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# Preparation of W-modified Fe—Mo catalyst and its applications in the selective oxidization of *p*-xylene to terephthalaldehyde

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## HIGHLIGHTS

- W-modified Fe—Mo catalyst was prepared by sol–gel method.
- Fe—Mo—W catalyst exhibited a higher activity stable.
- Fe—Mo—W exhibite higher oxidation performance than Fe—Mo catalyst.
- Selective oxidation of PX on Fe—Mo—W catalyst is a Mars and van Krevelen type.

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## ABSTRACT

Fe—Mo—W catalysts were prepared by a sol–gel method and used in the catalytic selective oxidation of *p*-xylene (PX) to prepare terephthalaldehyde (TPAL). The results showed that Mo, Fe, and W exist as oxides in the composite, and the Fe—Mo and Fe—Mo—W catalysts were stable between 400 and 600 °C. The Fe—Mo—W catalyst was more easily reduced to a lower valence state, and the lattice oxygen of the Fe—Mo—W catalyst was higher than that of the Fe—Mo catalyst. These phenomena demonstrated a higher oxidation performance than the Fe—Mo catalyst. The Fe—Mo—W catalyst calcined at 550 °C was reacted at 500 °C for 3 h with a catalyst dosage of 0.5 g, an air flow rate of 1000 mL $min^{-1}$, and a PX liquid hourly space velocity of 1.2 mL $g_{cat}^{-1}$ $h^{-1}$, the conversion of PX, the selectivity and the yield of TPAL was 99.5%, 74.0%, and 73.6%, respectively, and the Fe—Mo—W catalyst was stable after 50 h.

## 1. Introduction

Terephthalaldehyde (TPAL) is an aromatic compound that has two aldehyde groups in para-positions, providing a unique reactivity. This unique reactivity makes TPAL a promising material in the production of pharmaceutical products, agrochemicals, and dyestuffs. It also plays a key role as an intermediate in organic synthesis and high polymer synthesis [1,2].

The conventional TPAL production process has two parts. The first part uses *p*-xylene (PX) and chlorine gas to produce chlorinated xylenes. The second part uses hydrolysis to produce TPAL as well as HCl as a by-product. As a result, the entire process has a serious problem of toxicity that is a significant threat to production safety and to the environment. Thus, the development of a gas-phase catalytic process over a highly catalytic activity process for TPAL syntheses becomes ever more important from the commercial application and the environmental protection aspects, especially because PX is inexpensive and easy to obtain as a raw material.

At present, the newly developed LG Chem technology uses PX and air in a one-step oxidation process, which vastly simplifies the process and makes the process more environmentally friendly. Finally, the LG method achieves a reduction in cost of over 30% compared to the conventional production process at high volumes of production [3,4]. The reaction in this one-step oxidation process is a kind of selective oxidation reaction, and selective oxidation reaction is an importance reaction the chemical industrial. Most of the selective oxidation catalyst used in the industry from a variety of metal or metal oxides, these oxides may be a solid solution or a composite oxide, such as TS-1(Titanium silicalite-1)-Coated Structured Packing Materials for Styrene Oxidation Reaction [5,6]; Au/$Al_2O_3$, Au/C [7], Pd/C and Pt/C [8], Pd—Te/$SiO_2$ and Pd—Te/$Al_2O_3$ [9] and Au supported on carbonaceous material-based catalysts [10,11] for selective oxidation of glucose, Pd/CuO—$Ce_{0.5}Mn_{0.5}O_2$ for selective oxidation of methyl glucoside

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[12]; and carbon nanotubes for Selective liquid phase oxidation of benzyl alcohol [13]. The Fe—Mo catalyst is necessary for the LG Chem's newly developed production process, which is the key component to providing this new technology with great price competitiveness and environmentally friendly TPAL production. Thus, the Fe—Mo catalyst is considered to be one of the better performance catalysts [14,15]. However, the method of preparing the Fe—Mo catalyst is complex and produces heavy environmental pollution, and the activity of the catalyst is somewhat low [16].

Based on previous studies of the Fe—Mo [17] and Ni-modified Fe—Mo catalysts [18], this work focuses on the preparation of the W-modified Fe—Mo catalyst through a sol–gel method and its application in the reaction of the selective oxidation of PX to TPAL to improve the performance of the Fe—Mo catalyst.

## 2. Experimental

### 2.1. Preparation of catalysts

$(NH_4)MoO_4$, $Fe(NO_3)_3$, $(NH_4)_{10}W_{12}O_{41}$, $Cr(NO_3)_3$, $Cu(NO_3)_2$, and $Co(NO_3)_2$ were weighted in the molar ratio of $n(Mo):n(Fe) = 3:1$ and $n(M$, where M was W, Co, Cr, Cu$) = 5\%\cdot n(Mo)$, and dissolved by deionized water. When the $(NH_4)MoO_4$ and $Fe(NO_3)_3$ solution and one of the other solutions were mixed, a precipitate resulted. After reacting for 10 min, a known amount of citric acid was added to the mixed solution while stirring until the precipitate dissolved, and the solution was adjusted to pH = 2–3 by adding 0.5 mol $L^{-1}$ $NH_4OH$ solution while stirring. The solution was placed into a thermostat water bath and was heated and stirred to promote the metal ion hydrolysis. When most of the water in the solution evaporated at 80 °C, the original solution polymerized into sol, and the sol was standed for 12 h to obtain an elastic gel. The gel was dried in air at 120 °C for 12 h to obtain the dried gel or precursor. The dried gel was ground and calcined at 400–600 °C for 4 h to obtain the Fe—Mo—M composite oxide.

### 2.2. Catalytic selective oxidation of PX to TPAL

Gas phase catalytic selective oxidation of PX to TPAL on Fe—Mo and Fe—Mo—M (where M was W, Co, Cr, Cu) catalysts was conducted in a WFS-3010 fixed-bed reactor (Tianjing Xianquan Instrument Co., Ltd.). A 0.5 g amount of catalyst was added to the reactor. The PX was pumped into the vaporizer at 0.01 mL $min^{-1}$ and vaporized at 300 °C, and the air was fed into the reactor using another line. After 3 h, the product was collected at the outlet using a test tube cooled by ice water.

The product was analyzed by an Agilent 4890D gas chromatograph, which was equipped with a flame ionization detector (FID) and a HP-5 capillary column (30 m × 0.32 mm). The initial temperature of the column was 95 °C, which was held for 3 min. The temperature was then raised to 140 °C at a rate of 5 °C $min^{-1}$, and held for 1 min. The injector and detector temperatures were 280 °C and 230 °C, respectively. An internal standard method was used for quantitative analysis with 1,2-dichlorobenzene as an internal standard. The conversion of PX, the selectivity and the yield of the TPAL were adopted as the evaluation indices of catalyst activity.

### 2.3. Characterization of catalysts

Thermal analysis was conducted on a SDT Q600 Simultaneous TGA/DSC (TA Instruments) with an initial temperature of 50 °C and a heating rate of 20 °C $min^{-1}$. Fourier transform infrared spectrum analysis (FT-IR) was performed using a Thermo Nicolet Nexus 470 Fourier transform infrared spectrometer, and KBr was used as background. X-ray diffraction (XRD) was conducted on a XD-3 X-ray diffractometer (Beijing Purkinje General Instrument Co., Ltd.) with a Cu Kα radiation at 36 kV, 20 mA using a graphite monochromator. The $H_2$-TPR ($H_2$ temperature programmed reduction) experiment was conducted on a TP-5000 multi-function adsorption instrument (Tianjin Xianquan Industry and Trade Development Co.) equipped with a (thermal conductivity detector) TCD detector, and $H_2$—$N_2$ (8% $H_2$) mixing gas was used in the $H_2$-TPR process. The oxidation state and surface composition were analyzed using an X-ray photoelectron spectrometer (XPS) (Kratos Ultra Axis DLD), equipped with an Al Kα radiation source. The energy resolution of the spectrometer was 0.48 eV. The peak positions were corrected for sample charging by setting the C 1s binding energy at 284.8 eV. The XPS analysis was conducted at 150 W with a pass energy of 40 eV.

## 3. Results and discussion

### 3.1. Effects of the modified metal on the selective oxidation

Fe—Mo, Fe—Mo—Co, Fe—Mo—Cr, Fe—Mo—Cu, and Fe—Mo—W catalysts were synthesized by the sol–gel method, and these catalysts were applied to the selective oxidation of PX to TPAL using the above reaction conditions. The effects of the Co-, Cr-, Cu-, and W-modified catalysts on the catalytic activities of Fe—Mo were investigated, and the results are shown in Table 1.

For comparison, an Fe—Mo catalyst was prepared as described in previous work [8,9]. As shown in Table 1, the addition of Co, Cr, Cu, or W to the Fe—Mo catalyst greatly impacted the activity of the Fe—Mo catalyst. The conversion of PX decreased from 99.5% to 95.2%, and the selectivity of TPAL decreased from 59.6% to 34.5% when the Fe—Mo catalyst modified by Cr was used. When using Co- and Cu-modified Fe—Mo catalysts, the conversion of PX remained unchanged, but the selectivity and yield of the TPAL greatly decreased; the yield of the TPAL decreased from 59.2% to 48.0% and 34.6%, respectively. On the contrary, after modification using W, the conversion of PX remained unchanged, and the selectivity of TPAL increased from 59.6% to 72.0%, which was an increase of 12.4%. After modification using W, the Fe—Mo catalyst exhibited excellent catalytic activity; therefore, the Fe—Mo—W catalyst was further studied in this work.

### 3.2. Effects of calcination temperatures on the Fe—Mo—W catalyst

#### 3.2.1. Effects of calcination temperatures on the Fe—Mo—W selective oxidation of PX to TPAL

Fe—Mo—W catalysts were obtained by calcining the precursor, which was prepared by the sol–gel method, at 400, 450, 500, 550, and 600 °C. These catalysts were then used in the selective oxidation of PX to TPAL. The results are shown in Fig. 1.

Fig. 1 shows that the conversion of PX decreased from 99.3% to 86.7% as the calcination temperature increased from 400 to 550 °C. When the calcination temperature increased to 600 °C, the conversion of PX increased to 91.3%. As the calcination temperature continued to increased, the selectivity and yield of the TPAL increased at first, and then declined. As the calcination

**Table 1**
The effects of metals on the Fe—Mo—W selective oxidation of PX to TPAL.

| Catalysts | Conversion of PX/% | Selectivity of TPAL/% | Yield of TPAL/% |
|---|---|---|---|
| Fe—Mo | 99.5 | 59.6 | 59.2 |
| Fe—Mo—Co | 99.2 | 48.4 | 48.0 |
| Fe—Mo—Cr | 95.2 | 34.5 | 32.8 |
| Fe—Mo—Cu | 99.4 | 34.8 | 34.6 |
| Fe—Mo—W | 99.0 | 72.0 | 71.3 |