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## Article

# Synthesis of anisole by vapor phase methylation of phenol with methanol over catalysts supported on activated alumina



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## ABSTRACT

The synthesis of anisole by vapor phase methylation of phenol with methanol over activated alumina (AA) supported catalysts was investigated in a fixed bed reactor.  $\text{KH}_2\text{PO}_4/\text{AA}$  gave the best performance among the eight tested catalysts. The catalyst was prepared by loading  $\text{KH}_2\text{PO}_4$  on AA and then calcining at the optimized temperature of 700 °C for 8 h. In the vapor phase reaction, the level of anisole yield (LAY) has a maximum at 400–450 °C when the temperature varied from 300 to 500 °C, which decreased slightly with increasing WHSV and increased distinctly with increasing mole fraction of methanol. On comparing O-methylation and C-methylation of phenol, a low temperature, high WHSV (short residence time), and a low methanol concentration over the  $\text{KH}_2\text{PO}_4/\text{AA}$  catalyst with higher K contents were found to increase anisole selectivity by O-methylation of phenol. The reaction routes to the major products and the catalytic mechanism were suggested, and a ‘K-acid’ bifunctional process may be a critical factor to the formation of anisole.

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## 1. Introduction

Anisole is an important industrial chemical and intermediate product used for perfumes, flavoring agents, and organic synthesis [1,2]. Anisole is usually synthesized by a liquid phase process in an alkaline environment, such as the reaction between sodium phenolate and dimethyl sulfate, the reaction between bromobenzene and methanol, and the reaction between sodium phenolate and chloromethane [2]. However, these processes have been severely restricted in recent years because the alkali used are harmful to the environment and the extremely toxic raw materials like dimethyl sulfate and bromobenzene are dangerous to human health. So, a green process for anisole synthesis is needed, and a vapor phase catalytic reaction was proposed.

The synthesis of anisole by a vapor phase reaction between

phenol and dimethyl carbonate (DMC) has been investigated [2–5]. DMC, a green chemical material that is used for methylation, can be synthesized from the oxidative carbonylation of methanol [6], but the synthesis of DMC increases the complexity and cost of the anisole synthetic process. So, another method that uses methanol for direct methylation to replace DMC was studied [1,7–9]. However, in the reaction between phenol and methanol, the product composition is more complicated, and the product from O-methylation (methylation on the oxygen atom of the phenolic hydroxyl group) of phenol is more difficult to obtain compared to that from C-methylation (methylation on the carbon atom of the aromatic ring) [10–16]. Kirichenko et al. [1] obtained a high anisole selectivity of 93.9% with a phenol conversion rate of 81% with the catalysis of NaX at 320 °C. Sarala et al. [16] found that the existence of cesium in samarium phosphate enhanced anisole selectivity by suppressing

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C-alkylated side products. A high anisole yield of 83% was obtained at 350 °C. Generally, compared to the DMC approach, the synthesis of anisole from the methylation of phenol with methanol is less satisfactory, and the mechanism is rather vague. Therefore, further study on the vapor phase catalytic reaction for anisole preparation is of great significance.

In this paper, the synthesis of anisole by vapor phase methylation of phenol with methanol over a  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> supported catalyst was studied. The vapor phase reaction conditions of temperature, space velocity, feed ratio of phenol to methanol, and catalyst synthesis conditions including the type and loading amount of the metal salts, and the calcination temperature were examined for level of anisole yield optimization. A catalytic mechanism was deduced.

## 2. Experimental

### 2.1. Catalyst preparation

The catalyst was prepared by the impregnation method in which a metal salt was loaded on the support of activated alumina (AA,  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>) granules (diameter around 2 mm).  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> granules was washed with distilled water and dried at 120 °C for 12 h first, and then cooled to room temperature for use. A salt solution was slowly added to a known amount of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> granules according to the isopycnic impregnation rules. The impregnated  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> granules were then placed in open air at room temperature for 24 h, and finally calcined in a muffle furnace for 8 h (the calcining temperature was 700 °C unless otherwise specified).

### 2.2. Catalyst characterization

The metal content on the  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> support was measured by inductively coupled plasma-atomic emission spectrometry (ICP-AES, IRIS Intrepid II XSP). The chemical phase of the catalyst was analyzed by X-ray diffraction (XRD) with a D/teX-Ultra detector and Cu K $\alpha$  radiation.

### 2.3. Apparatus and procedure for the vapor phase reaction

The schematic of the experimental system is shown in Fig. 1. The liquid reactant mixture of phenol and methanol and a stream of nitrogen as carrier gas were introduced into a fixed bed reactor by a peristaltic pump and mass flowmeter, respectively. The fixed bed reactor was a quartz tube (length of 600 mm and inner diameter of 27 mm) placed coaxially in an electric furnace. About 20 g catalyst granules were loaded inside the reactor. When the set temperature was reached, the carrier gas of nitrogen (100 mL/min) was introduced into the reactor to purge out air. Then the liquid reactants were fed into the reactor. The products were taken out of the reactor and sent to a condensing unit, which comprised a Graham condenser and two bottles located in an ice-water bath. The product was condensed to liquid and collected in the bottles. In each run, the time on stream was 3 h.

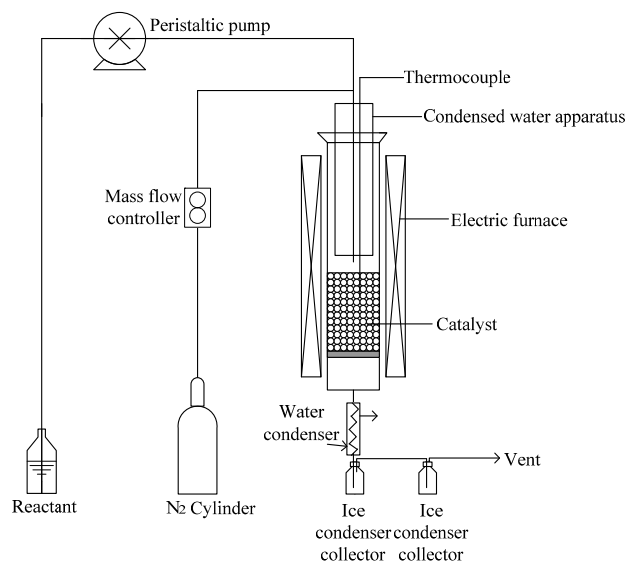


Fig. 1. Schematic of the lab scale apparatus for vapor phase synthesis of anisole.

### 2.4. Product analysis

To get the conversion of phenol and selectivity for anisole, the total liquid in the two bottles were weighed after the experiment. The liquid composition was analyzed by GC/MS (gas chromatography combined with mass spectrometry). The absolute amount of phenol remaining in the liquid product was determined by the internal standard method. The compound of isoamyl acetate (IAA) was used as the internal standard. The conversion of phenol was defined as the ratio of the mass of converted phenol to the original mass of phenol fed into the reaction system. However, the amounts of other components were not quantified by the internal standard because the correlation was not as good as that for phenol. Therefore, the selectivity of a liquid product was denoted by its area percentage among the major products, and accordingly the arithmetic product by multiplication between the phenol conversion rate (wt%) and the anisole selectivity (area%) was used to represent the level of anisole yield (LAY). The analytical conditions by GC/MS (Varian 3800GC/300MS with FFAP column of 25 mm  $\times$  0.25 mm  $\times$  0.2  $\mu$ m) were as follows: oven temperature started from 40 °C, hold for 3 min, then increased by 4 °C/min to 100 °C, hold for 3 min, and finally increased to 240 °C by 6 °C/min and hold for 10 min; the injector temperature was 240 °C and the ion source temperature was 250 °C. The error analysis of the experimental system was conducted by three repeated experiments. The standard deviation of phenol conversion rate was 1.88%. The standard deviation of anisole selectivity was 0.42%.

## 3. Results and discussion

### 3.1. Catalyst preparation conditions

#### 3.1.1. Influence of the type of metal salt on catalyst performance

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