

# Direct Benzyl Alcohol And Benzaldehyde Synthesis from Toluene Over Keggin-Type Polyoxometalates Catalysts: Kinetic and Mechanistic Studies

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## **Catalysts preparation**

The heteropolyacid  $\text{H}_3\text{PMo}_{12}\text{O}_{40}\cdot\text{aq}$  (noted  $\text{HPMo}_{12}$ ) prepared in two steps:

The first is the preparation of the disodium salt  $\text{Na}_2\text{HPMo}_{12}\text{O}_{40}\cdot 16\text{H}_2\text{O}$ , and the second stage consists of isolating the heteropolyacid  $\text{H}_3\text{PMo}_{12}\text{O}_{40}$  by extraction with diethyl-ether ( $\text{Et}_2\text{O}$ ).

Step 1: 290 g (1.2 mol) of  $\text{Na}_2\text{MoO}_4\cdot 2\text{H}_2\text{O}$  (99% purity) was dissolved in 420 ml distilled water. Then 6.8 mL of 85 %  $\text{H}_3\text{PO}_4$  (0.1 mol) and 284 mL of 70 %  $\text{HClO}_4$  (3.3 mol) were added successively. After the mixture was cooled to room temperature, the disodium salt  $\text{Na}_2\text{HPMo}_{12}\text{O}_{40}$  was precipitated and filtered.

Step 2:  $\text{H}_3\text{PMo}_{12}\text{O}_{40}\cdot 14\text{H}_2\text{O}$  was obtained from an aqueous solution of  $\text{Na}_2\text{HPMo}_{12}\text{O}_{40}\cdot 16\text{H}_2\text{O}$  (250 g/200 mL), acidified by 50 mL of 12 M  $\text{HCl}$  (37%) and extracted by 400 mL of  $\text{Et}_2\text{O}$  (99.5% purity). The heavy layer (300 mL), added with half its volume of water, gave yellow crystals after desiccation (200 g).

$\text{H}_4\text{PMo}_{11}\text{VO}_{40}$  (noted  $\text{HPMo}_{11}\text{V}$ ) was prepared from an appropriate mixture solution of 17.8 g of sodium monohydrogenophosphate ( $\text{Na}_2\text{HPO}_4\cdot 2\text{H}_2\text{O}$ ),  $\text{Na}_2\text{MoO}_4\cdot 2\text{H}_2\text{O}$  (99% purity) (246 g),  $\text{Na}_2\text{VO}_4\cdot 2\text{H}_2\text{O}$  (99% purity) (12.2 g) and  $\text{HClO}_4$  (70%) in 400 mL of distilled water. The mixture was then acidified by 40 mL of 37%  $\text{HCl}$  (12M), and the acidic  $\text{H}_4\text{PMo}_{11}\text{VO}_{40}$  was extracted by 400 mL of diethyl-ether.

The heteropolysalt  $(\text{NH}_4)_{2.5}\text{Fe}_{0.08}\text{H}_{0.26}\text{PMo}_{12}\text{O}_{40}$  (noted  $\text{FePMo}_{12}$ ) was prepared an aqueous solution ( $0.08\text{ mol}\cdot\text{l}^{-1}$ ) of  $\text{Fe}(\text{NO}_3)_3$  (0.17 g) was added dropwise to an aqueous solution of  $\text{HPMo}_{12}$  ( $0.06\text{ mol}\cdot\text{l}^{-1}$ ) (10 g) at  $50^\circ\text{C}$ , followed by the addition of an aqueous solution ( $0.08\text{ mol}\cdot\text{l}^{-1}$ ) of  $(\text{NH}_4)_2\text{CO}_3$  (1.28g) under vigorous stirring, resulting in immediate precipitation of  $\text{KFePMo}_{12}$  salt. Stirring continued until complete evaporation of the solvent at room temperature. Powder was collected without washing and ground in the mortar.

The heteropolysalt  $(\text{NH}_4)_4\text{PMo}_{11}(\text{H}_2\text{O})\text{FeO}_{39}$  (noted  $\text{PMo}_{11}\text{Fe}$ ) was obtained from an aqueous solution of 48.75 g of ammonium molybdate,  $\text{H}_3\text{PO}_4$  (1M),  $\text{HNO}_3$  (0.5 M) and  $\text{Fe}(\text{NO}_3)_3$  (1M) at  $0^\circ\text{C}$ , using  $\text{NH}_4\text{NO}_3$  as precipitating agent.

### Catalytic test

Catalyst performances will be expressed as follow:

$$\text{Toluene Conversion (\%)} = \frac{\text{moles of Toluene}_{\text{in}} - \text{moles of Toluene}_{\text{out}}}{\text{moles of Toluene}_{\text{in}}} \times 100$$

$$\text{Product (Pi) Selectivity (\%)} = \frac{\text{moles of Pi}_{\text{out}}}{\text{moles of all products}_{\text{out}}} \times 100$$