Article

Study on the Development of High-Performance P-Mo-V Catalyst and the Influence of Aldehyde Impurities on Catalytic Performance in Selective Oxidation of Methacrolein to Methacrylic Acid

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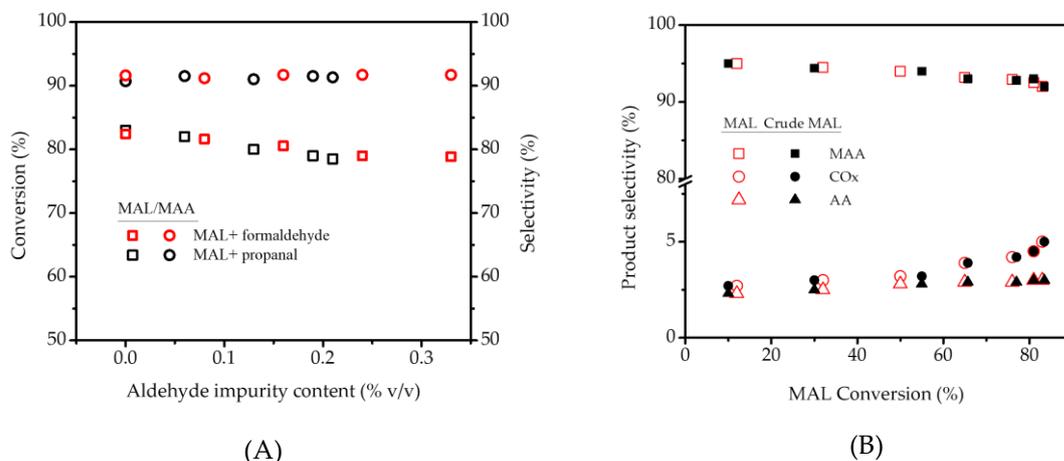
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1. Co-feeding experiments with aldehyde impurities

According to the C_2 process, MAL feedstock contains formaldehyde and propanal impurities. Aldehyde impurities are likely to have detrimental effects on the catalytic performance. Cofeeding experiments with formaldehyde and propanal performed on $K_{0.6}CuCsNH_4PAV$ is of great significance for the industrial application. The catalytic performance was inspected with inlet concentrations of aldehyde impurities ranging from 0 to 5 wt% at 310 °C. The results were shown in Figure S1 (A). The conversion of MAL decreased from 83% to 80% with the increase of aldehyde impurities content. Interestingly, the selectivity of MAA is almost unaffected. The parallel oxidation experiments of pure MAL and crude MAL were carried out. The results were shown in Figure S1 (B). Co-feeding of aldehyde impurities indicated Formaldehyde and propanal had little effect on the path of MAL oxidation. Small molecules are very easy to absorb on the surface of the catalyst, which would decrease the activity of the catalyst. Moreover, formic acid and propionic acid were detected at the reactor outlet. The results showed that the oxidation of formaldehyde and propanal occurred on the catalyst. The decrease of MAL conversion could be attributed to the competitive adsorption of MAL and aldehyde impurities.


(A)

(B)

2. Transient response

In the initial 420 min, the reaction was carried out in pure MAL, and then the feed was changed to crude MAL feedstock. After that, the conversion of MAL was gradually reduced from 83% to about 79%. After the oxidation reaction reached a stable level, the feed switched back to pure MAL at 840 min. At the same time, the conversion of MAL gradually returned to the original level (from 79% to 83%).

3. The changes of the catalyst structure in transient response
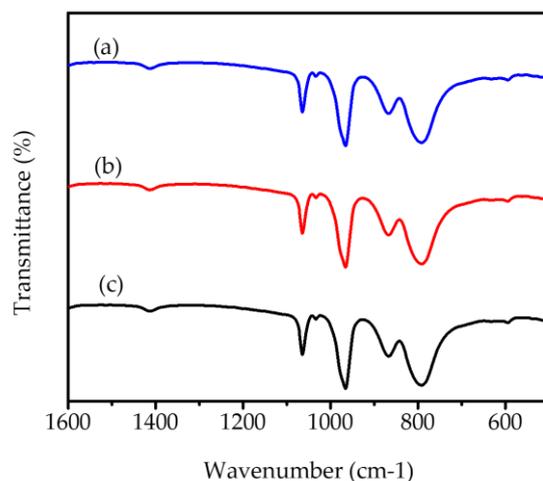
Figure S2. IR spectra recorded with $K_{0.6}CuCsNH_4PVA$ experienced in the transient responses in Figure 11 (A) (a) 0 min, the sample of (b) was obtained for the reaction in the presence of aldehyde impurities and that of (c) in the absence of aldehyde impurities.

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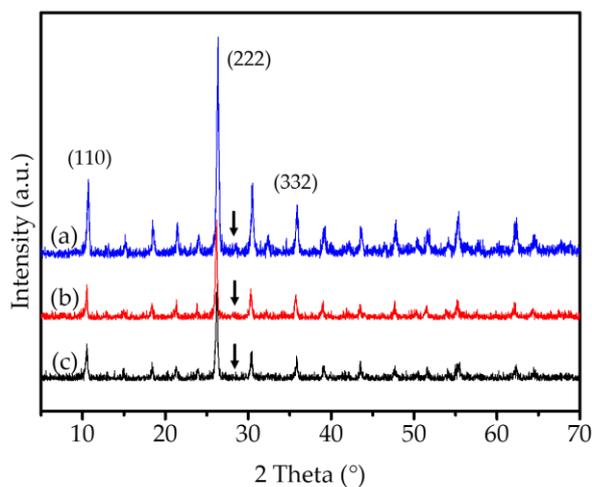
Figure S3. X-ray diffraction spectrogram recorded with $K_{0.6}CuCsNH_4PVA$ experienced in the transient responses in Figure 11 (A) (a) 0 min, the sample of (b) was obtained for the reaction in the presence of aldehyde impurities and that of (c) in the absence of aldehyde impurities.

Table S1. Specific surface area and atomic Ratio of Mo and V in the bulk of $K_{0.6}CuCsNH_4PVA$ before and after the treatments in the presence and absence of aldehyde impurities.

	Surface area $(m^2 \cdot g^{-1})$[a]	Atomic Ratio[b]	
		V/P	Mo/P
0 min	2.46	1.0	11.0
Presence of aldehyde impurities.	2.47	0.9	11.0
Absence of aldehyde impurities.	2.46	1.0	10.9

[a] BET Surface Area.

[b] ICP Determination of element content.