

Synthesis of 2-butoxy ethanol with narrow-range distribution catalyzed by supported heteropolyacids

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Abstract

A supported heteropolyacid (HPA), $\text{H}_3\text{PMo}_{12}\text{O}_{40}/\text{SiO}_2$, calcined in vacuum at 150°C , has been shown to be an efficient solid acid catalyst for the synthesis of 2-butoxy ethanol with high selectivity. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

2-Butoxy ethanol (BE) is a valuable fine chemical material. With its unique physical properties and chemical characteristics, BE can be developed into a superior solvent. In general, BE is synthesized from the ethoxylation of *n*-butanol with ethylene oxide (EO) according to a proper molar ratio in the presence of KOH catalyst [1,2]. It has been found that the product distribution follows the Weibull law [3]. Usually the selectivity for BE is very low. Acid catalysts, such as BF_3 , heteropoly acid and solid acid, can also be used for this purpose. They appear to exhibit good catalytic activity, but they are inevitable to produce undesirable 1,4-dioxane and other by-products [4,5]. The uncatalyzed reaction of ethoxylation is unacceptably

slow even under a fairly high reaction pressure (e.g., 2.0–2.5 MPa) [6].

Supported HPA catalyst is important for ethoxylation because bulk HPA have a low specific surface area ($1\text{--}5\text{ m}^2/\text{g}$) [7–10]. The acidity and catalytic activity of supported HPA depend on the type of the carrier, the HPA loading, the pretreatment conditions, etc. Acidic or neutral substances such as SiO_2 [11,12], active carbon [13,14], acidic ion-exchange resin [15], etc., are suitable supports, and the most often used being SiO_2 . Basic solids like MgO tend to decompose HPA [8,9,16]. We have recently reported that heteropoly anions play an important role in the efficient catalysis of HPA for homogeneous liquid-phase reactions such as ethanol ethoxylation [17,18]. HPA is usually employed in the liquid phase as soluble catalyst, as well as in the vapor phase as supported catalysts. Since HPA is extraordinarily soluble in water and very soluble in several organic solvents as well, it is therefore of significance

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from the practical viewpoint to develop those supported HPA catalysts with no leakage of HPA in the liquid phase or in the vapor phase [19].

In recent years, several new catalysts for ethoxylation have been proposed, and nearly 100 patents have been issued on the subject. They are expected to allow the polyoxyethylene chain distribution to be narrowed without formation of excessive amounts of polyglycols and other undesirable molecules. Some of the new catalytic systems proposed for alcohol ethoxylation have been investigated. Such a catalyst was also proposed by some authors [20–23].

The aim of this work is to study the synthesis of 2-butoxy ethanol with narrow-range distribution catalyzed by supported heteropolyacids and to discuss the influences of various factors on the distribution.

2. Experimental

2.1. Materials

The following substances were used for ethoxylation: (1) *n*-butanol, purity 99.5%; ethylene oxide (EO, Liaohua petrochemical works, Liaoning, China); (2) $H_3PW_{12}O_{40} \cdot xH_2O$ (PW); $H_4SiW_{12}O_{40} \cdot xH_2O$ (SiW); $H_3PMo_{12}O_{40} \cdot xH_2O$ (PMo); $H_4SiMo_{12}O_{40} \cdot xH_2O$ (SiMo); $H_4GeMo_{12}O_{40} \cdot xH_2O$ (GeMo); and sodium hydroxide. Some other catalytic systems were also used.

2.2. Synthesis of ethoxylates

Ethoxylation was performed in a 1-l stainless-steel jacketed reactor, equipped with a driven stirrer and cooling coil. In each synthesis, the reactor was charged with *n*-butanol mixture (150 g and a weighed amount of catalyst 0.2% NaOH with respect to the *n*-butanol substrate). Then the reactor was closed, vented with nitrogen, and heated to the reaction temperature (50–100°C and 130°C for HPA and

NaOH, respectively). After preheating, ethylene oxide was admitted to the reactor from the bottle, which was pressurized with nitrogen at 0.6 MPa. Ethylene oxide pressure in the reactor was kept constant by opening and closing a micrometric valve. Samples were withdrawn at intervals and analyzed by gas chromatography.

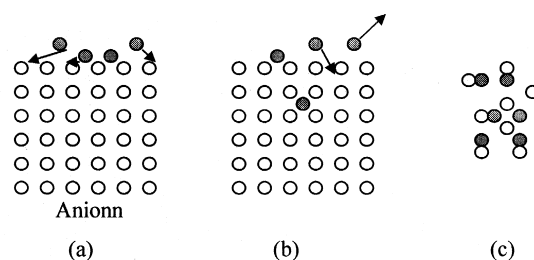
2.3. Gas chromatography

Homologue distributions of ethoxylates were determined in a chromatograph (HP-5890-2) with a flame-ionization detector. Separation was carried out in a cross-linked methyl silicone column of 25 m \times 0.32 mm \times 0.52 μ m film thickness. Nitrogen was used as the carrier gas. Temperatures of the detector and injector were 280°C and 260°C, respectively. Analyses were started with a column temperature of 140°C, which was programmed after 1 min at a rate of 15°C/min up to 280°C.

3. Results and discussion

3.1. Supported HPA

Supported HPA form ionic crystals composed of heteropolyanions, counterions (H^+ ,



a — surface reaction; b c — stereospecific reaction

● : Supported HPA

○ : *n*-butanol molecules

Scheme 1.

Table 1
Composition of *n*-butanol ethoxylates obtained with various catalysts (*n*-butanol/EO = 5/1, molar ratio)

Catalytic system	<i>n</i> -butanol %	Product distribution (%)				By products (%)	C ₄ H ₉ OH (%) conversion ^a	Selectivity (%) ^b		
		EO	1	2	3			1	2	3
NaOH	80.21	0	14.75	3.48	0.56	0.55	19.29	76.46	18.04	2.9
BF ₃	81.65	0.77	15.62	1.32	0	0.60	17.85	87.51	7.39	0
PW	82.79	0	14.75	1.22	0	0.70	16.71	88.27	7.30	0
PMo	79.46	0	17.37	2.43	0	0.20	20.04	86.67	12.13	0
SiW	77.91	0	17.59	1.92	0	0.50	21.58	81.51	8.90	0
PMo/SiO ₂	76.66	0	20.76	1.00	0	0.12	21.84	95.06	4.66	0

^aConversion = C₄H₉OH (initial, %) – C₄H₉OH (product, %).

^bSelectivity = 2-butoxy ethanol (product distribution, %)/conversion, %.

H₃O⁺, H₅O₂⁺, etc.) and hydration water. The crystal structure of HPA depends on the amount of hydration water. This water can be easily removed on heating, whereby the acid strength is increased due to the dehydration of protons. This is a reversible process accompanied by the changing of the volume of the crystal cell. Unlike the rigid network structure of zeolites, in HPA crystals the Keggin anions are quite mobile. Not only water but also a variety of polar *n*-butanol molecules can enter and leave the HPA crystal (Scheme 1).

3.1.1. HPA on silica

SiO₂ is relatively inert towards HPA, at least above a certain loading level, although some chemical interaction takes place between HPA and SiO₂. The thermal stability of HPA on SiO₂ seems to be comparable to or slightly lower than that of the parent HPA. On the other hand,

a thermally decomposed Keggin structure on the silica surface may be reconstructed on exposure to water vapor [24,25]

SiO₂-supported molybdenum HPA, such as PMo, SiMo and GeMo, retain the Keggin structure at high loading but decompose at very low loading due to their interaction with silanol groups [26–29]. At high loading, supported HPA behave similarly to bulk HPA, while in contrast, at low loading, HPA decompose to MoO₃, losing the acidity.

Composition of *n*-butanol ethoxylates obtained with various catalysts is listed in Tables 1 and 2. Composition of *n*-butanol ethoxylates obtained with various catalysts is also presented in Figs. 1 and 2. The results obtained in the presence of PMo, PMo/SiO₂, NaOH and BF₃ are given. Narrowing the homologue distribution in comparison with the product obtained in the presence of NaOH is clearly observed. The

Table 2
Composition of *n*-butanol ethoxylates obtained on the PMo/SiO₂ catalyst (*n*-butanol/EO = 5/1, molar ratio)

Catalytic system	<i>n</i> -butanol %	Product distribution (%)		By products (%)	C ₄ H ₉ OH (%) conversion ^a	Selectivity (%) ^b	
		1	2			1	2
Fresh	76.66	20.76	1.00	0.12	21.84	95.06	4.66
Reused once	76.76	19.51	2.11	0.20	22.64	86.33	13.60
Reused two times	77.76	19.06	1.89	0.17	22.24	85.70	14.28
Reused three times	77.85	18.68	1.63	0.19	22.15	84.33	15.66
Reused four times	78.71	17.32	1.69	0.18	21.29	81.35	18.65

^aConversion = C₄H₉OH (initial, %) – C₄H₉OH (product, %).

^bSelectivity = 2-butoxy ethanol (product distribution, %)/conversion, %.

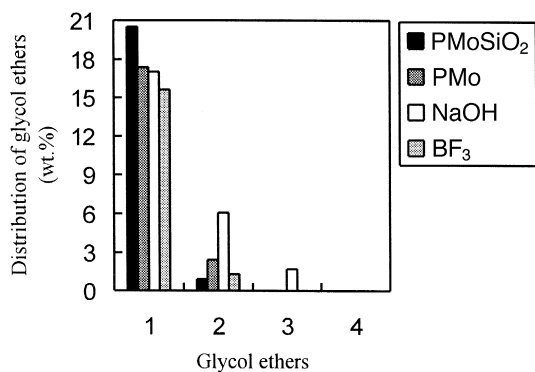


Fig. 1. Effect of PMoSiO₂, PMo, NaOH and BF₃ catalysts on HOCH₂CH₂OC₄H₉ distribution. (1) HOCH₂CH₂OC₄H₉. (2) HO(CH₂CH₂O)₂C₄H₉. (3) HO(CH₂CH₂O)₃C₄H₉. Reaction conditions: time, 0.5 h; temperature, 100°C; pressure, 0.1–0.4 Mpa; *n*-C₄H₉OH/EO = 5/1 (molar ratio).

exception is the product obtained in the presence of PMo/SiO₂. A 100% EO conversion and 95% BE selectivity can be obtained.

3.1.2. HPA on molecular sieve

Incorporation of HPA into zeolite pores to obtain shape-selective catalysts has long been a challenge. However, conventional zeolites are not suitable for this because their pores are too small to accommodate large (1.2 nm) HPA molecules. Recently, HPA supported on the molecular sieve HZSM-5 (BET surface area 290 m²/g, uniform pores 1.5 nm in size) was prepared. The PW/HZSM-5 compositions with PW loadings from 10 to 50 wt.% have 1.5-nm uni-

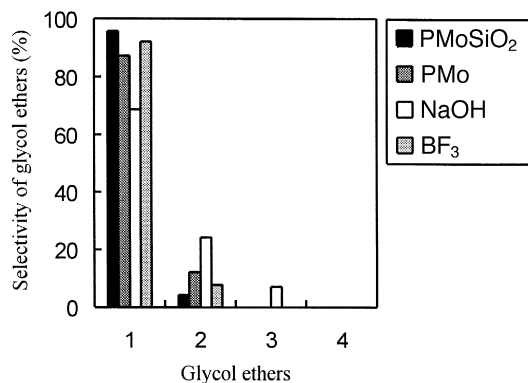


Fig. 2. Effect of PMoSiO₂, PMo, NaOH and BF₃ catalysts on HOCH₂CH₂OC₄H₉ selectivity. (1) HOCH₂CH₂OC₄H₉. (2) HO(CH₂CH₂O)₂C₄H₉. (3) HO(CH₂CH₂O)₃C₄H₉. Reaction conditions are the same as in Fig. 1.

formly sized pores. HPA retains the Keggin structure on the HZSM-5 surface at an HPA loading above 20 wt.%, while at lower loading a partial decomposition of PW was observed, as in the case of amorphous SiO₂. HPA are finely dispersed on the HZSM-5 surface. As shown by TEM, the PW species are mainly located inside the HZSM-5 pores rather than on the outer surface. PW/HZSM-5 exhibits a higher catalytic activity in liquid-phase *n*-butanol ethoxylation. Other HPA/HZSM-5 catalysts have been tested in the ethoxylation of ethylene oxide with *n*-butanol. Those catalysts are very similar to PMo/SiO₂.

3.2. Acid properties

Supported HPA possess purely Bronsted acid which is stronger than such conventional solid acids as SiO₂-Al₂O₃, H₃PO₄/SiO₂, and HY zeolite. The acid strength of crystalline HPA which is identical to that in solution decreases in the series PW > SiW ≥ PMo > SiMo [8] (Table 3).

Usually, relative catalytic activities of HPA are consistent with this order both in homogeneous and in heterogeneous systems. Like other strong solid acids, HPA is capable of generating carbon from adsorbed organic compounds.

3.3. Thermal stability of supported HPA

Supported HPA have a fairly high thermal stability. The Keggin-type PW, SiW, PMo, and SiMo decompose at 465, 445, 375, and 350°C, respectively. The thermal decomposition causes the loss of their acidity.

Table 3
Dissociation constants of HPA in acetone at 25°C

Acid	pK ₁	pK ₂	pK ₃
H ₃ PW ₁₂ O ₄₀	1.6	3.0	4.0
H ₄ SiW ₁₂ O ₄₀	2.0	3.6	5.3
H ₃ PMo ₁₂ O ₄₀	2.0	3.6	5.3
H ₄ SiMo ₁₂ O ₄₀	2.1	3.9	5.9
H ₂ SO ₄	6.6		
HCl	4.3		
HNO ₃	9.4		

4. Conclusion

The ethoxylation of ethylene oxide with *n*-butanol to form 2-butoxy ethanol is efficiently catalyzed by heterogeneously supported heteropolyacid catalyst.

The heterogeneously supported heteropolyacid catalyst is highly selective (> 95%), and has purely Bronsted acid which is stronger than such conventional solid acid, and its total amount of acidity decreases rapidly with increase of calcination temperature. The ethoxylation is found to be a surface and stereospecific reaction.

The composition and active phase of fresh and reused catalysts have no evident change in the X-ray diffraction spectra. In almost all cases, the supported heteropolyacid could be regenerated and reused several times in the ethoxylation.

Acknowledgements

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