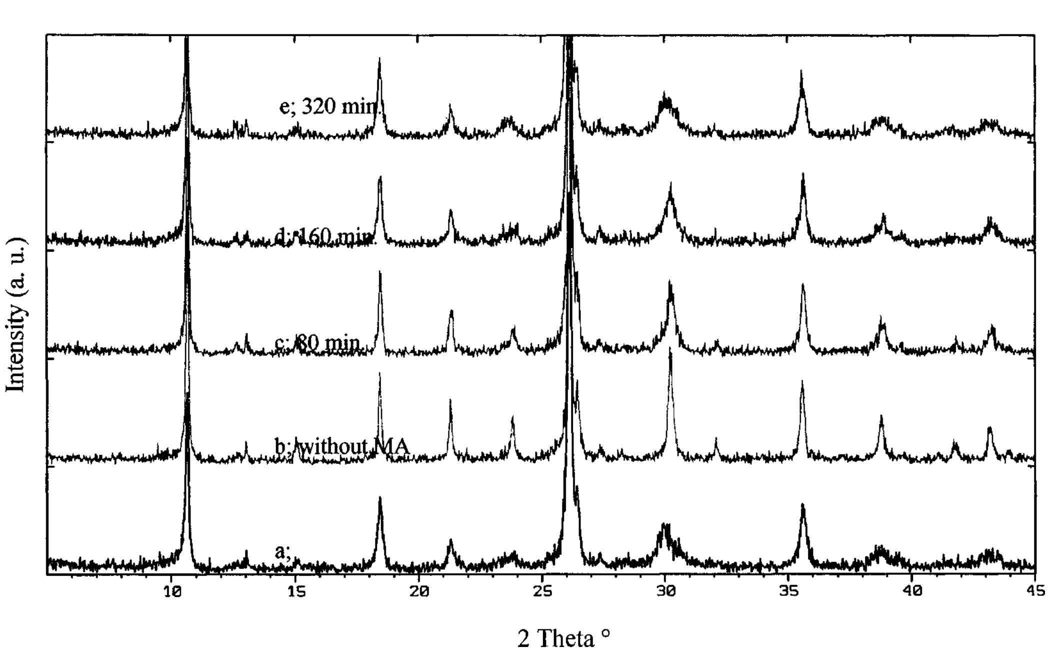

Figure 2. *In situ* X-ray diffraction patterns obtained under reaction conditions (a) and after turning off (b), and turning on (c)–(e) the MA supply.

is an excessive broadening of the diffraction lines with increasing time on stream indicating that the original degree of perfection has been lost under operating conditions. It is noteworthy that this effect only can be observed under the conditions of the catalytic reaction: figure 2(b) shows that by turning off the MA supply the line broadening disappears within a few hours. When the supply of MA was turned on again the lines broadened to their previous values after only 320 min time on stream. When turning the MA supply repeatedly on and off the line broadening appeared and disappeared in a rather reversible and reproducible way.

The analysis of the line profiles based on the variation of the integral line breadths with the Bragg angle shows, that both lattice distortions and crystallite size effects are responsible for the observed line broadening effect and that their individual contribution to the integral line breadths changes with time.

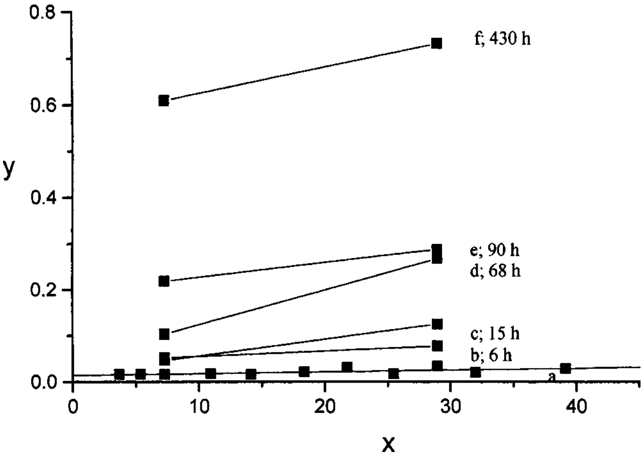

Figure 3. Development of line breadths with increasing time on stream. x-axis $= (\sin\theta/\lambda)^2$, y-axis $= (\beta^*\cos\theta)^2$. (a) Without MA supply, 613 K, all diffraction lines included, (b)–(f) (200) and (400) diffraction lines at the indicated time on stream.

Figure 3 shows the development of the corrected integral line breadths (β) with increasing time on stream in a $(\beta^*\cos\theta)^2$ vs. $(\sin\theta/\lambda)^2$ plot, where θ is the glancing angle of diffraction and λ the wavelength of the X-rays. The (200) and (400) reflections are used to define a straight line providing size and strain parameters in the [h00] direction. In this representation the slope of the lines is proportional to the strain parameter and the ordinate intercept corresponds to the reciprocal value of the crystallite size [8].

Both parameters show a strong dependence on the time on stream under the conditions of the reaction. With increasing time on stream the ordinate intercept increases continuously indicating the disintegration of the HPA to small crystallites of about 10 nm in size.

The decrease in the crystallite size is accompanied by a significant increase in activity (figure 4). The conversion increases from 27.4 to 37.6% whilst the selectivity value remains nearly unchanged 78%.

4. Discussion

Our novel *in situ* XRD study showed that in V-containing HPA catalysts under the conditions of the MA to MAA oxidation reaction lattice defects are formed. With prolonged time on stream the lattice distortions become more and more pronounced and the increase in lattice distortions finally results in the disintegration of the HPA to small crystallites of about 10 nm in size. The observed increase in activity can be related to the increase of the specific surface area due to the formation of smaller crystallites. As far as the lattice distortions are concerned, at present we can only speculate upon the role of the lattice defects on activity, although in

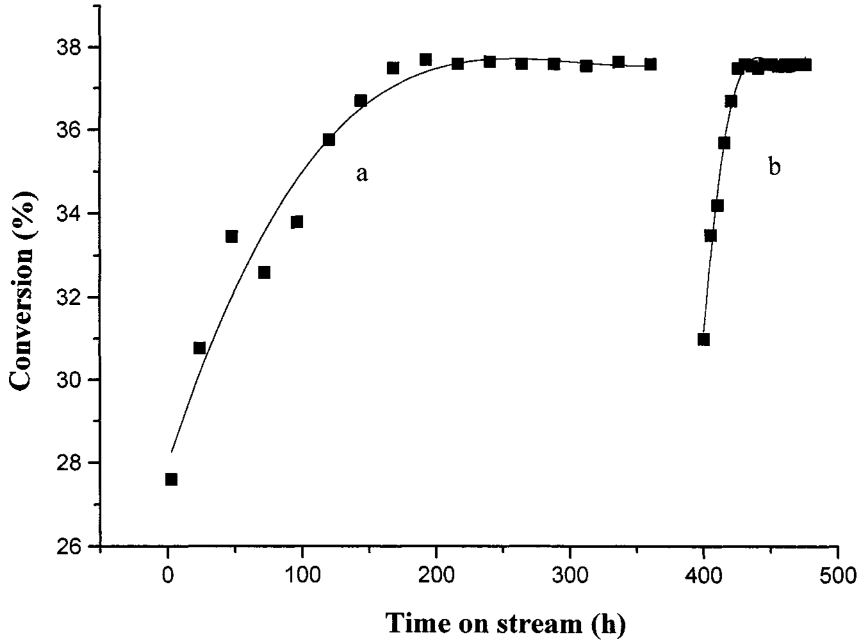

Figure 4. Activity vs. time at 613 K: (a) first run and (b) second run after turning off the MA supply.

catalytic reactions defects always have been suspected as the active sites of the catalytic interaction. It appears likely that the dynamic adsorption–reaction–desorption cycles in the interior of the HPA crystallites initialize the formation of lattice distortions which finally lead to crystal disintegration.

The reported line broadening effect shows some similarities to the formation of a so-called quasiliquid phase by the interaction of pyridine and ethanol with $H_3PW_{12}O_{40}$ heteropolyacid. X-ray diffraction data show that the crystalline structure of $H_3PW_{12}O_{40}$ is lost on exposure to excess of pyridine or ethanol [9–13]. In case of $Cs_xH_{3-x}PW_{12}O_{40}$ the amounts of ethanol held by the solid under analogous reaction conditions were much smaller than that held by $H_3PW_{12}O_{40}$. However, the adsorbed quantities were still much greater than those expected for monolayer adsorption. This suggests that under the conditions of the catalytic reaction MA molecules penetrate into the interior of the crystallites. The amount of the adsorbed MA, however, is not sufficient for the complete dissolution of the HPA under formation of an amorphous quasiliquid phase. Due to the smaller amount of adsorbed MA under the conditions of the catalytic reaction the observed decrease in crystallinity occurs under maintenance of a highly disordered crystalline structure.

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