

# Synthesis of Bisphenol-A from Phenol and Acetone using Organic-Inorganic Modified Heteropoly Acid Catalyst

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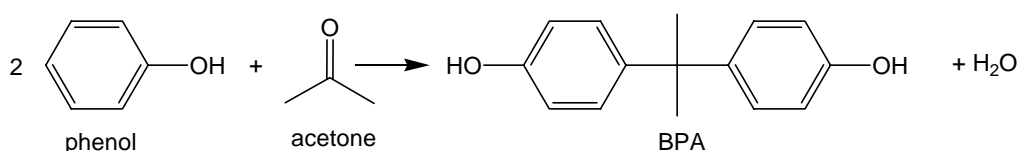
## ABSTRACT

For the synthesis of Bisphenol-A, an effective design of heteropoly acid catalysts by organic-inorganic dual modification is demonstrated. Dual modification of  $\text{H}_3\text{PWO}_{40}$  was made by partial Cs ion exchange ( $\text{Cs}_{2.5}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}$ ) for lowering acid strength and by immobilization of 2-diethylamino-ethanethiol (DEAT) adjacent to protonic acid sites. The Bisphenol-A yield of 94% was achieved on the designed heteropoly acid catalyst, which is comparable to the conventional ion-exchange resin catalyst (yield of 96%). Since such high performance was not achieved by homogeneous mixture of  $\text{Cs}_{2.5}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}$  and hexanethiol or mechanical mixture of  $\text{Cs}_{2.5}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}$  and  $\text{Cs}_{2.5}\text{DEAT}_{0.5}\text{PW}_{12}\text{O}_{40}$ , importance of microscopic interaction between protonic acid sites and mercapto group was suggested.

## 1. INTRODUCTION

Bisphenol-A (BPA, hereafter) is an important raw material for the production of epoxy resins and polycarbonates. BPA is conventionally produced through acid catalyzed condensation reaction between phenol and acetone by using ion-exchange resins promoted by mercapto compounds. The ion-exchange resins shows excellent performance on BPA synthesis. For example, it has been reported that modified ion-exchange resins, like Amberlyst, show very good activity for BPA synthesis with around 90% selectivity to the desired *p*, *p'* isomer [1]. However, thermal stability of resin catalysts is very limited and they cannot be used at higher reaction temperatures. Also fouling of the resin catalysts in the reaction medium is a problem. Some attempts have been made on the use of inorganic solid acids for BPA synthesis, such as heteropoly acids [1-4], zeolites [5], acid functionalized mesoporous silica [6-10], and clays [11]. Das et al. [6,7] have shown that sulfonic acid-functionalized mesoporous MCM-41 is very effective for BPA synthesis at a relatively low reaction temperature. Margelefsky et al. [9] successfully demonstrated that SBA-15 grafted with organic molecules having both sulfonic acid and thiol groups shows significantly higher catalytic activity than SBA-15 having randomly distributed sulfonic acid and thiol

group. Heteropoly acids, especially those supported on mesoporous silica, also show good performance on BPA synthesis [3,4]. However, the maximum BPA yields of these inorganic solid acids and organic functionalized solid acids are still lower than the conventional ion-exchange resins that show BPA yields of above 90%. A better strategy of catalyst design is required for modification of solid acid catalysts.



The aim of this study is to develop an effective strategy of catalyst design for BPA synthesis. First, the catalytic performances of typical solid acids are compared. Secondly, modification by organic molecules having thiol group is examined. To achieve cooperative functions by protonic acid sites on heteropoly acid and thiol groups of organic promoters, the organic promoters are immobilized by using amino-mercapto compounds. Finally, the designed heteropoly acid catalyst is characterized and the catalytic performance is compared with ion-exchange resin catalysts.

## 2. EXPERIMENTAL

### 2.1 Catalyst preparation

$\text{H}_3\text{PW}_{12}\text{O}_{40}$  and  $\text{H}_4\text{SiW}_{12}\text{O}_{40}$  were purchased from Nippon Inorganic Color and Chemicals Co. Ltd. Acidic cesium salts,  $\text{Cs}_x\text{H}_{3-x}\text{PW}_{12}\text{O}_{40}$ , were prepared by a titration method as Okuhara reported [12, 13]. An appropriate amount of an aqueous solution of  $\text{Cs}_2\text{CO}_3$  (Mitsuwa,  $0.10 \text{ mol dm}^{-3}$ ) was added dropwise with a constant rate to an aqueous solution of  $\text{H}_3\text{PW}_{12}\text{O}_{40}$  at room temperature with vigorous stirring. The Cs content,  $x$  in  $\text{Cs}_x\text{H}_{3-x}\text{PW}_{12}\text{O}_{40}$ , was adjusted by the amount of  $\text{Cs}_2\text{CO}_3$  solution added. From the beginning of addition of  $\text{Cs}_2\text{CO}_3$ , very fine precipitates were formed. After aging at room temperature overnight, the water was removed in rotary-evaporator at  $60 \text{ }^\circ\text{C}$  under vacuum. Proton-type beta-zeolite (H-BEA) was supplied from the Catalysis Society of Japan (JRC-Z-HB25,  $\text{SiO}_2/\text{Al}_2\text{O}_3 = 25 \pm 5$ ). Montmorillonite K10 clay (surface area  $220 \text{ m}^2 \text{ g}^{-1}$ ) was purchased from Aldrich. In order to remove residual metal cations in the cation-exchange site, 1 g of K10 clay was treated in an aqueous solution of  $\text{NH}_4\text{NO}_3$  (1 M, 10 mL) at room temperature for 3 h, followed by the calcination at  $500 \text{ }^\circ\text{C}$  for 1 h. Ion-exchange resin of Amberlyst 15 (1.70 eq/L) was purchased from Aldrich. For the addition of a promoter, Amberlyst 15 and 3.7 wt% of 2-Diethylamino-ethanethiol were mixed in distilled water. After 1 h aging, the solid was separated by a centrifugal separator, and washed with phenol three times.

Organic promoters were immobilized on  $\text{Cs}_x\text{H}_{3-x}\text{PW}_{12}\text{O}_{40}$  as follows.  $\text{Cs}_x\text{H}_{3-x}\text{PW}_{12}\text{O}_{40}$  was

dissolved into distilled water and an aqueous solution of hydrochlorides of promoter (2-Amino-benzenethiol, 2-Amino-ethanethiol, and 2-Diethylamino-ethanethiol (Tokyo Kasei, > 95 %)) was slowly added. After stirring for 1 h at room temperature, the precipitate was collected by a centrifugal separator. The obtained precipitate was dried at 80°C overnight.

## 2.2 Characterizations

X-ray diffraction patterns of the powdered catalysts were recorded with a Rigaku RINT 1200 diffractometer with Cu K $\alpha$  radiation. Microcalorimetric measurement on NH<sub>3</sub> adsorption was performed at 150 °C using a calorimeter (Tokyo Rikou Co., HAC-450G) connected to a volumetric glass line (35 °C) with on-line injection system for pulsing NH<sub>3</sub> gas. Before the adsorption experiments the sample (0.1 g) was pretreated under vacuum overnight at 150 °C. <sup>13</sup>C MAS NMR spectrum at 75.4768 MHz was measured by a Bruker DMX500 with the following conditions: Spinning rate 5kHz, contact time 1.75 msec, interval 4 sec, accumulation 5000 times, and glycine as an external standard of chemical shift. Before the measurement, the sample was dried at 100 °C overnight.

## 2.3 Catalytic tests

Synthesis of Bisphenol-A (BPA) was carried out in the liquid phase under atmospheric pressure in a 100-mL tubular glass reactor equipped with a condenser and a magnetic stirrer. A 100 mg of solid catalyst was dried at 60 °C overnight and put into the reactor with phenol (20 mmol). After purging of gas phase in the reactor with dried nitrogen for 3 times, the reactor was heated to 80°C with stirring. Then, acetone (2 mmol) was added by a microsyringe to start the BPA synthesis. Yields were determined by a gas chromatography with VF-5ms capillary column using *n*-dodecane as an internal standard. The kinetic parameters are defined as follows.

Rate(BPA): Initial rate of BPA production after 1 h.

TOF (Turnover frequency): Initial rate of BPA production after 1 h per acid amount.

TON (Turnover number): Amount of produced BPA per acid amount.

## 3. RESULTS AND DISCUSSION

### 3.1 Modification by ion-exchange

First of all, the effects of types of heteropoly acids and ion-exchange were examined. Fig. 1 shows the differential heat of ammonia adsorption determined by micro-calorimeter. H<sub>2</sub>PW<sub>12</sub>O<sub>40</sub> shows very high heat of adsorption, i.e., the initial heat was 200-180 kJ mol<sup>-1</sup>. Since an error range at the first and second points is relatively high, the initial heat of adsorption was determined as an intersection of the slope of heat of adsorption of several points (NH<sub>3</sub> doping of 0.2-0.6 mmol g<sup>-1</sup>) at 0 mmol g<sup>-1</sup> of NH<sub>3</sub> doping. The heat of ammonia adsorption was in the sequence of H<sub>3</sub>PW<sub>12</sub>O<sub>40</sub> > H<sub>4</sub>SiW<sub>12</sub>O<sub>40</sub> > Cs<sub>2.5</sub>H<sub>0.5</sub>PW<sub>12</sub>O<sub>40</sub> >> H-BEA

> montmorillonite K10. For the quantification of acid amount, the strong acid sites having the heat of adsorption above  $100 \text{ kJ mol}^{-1}$  was taken into account. Since Siril et al. reported that the calorimetric profile of typical ion-exchange resins such as Amberlyst 15, Amberlyst 35, and C100H show the initial heat of adsorption at around  $120 \text{ kJ mol}^{-1}$  and inflection points at around  $100 \text{ kJ mol}^{-1}$  [14], the effective acid strength for BPA synthesis over ion-exchange resin is thought to be above  $100 \text{ kJ mol}^{-1}$ .

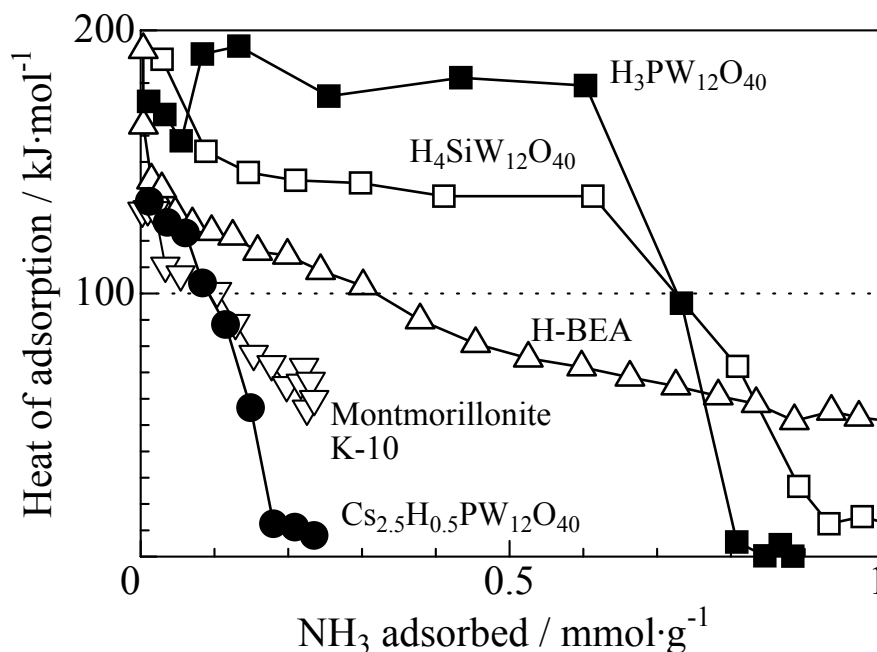


Fig. 1. Differential heat of adsorption of ammonia on various solid acid catalysts.

Table 1 Results on Bisphenol-A synthesis and acid properties of various solids acid catalysts.

Catalyst	BPA synthesis		NH <sub>3</sub> adsorption		TOF /h <sup>-1</sup>
	BPA Yield <sup>a)</sup> %	Rate(BPA) /mmol g <sup>-1</sup> h <sup>-1</sup>	Initial heat <sup>b)</sup> /kJ mol <sup>-1</sup>	Amount <sup>c)</sup> /mmol g <sup>-1</sup>	
H <sub>3</sub> PW <sub>12</sub> O <sub>40</sub>	42	3.2	185	0.7	4.3
H <sub>4</sub> SiW <sub>12</sub> O <sub>40</sub>	38	2.8	160	0.7	3.8
Cs <sub>2.5</sub> H <sub>0.5</sub> PW <sub>12</sub> O <sub>40</sub>	35	1.4	150	0.1	25.0
H-BEA	2	0.1	130	0.3	1.1
Montmorillonite K10	0	0.0	115	0.1	0.0

<sup>a)</sup> Total BPA yield after 6 h. <sup>b)</sup> The initial heat of NH<sub>3</sub> adsorption determined as an intersection of the slope of heat of adsorption at 0 mmol g<sup>-1</sup> of NH<sub>3</sub> doping. <sup>c)</sup> The amount of NH<sub>3</sub> adsorbed with the heat above  $100 \text{ kJ mol}^{-1}$ .

Table 1 shows the results of BPA synthesis by using various acid catalysts. Basically, heteropolyacids showed higher catalytic performances, and the final BPA yield was in the

sequence of  $\text{H}_3\text{PW}_{12}\text{O}_{40} > \text{H}_4\text{SiW}_{12}\text{O}_{40} > \text{Cs}_{2.5}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40} \gg \text{H-BEA} > \text{montmorillonite K10}$ . This sequence was the same to the initial heat of  $\text{NH}_3$  adsorption. The results indicate that strong acid sites are required for BPA synthesis. The initial reaction rates were also in the same order. The catalytic performances were compared with acid properties determined by the differential heat of ammonia. The acid amount was not well correlated with the activity of BPA synthesis because H-BEA having higher acid amount than  $\text{Cs}_{2.5}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}$  showed poorer activity in the BPA synthesis. Table 1 also shows turnover frequency (TOF) determined by initial reaction rate per acid amount determined by micro-calorimeter. Different from the apparent catalytic activity,  $\text{Cs}_{2.5}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}$  having relatively moderate acid strength showed markedly higher TOF, indicating the efficiency of individual acid sites is the highest when acid strength is around  $150 \text{ kJ mol}^{-1}$ . The further investigation is carried out by using  $\text{Cs}_{2.5}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}$  as a base-catalyst.

### 3.2 Modification by amino-mercapto compounds

The effect of organic mercapto compounds as promoters was examined. Table 2 shows the effect of homogeneous mixture of *n*-hexanethiol with  $\text{H}_3\text{PW}_{12}\text{O}_{40}$  and  $\text{Cs}_{2.5}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}$ . The addition of *n*-hexanethiol increased the activity, i.e., TOF for both  $\text{H}_3\text{PW}_{12}\text{O}_{40}$  and  $\text{Cs}_{2.5}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}$  significantly increased. However, the selectivity of BPA is only slightly increased. As a result, the promotion effect on BPA yield is limited.

Table 2 Effect of homogeneous mixture of *n*-hexanethiol with heteropoly acids.

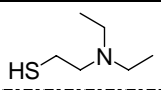
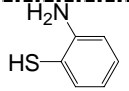
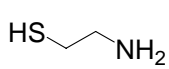
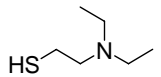
Catalyst <sup>a)</sup>	Time /h	BPA Yield / %	BPA selectivity / %	TOF / h <sup>-1</sup>
$\text{H}_3\text{PW}_{12}\text{O}_{40}$	3	42	46	3
$\text{H}_3\text{PW}_{12}\text{O}_{40} + n\text{-hexanethiol}$	1	56	56	33
$\text{Cs}_{2.5}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}$	9	34	40	25
$\text{Cs}_{2.5}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40} + n\text{-hexanethiol}$	9	40	57	82

<sup>a)</sup> *n*-hexanethiol/ $\text{H}_3\text{PW}_{12}\text{O}_{40}$  or *n*-hexanethiol/ $\text{Cs}_{2.5}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}$  = 0.25 in molar ratio.

Then, the immobilization of organic amino-mercapto compounds is examined as show in Table 3. When total proton was substituted with 2-diethylamino-ethanethiol, the catalyst shows only poor activity and almost no selectivity. This indicates that the amino-mercapto compounds (NS) should work with protonic acid concertedly. When the composition of catalyst was  $\text{NS}_{2.5}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}$ , 2-amino-benzenethiol modified catalyst shows moderate conversion of acetone, but the selectivity of BPA was low. Although the immobilization of 2-amino-ethanethiol shows high BPA activity, the activity was very poor. The catalyst modified with 2-diethylamino-ethanethiol (DEAT, hereafter) shows high activity and fairly good selectivity. The BPA yield of DEAT modified  $\text{H}_3\text{PW}_{12}\text{O}_{40}$  (65%) was improved than

non-modified catalyst (42 %). It can be expected that various factors of DEAT, such as basicity of amino group and flexibility of thiol group, are preferable for the promotion effect of thiol group on the production of BPA

Table 3 Effect of immobilized amino-mercapto compounds (NS) on  $\text{NS}_{2.5}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}$  on BPA synthesis for 6 h.

Promoter	Composition	BPA Yield / %	Acetone conversion / %	BPA selectivity / %
	$\text{NS}_3\text{H}_0$	0.1	12	1
	$\text{NS}_{2.5}\text{H}_{0.5}$	28	60	56
	$\text{NS}_{2.5}\text{H}_{0.5}$	48	59	82
	$\text{NS}_{2.5}\text{H}_{0.5}$	65	88	74

### 3.3 Combined modification by ion-exchange and amino-mercapto compound

The combination of above two modifications, i.e., Cs-ion exchange and immobilization of amino-mercapto compound, is investigated in this section. Table 4 shows the effect of ratio of DEAT to protonic acid on  $\text{Cs}_{2.5}\text{H}_{(0.5-x)}\text{DEAT}_x\text{PW}_{12}\text{O}_{40}$ . It is clear that the addition of DEAT to  $\text{Cs}_{2.5}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}$  increased the selectivity of BPA up to DEAT/ $\text{H}^+$  ratio of unity. The further addition of DEAT significantly decreased the conversion of acetone. The suppression of the activity suggests entire neutralization of protonic acid sites by DEAT. When the DEAT/ $\text{H}^+$  ratio is from 0 to 1, the effect of DEAT addition on the activity is rather complicated. The conversion once decreased at DEAT/ $\text{H}^+$  ratio of 0.5, and increased at DEAT/ $\text{H}^+$  ratio of 1.0. The former can be attributed to the partial neutralization of protonic acid sites, and the latter can be due to the promotion effect by thiol groups. Actually, TOF monotonously increased with the addition of DEAT, indicating the individual activity of acid sites on heteropoly acid was promoted by thiol groups of DEAT. The best performance was obtained by  $\text{Cs}_{2.5}\text{H}_{0.25}\text{DEAT}_{0.25}\text{PW}_{12}\text{O}_{40}$ , having the DEAT/ $\text{H}^+$  ratio of 1.0.

Finally, the catalytic performance on BPA synthesis was compared with a conventional ion-exchange resin catalyst. Amberlyst 15 was also modified with 3.7 wt% of DEAT, of which the loaded amount corresponds to 20 mol% of acid sites. As shown in Table 5, the final BPA yield, BPA selectivity, and *p,p'*-selectivity of  $\text{Cs}_{2.5}\text{H}_{0.25}\text{DEAT}_{0.25}\text{PW}_{12}\text{O}_{40}$  were comparable to that of corresponds to DEAT-modified Amberlyst 15. It should be noted that the BPA yield of 94 % is the best one among solid acid based catalysts ever reported. Although the conversion is rather lower than Amberlyst 15, this can be due to lower amount of acid sites per gram of catalyst. Actually, TOF of BPA production is around 30 times higher on  $\text{Cs}_{2.5}\text{H}_{0.25}\text{DEAT}_{0.25}\text{PW}_{12}\text{O}_{40}$ , indicating the individual activity of active sites is higher on

$\text{Cs}_{2.5}\text{H}_{0.25}\text{DEAT}_{0.25}\text{PW}_{12}\text{O}_{40}$ . From this fact, the strategy of catalyst design by the organic-Inorganic dual mediation of heteropoly acid was verified.

Table 4 Effect of ratio of DEAT to protonic acid on  $\text{Cs}_{2.5}\text{H}_{(0.5-x)}\text{DEAT}_x\text{PW}_{12}\text{O}_{40}$ .

$\text{H}^+$	DEAT	DEAT/ $\text{H}^+$	Time /h	BPA yield %	Conv. %	BPA Select. %	<i>p,p'</i> - Select. %	TON	TOF $\text{h}^{-1}$
0.50	0	0	6	34	85	40	87	41	8.5
0.33	0.17	0.5	9	51	58	88	97	95	34
0.25	0.25	1.0	9	94	94	97	96	236	87
1.00	1.50	1.5	6	0	39	0	-	0	0
0.17	0.33	2.0	6	0	27	0	-	0	0

Table 5 BPA synthesis by  $\text{Cs}_{2.5}\text{H}_{0.25}\text{DEAT}_{0.25}\text{PW}_{12}\text{O}_{40}$  and DEAT/Amberlyst 15.

Catalyst	Time /h	BPA yield /%	Conv. /%	BPA Select. /%	<i>p,p'</i> - Select. /%	TON	TOF $\text{h}^{-1}$
$\text{Cs}_{2.5}\text{H}_{0.25}\text{DEAT}_{0.25}\text{PW}_{12}\text{O}_{40}$	9	94	94	97	96	236	87
3.7wt% DEAT/Amberlyst 15 <sup>a)</sup>	6	97	99	98	97	9.7	3.1

Catalyst weight 1.0 g, <sup>a)</sup> Dehydrated at 100°C.

Fig. 2 shows the results of leaching test. After a removal of solid catalysts, the formation of BPA was terminated. The results clearly show that  $\text{Cs}_{2.5}\text{DEAT}_{0.25}\text{H}_{0.25}\text{PW}_{12}\text{O}_{40}$  acts as a solid catalyst.

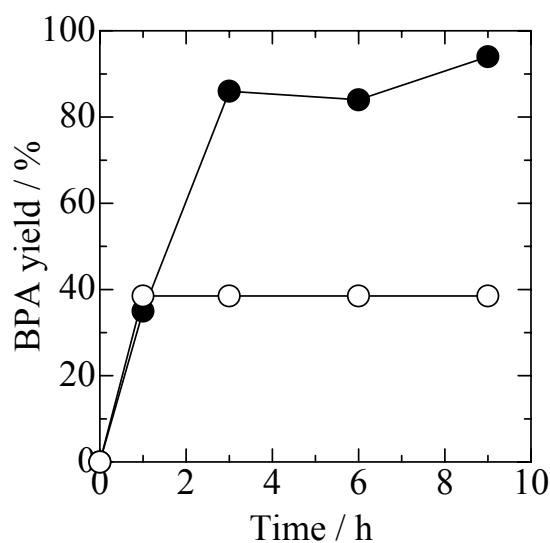


Fig. 2. Time course of BPA yield over  $\text{Cs}_{2.5}\text{H}_{0.25}\text{DEAT}_{0.25}\text{PW}_{12}\text{O}_{40}$  as a function of time. The catalyst was in flask for 9 h (●), and filtered at the reaction time of 1 h (○).

### 3. 4 Structure of $\text{Cs}_{2.5}\text{H}_{0.25}\text{DEAT}_{0.25}\text{PW}_{12}\text{O}_{40}$

Fig. 3 shows XRD patterns of  $\text{H}_3\text{PW}_{12}\text{O}_{40}$  and modified catalysts. The diffraction lines assignable to bcc-type of Keggin structure of  $\text{H}_3\text{PW}_{12}\text{O}_{40}$  [15] are observed, and the lines are shifted to higher angle after partial Cs-ion exchange. Even after the doping of DEAT, there is not much change in the XRD patterns and no other diffraction lines are observed. The results show that the addition of DEAT does not change the bulk structure of  $\text{Cs}_{2.5}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}$ .

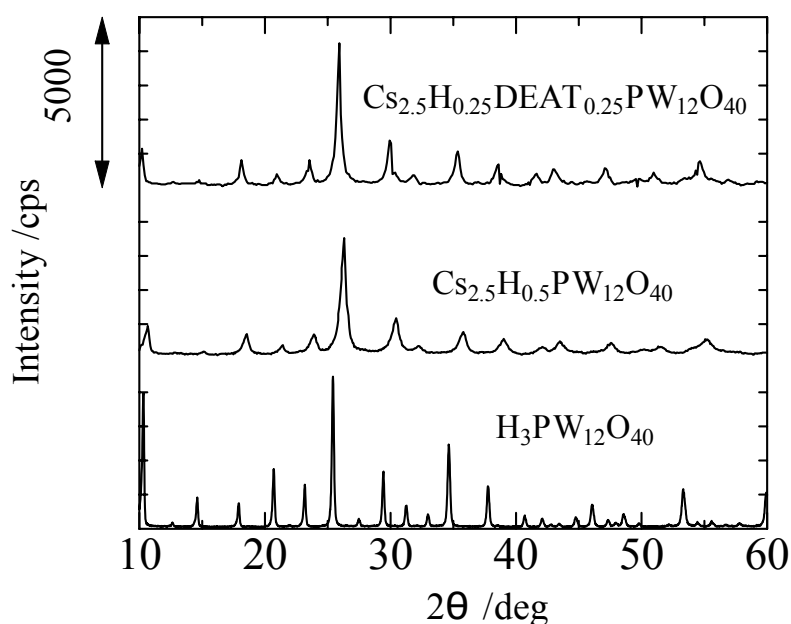


Fig. 3. XRD patterns of  $\text{H}_3\text{PW}_{12}\text{O}_{40}$ ,  $\text{Cs}_{2.5}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}$ , and  $\text{Cs}_{2.5}\text{H}_{0.25}\text{DEAT}_{0.25}\text{W}_{12}\text{O}_{40}$ .

In order to examine the interaction between DEAT and heteropoly acid,  $^{13}\text{C}$ -MAS-NMR was measured as shown in Fig. 4. The  $^{13}\text{C}$  NMR spectrum of DEAT shows 4 resonance signals at 13.7, 25.6, 46.0, and 57.8 ppm, of which the assignments are indicated in the figure. After the immobilization of DEAT, the resonance signal at 25.6 ppm assignable to carbon adjacent to SH group was not much affected. On the other hand, the upfield shifts of the carbons adjacent to amino group were observed (from 57.8 ppm to 53.2 ppm and from 46.0 ppm to around 36 ppm) with broadening of the signals. The signal at 25.6 ppm was slightly shifted to 11.3 ppm). Motokura et al. also reported such upfield shifts of amino group of 3-(diethylamino)propyltrimethoxysilane through the immobilization on silica-alumina [16]. The similar upfield shifts in this study also indicates the immobilization of DEAT on  $\text{Cs}_{2.5}\text{H}_{0.25}\text{PW}_{40}$ . The degree of the upfield shifts was larger on the signals at 46.0, and 57.8 ppm assignable to carbons around amino group, but negligible on the signal at 25.6 ppm assignable to carbon adjacent to SH group. From these results, DEAT is immobilized on  $\text{Cs}_{2.5}\text{H}_{0.25}\text{PW}_{40}$  by the interaction between amine group and acid site of heteropoly acid, branching a rather free SH functional group on the surface, as depicted in Scheme 1. Free -SH group on immobilized DEAT may effectively promote acid catalyzed condensation of one acetone and two phenol molecules. This concept is similar to that proposed by Margelefsky et

al. [9]. They designed co-presence of acid and thiol group in the same molecule grafting on SBA-15, and elucidated that the distance between acid site and thiol groups is the important factor. In our research, on the other hand, the active sites are composed of acid site on solid catalyst and thiol group on the immobilized organic molecule. It was demonstrated that BPA is effectively produced on the organic-inorganic concerted active sites on  $\text{Cs}_{2.5}\text{H}_{0.25}\text{DEAT}_{0.25}\text{PW}_{12}\text{O}_{40}$ .

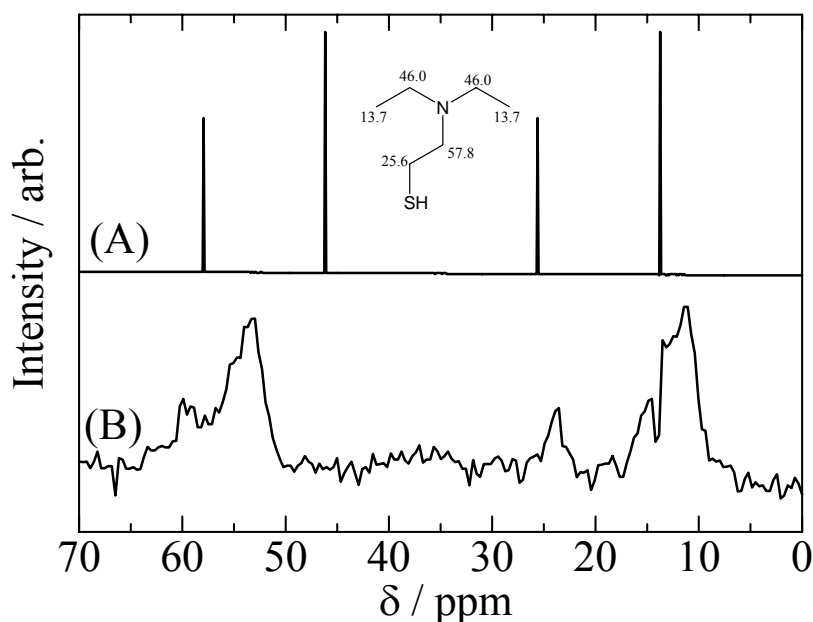
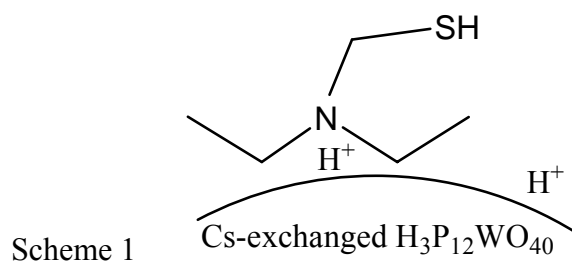


Fig. 4. (A)  $^{13}\text{C}$  NMR spectrum of DEAT in  $\text{CDCl}_3$ . (B) Solid-state  $^{13}\text{C}$  MAS NMR spectrum of  $\text{Cs}_{2.5}\text{H}_{0.25}\text{DEAT}_{0.25}\text{PW}_{12}\text{O}_{40}$ .



#### 4. CONCLUSION

The effective design of heteropoly acid catalysts by organic-inorganic dual modification was demonstrated. After partial Cs-ion exchange followed by immobilization of 2-diethylamino-ethanethiol (DEAT), the dual modified  $\text{Cs}_{2.5}\text{H}_{0.25}\text{DEAT}_{0.25}\text{W}_{12}\text{O}_{40}$  showed very high catalytic activity for the synthesis of Bisphenol-A (BPA) by condensation reaction of phenol and acetone. The final BPA yield was 94%, which is comparable to the

conventional DEAT-modified Amberlyst 15 (96%). The reaction rate per acid site (TOF) of  $\text{Cs}_{2.5}\text{H}_{0.25}\text{DEAT}_{0.25}\text{PW}_{12}\text{O}_{40}$  was around 30 times higher than that of DEAT-modified Amberlyst 15, indicating the individual activity of active sites is higher on  $\text{Cs}_{2.5}\text{H}_{0.25}\text{DEAT}_{0.25}\text{PW}_{12}\text{O}_{40}$ . The result of  $^{13}\text{C}$  NMR indicated that DEAT is immobilized on heteropoly acid surface by the interaction between amino group and acid site of heteropoly acid, branching a rather free SH functional group on the surface. It was demonstrated that BPA is effectively produced on the organic-inorganic concerted active sites on  $\text{Cs}_{2.5}\text{H}_{0.25}\text{DEAT}_{0.25}\text{PW}_{12}\text{O}_{40}$ .

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