



# Etherification of n-butanol to di-n-butyl ether over $H_3PMo_{12-x}W_xO_{40}$ ( $x = 0, 3, 6, 9, 12$ ) Keggin and $H_6P_2Mo_{18-x}W_xO_{62}$ ( $x = 0, 3, 9, 15, 18$ ) Wells–Dawson heteropolyacid catalysts

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## ABSTRACT

Etherification of n-butanol to di-n-butyl ether was carried out over  $H_3PMo_{12-x}W_xO_{40}$  ( $x = 0, 3, 6, 9, 12$ ) Keggin and  $H_6P_2Mo_{18-x}W_xO_{62}$  ( $x = 0, 3, 9, 15, 18$ ) Wells–Dawson heteropolyacid (HPA) catalysts. Acid strength of  $H_3PMo_{12-x}W_xO_{40}$  Keggin and  $H_6P_2Mo_{18-x}W_xO_{62}$  Wells–Dawson HPA catalysts was determined by  $NH_3$ -TPD (temperature-programmed desorption) measurements. The correlations between desorption peak temperature (acid strength) of the HPA catalysts and catalytic activity revealed that conversion of n-butanol and yield for di-n-butyl ether increased with increasing acid strength of the catalysts, regardless of the identity of HPA catalysts (without HPA structural sensitivity).

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## 1. Introduction

Addition of suitable fuel additive to diesel fuel is the most effective way to reduce diesel exhausts such as CO,  $NO_x$ , and particulates [1,2]. It has been reported that linear ethers (total number of atoms  $\geq 9$ ) can be used as an effective diesel additive, resulting in reduction of CO,  $NO_x$ , and particulates [2,3]. Among various linear ethers, di-n-butyl ether, which can be directly synthesized from biobutanol, has attracted recent attention as an octane booster and cetane number enhancer for diesel fuel [4]. However, many previous researches have been focused on dimethyl ether and diethyl ether production [5–8], and much progress has not been made on linear ethers (total number of atoms  $\geq 9$ ) production.

Conventional catalytic process for the production of linear ether is based on dehydration of linear alcohol over sulfuric acid [9]. Concentrated sulfuric acid shows quite high catalytic activity for linear ether production. However, considerable olefins and heavy products such as alkyl sulfates are generally formed as by-products. Its corrosive and homogeneous nature also causes corrosion of reaction system and disposable problem. In order to overcome these problems, linear ether production over solid acid catalysts such as zeolite [10], alumina [11], and silica-alumina [12] has been attempted. However, conversion of linear alcohol and selectivity for linear ether were too low over these catalysts.

Heteropolyacids (HPAs) are early transition metal–oxygen anion clusters that have been employed as acid catalysts for both homogeneous and heterogeneous reactions [13–15]. Excellent acid property and thermal stability of HPAs make them well suitable for acid catalysis that may require harsh environments. Among various HPA structural classes, Keggin and Wells–Dawson HPAs have attracted significant interest as promising catalysts for acid-catalyzed reactions, including hydration of propylene [16], esterification of *iso*-butene and methanol [17], and alkylation of *iso*-butane [18]. One of the great advantages of HPAs is that their catalytic properties can be easily tuned by changing the counter-cation, heteroatom, or framework polyatom.

In this work,  $H_3PMo_{12-x}W_xO_{40}$  ( $x = 0, 3, 6, 9, 12$ ) Keggin and  $H_6P_2Mo_{18-x}W_xO_{62}$  ( $x = 0, 3, 9, 15, 18$ ) Wells–Dawson HPAs were employed as catalysts for etherification of n-butanol to di-n-butyl ether. Effect of reaction temperature on the catalytic performance was investigated. Acid strength of  $H_3PMo_{12-x}W_xO_{40}$  Keggin and  $H_6P_2Mo_{18-x}W_xO_{62}$  Wells–Dawson HPA catalysts was measured by  $NH_3$ -TPD experiments. The measured acid strength of  $H_3PMo_{12-x}W_xO_{40}$  Keggin and  $H_6P_2Mo_{18-x}W_xO_{62}$  Wells–Dawson HPA catalysts was then correlated with conversion of n-butanol and yield for di-n-butyl ether.

## 2. Experimental

### 2.1. Catalyst

$H_3PMo_{12-x}W_xO_{40}$  ( $x = 0, 3, 6, 9, 12$ ) Keggin and  $H_6P_2Mo_{18-x}W_xO_{62}$  ( $x = 0, 3, 9, 15, 18$ ) Wells–Dawson HPA catalysts were prepared according

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to the method reported in a literature [19,20] using  $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$  (Junsei Chem.),  $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$  (Junsei Chem.),  $\text{NaH}_2\text{PO}_4$  (Samchun Chem.), diethyl ether (Samchun Chem.), nitric acid (Samchun Chem.), and hydrochloric acid (Sigma-Aldrich). The ratios of  $x$  were controlled during the synthesis of HPA catalysts not after the synthesis of HPA catalysts. Successful formation of  $\text{H}_3\text{PMo}_{12-x}\text{W}_x\text{O}_{40}$  Keggin and  $\text{H}_6\text{P}_2\text{Mo}_{18-x}\text{W}_x\text{O}_{62}$  Wells–Dawson HPA catalysts was confirmed by FT-IR (Nicolet, Nicolet 6700) and ICP-AES (Shimadzu, ICPS-1000IV) analyses, as reported in our previous work [21]. In this work,  $\text{H}_3\text{PMo}_{12-x}\text{W}_x\text{O}_{40}$  Keggin HPA catalysts with  $x=0, 3, 6, 9,$  and  $12$  were denoted as  $\text{PMo}_{12}, \text{PMo}_9\text{W}_3, \text{PMo}_6\text{W}_6, \text{PMo}_3\text{W}_9,$  and  $\text{PW}_{12}$ .  $\text{H}_6\text{P}_2\text{Mo}_{18-x}\text{W}_x\text{O}_{62}$  Wells–Dawson HPA catalysts with  $x=0, 3, 9, 15,$  and  $18$  were denoted as  $\text{P}_2\text{Mo}_{18}, \text{P}_2\text{Mo}_{15}\text{W}_3, \text{P}_2\text{Mo}_9\text{W}_9, \text{P}_2\text{Mo}_3\text{W}_{15},$  and  $\text{P}_2\text{W}_{18}$ .

## 2.2. $\text{NH}_3$ -TPD measurement

Acid strength of  $\text{H}_3\text{PMo}_{12-x}\text{W}_x\text{O}_{40}$  ( $x=0, 3, 6, 9, 12$ ) Keggin and  $\text{H}_6\text{P}_2\text{Mo}_{18-x}\text{W}_x\text{O}_{62}$  ( $x=0, 3, 9, 15, 18$ ) Wells–Dawson HPA catalysts was determined by  $\text{NH}_3$ -TPD (temperature-programmed desorption) measurements. Each HPA catalyst (50 mg) was charged into a tubular quartz reactor of the conventional TPD apparatus. The HPA catalyst was pretreated at  $150^\circ\text{C}$  for 1 h under flow of He (20 ml/min) to remove any physisorbed molecules such as water. Ammonia (20 ml/min) was then pulsed into the reactor every minute at room temperature under a flow of He (5 ml/min), until the acid sites were saturated with ammonia. The physisorbed ammonia was removed by evacuating the catalyst sample at  $100^\circ\text{C}$  for 1 h. The furnace temperature was increased from room temperature to  $700^\circ\text{C}$  at a heating rate of  $5^\circ\text{C}/\text{min}$  under a flow of He (10 ml/min). The desorbed ammonia was detected using a GC-MSD (Agilent, MSD-6890N GC). Furthermore, TGA-DTA (TA instrument, Q600) analyses were carried out to confirm the thermal stability of the HPAs.

## 2.3. Etherification of n-butanol

Etherification of n-butanol to di-n-butyl ether was carried out over  $\text{H}_3\text{PMo}_{12-x}\text{W}_x\text{O}_{40}$  ( $x=0, 3, 6, 9, 12$ ) Keggin and  $\text{H}_6\text{P}_2\text{Mo}_{18-x}\text{W}_x\text{O}_{62}$  ( $x=0, 3, 9, 15, 18$ ) Wells–Dawson HPA catalysts in a stainless steel autoclave reactor (200 ml). 1 g of each HPA catalyst and a mixture of n-butanol (80 ml) and toluene (20 ml, solvent) were charged into the reactor at room temperature. The reactor was purged with nitrogen several times in order to remove oxygen. The reactor was then heated to reaction temperature. The reaction was carried out for 3 h at nitrogen pressure of 30 bar in order to prevent vaporization of reaction mixture. After 3 h-reaction, reaction products were sampled and analyzed using a gas chromatograph (HP 5890, FID) equipped with a capillary column (Supelco, VO COL,  $60\text{ m} \times 1.5\ \mu\text{m} \times 0.25\ \text{mm}$ ). Conversion of n-butanol and selectivities for di-n-butyl ether and butenes were calculated according to the following equations on the basis of carbon balance. Yield for di-n-butyl ether was calculated by multiplying conversion of n-butanol and selectivity for di-n-butyl ether. Yield for butenes was calculated by multiplying conversion of n-butanol and selectivity for butenes.

$$\text{Conversion of n-butanol (\%)} = \frac{\text{mole of n-butanol reacted}}{\text{mole of n-butanol in the feed}} \times 100 \quad (1)$$

$$\begin{aligned} \text{Selectivity for di-n-butyl ether (\%)} \\ = \frac{2 \times \text{mole of di-n-butyl ether formed}}{\text{mole of n-butanol reacted}} \times 100 \end{aligned} \quad (2)$$

$$\text{Selectivity for butenes (\%)} = \frac{\text{mole of butenes formed}}{\text{mole of n-butanol reacted}} \times 100 \quad (3)$$

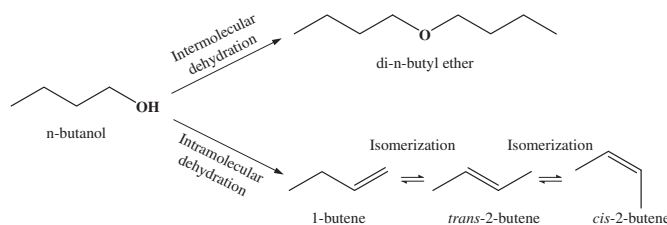


Fig. 1. Scheme for dehydration of n-butanol.

## 3. Results and discussion

### 3.1. Effect of reaction temperature on the catalytic performance

Fig. 1 shows the scheme for dehydration of n-butanol. It is known that dehydration of linear alcohol follows parallel reaction paths [22]. Dehydration of n-butanol over acid catalysts mainly produces di-n-butyl ether and butenes (1-butene, *cis*-2-butene, and *trans*-2-butene). Intermolecular dehydration (etherification) of n-butanol yields di-n-butyl ether. Intramolecular dehydration of n-butanol gives 1-butene, which can be isomerized to *cis*- and *trans*-2-butenes. In a previous work on the dehydration of linear ethers [1], it has been reported that products such as olefins, water, and alcohols further react to form other ethers or alcohols. In this work, however, di-n-butyl ether, butenes (1-butene, *cis*-2-butene, and *trans*-2-butene), and negligible amount of 1-butanol were only observed.

Fig. 2 shows the catalytic performance of  $\text{H}_3\text{PW}_{12}\text{O}_{40}$  catalyst in the etherification of n-butanol with respect to reaction temperature. Conversion of n-butanol increased with increasing reaction temperature. Selectivity for di-n-butyl ether was very high while that for butenes was very low at reaction temperature lower than  $200^\circ\text{C}$ . At reaction temperature higher than  $200^\circ\text{C}$ , however, selectivity for di-n-butyl ether drastically decreased while that for butenes suddenly increased with increasing reaction temperature. According to the literature [23], free energy values for each reaction path clearly showed that intramolecular dehydration (olefin formation) was thermodynamically favorable at high temperature. Moreover, free energy values for intramolecular dehydration (olefin formation) decreased more rapidly than free energy values for intermolecular dehydration (etherification) with increasing reaction temperature. It represented that intramolecular dehydration (olefin formation) was more favorable with increasing reaction temperature. Therefore, selection of appropriate reaction temperature is of great importance for efficient production of di-n-butyl ether via etherification of n-butanol. Based on the result in Fig. 2,  $200^\circ\text{C}$  at which maximum yield for di-n-butyl ether was observed was chosen as the reaction temperature for activity test of other HPA catalysts.

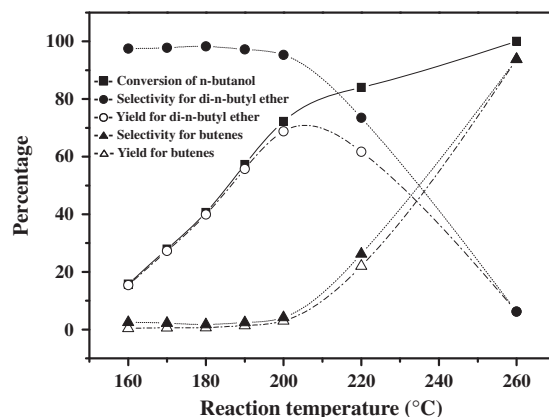


Fig. 2. Catalytic performance of  $\text{H}_3\text{PW}_{12}\text{O}_{40}$  catalyst in the etherification of n-butanol with respect to reaction temperature.

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