Condensation of benzene and aqueous formaldehyde to diphenylmethane in a biphasic system consisting of an aqueous phase of heteropolyacid

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Abstract

Synthesis of diphenylmethane ($PhCH_2Ph$) from benzene and formalin (aqueous HCHO) was investigated in a biphasic reaction system, which consisted of benzene and aqueous phases, where the latter phase contains HCHO and liquid acid as catalyst. Heteropolyacids such as $H_3PW_{12}O_{40}$, $H_3PMo_{12}O_{40}$, and $H_4SiW_{12}O_{40}$ exhibited significant activities for the formation of diphenylmethane, whereas typical mineral acids (H_2SO_4, HNO_3, and H_3PO_4), organic acids (*para*-toluenesulfonic acid (PTS) and CF_3COOH), and $Sc(CF_3SO_3)_3$ were inactive. The yields of diphenylmethane were proportional to the concentrations of both proton and the heteropoly anion ($PW_{12}O_{40}{}^{3-}$). Consequently, it can be presumed that the critical reaction step is the attack by a benzyl cation to a benzene molecule, in which the intermediate benzyl cation is stabilized by a heteropoly anion to accelerate the reaction. Since heteropolyacids exist in the aqueous phase exclusively, and the product diphenylmethane is concentrated in the benzene phase after the reaction, $H_3PW_{12}O_{40}$ can be readily recovered from the reaction solution. It was confirmed that $H_3PW_{12}O_{40}$ in the aqueous phase, after drying at room temperature, could be reused repeatedly without significant decreases in the activity.
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1. Introduction

Diphenylmethane ($C_6H_5CH_2C_6H_5$ or $PhCH_2Ph$) has been widely used as an important intermediate in synthesis of chemicals such as in the production of spices and pharmaceutics [1]. Furthermore, diphenylmethane dyes (e.g. auramine) are widely used in wool, paper, leather, and silk industries [2]. Recently, $PhCH_2Ph$ and its derivatives have attracted increased attention as insulating materials in place of PCB.

Typically, $PhCH_2Ph$ is obtained synthetically through the Friedel–Crafts reaction of benzene with benzyl chloride in the presence of aluminum-amalgam, $AlCl_3$, or $ZnCl_2$ as the catalyst [2–4]. However, the toxicity and corrosiveness of these catalysts and the resulting byproduct (HCl) make this process harmful to the environmental. Alternatively, solid acid catalysts such as zeolites [5,6] including H-ZSM-5 [7], sulfated ZrO_2 [8,9], Ga-MCM-41 [10], and TlO_x/ZrO_2 [11] have been reported for the benzylation of benzene with benzyl chloride.

In contrast to the traditional benzyl chloride process, synthesis of $PhCH_2Ph$ using benzene and for-

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malin (an aqueous solution of HCHO), shown by Eq. (1), is recognized to be environmentally friendly and economically favorable because the byproduct is ideally only water. The reaction between benzene and paraformaldehyde (water-free oligomers of HCHO) can be readily catalyzed by zeolites [7] and Aciplex–SiO$_2$ (one type of organic resins) [12]. However, energy consumption that is required in the production of paraformaldehyde or trioxane is high. On the other hand, when formalin (aqueous formaldehyde) was used as the source of formaldehyde in these reactions, the solid acids were significantly less active due to the strong inhibition by water [12].

$$2C_6H_6 + HCHO(\text{in water})$$
$$\rightarrow C_6H_5CH_2C_6H_5 + H_2O \qquad (1)$$
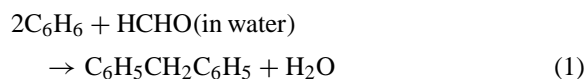
Since the use of formalin is more desirable for the synthesis of PhCH$_2$Ph, it remains an important challenge to develop a new catalytic system for PhCH$_2$Ph synthesis using formalin [13].

Heteropolyacids have enjoyed wide acceptance as active catalysts in both homogeneous and heterogeneous systems [13–23]. Herein, we present our investigations of the synthesis of PhCH$_2$Ph directly from benzene and aqueous HCHO using liquid acids. The catalytic property of liquid acids including heteropolyacids for the reaction was investigated as a biphasic reaction system (benzene and aqueous phases); specifically, the catalytic activities and selectivities of heteropolyacids were examined and compared with a variety of mineral and organic acids. Systematic investigations were carried out to determine the effects of the concentrations of proton, heteropoly anion, formaldehyde, and water. Furthermore, studies were conducted to establish the reusability of the heteropolyacid catalyst H$_3$PW$_{12}$O$_{40}$.

2. Experimental

2.1. Materials

Heteropolyacids (H$_3$PW$_{12}$O$_{40}$, H$_3$PMo$_{12}$O$_{40}$, H$_6$P$_2$W$_{18}$O$_{62}$, and H$_4$SiW$_{12}$O$_{40}$) in the solid state, and an aqueous solution of H$_4$SiMo$_{12}$O$_{40}$ (0.120 mol/kg) were obtained from Nippon Inorganic Color and Chemical Co. (Japan). Mineral acids (H$_2$SO$_4$, HNO$_3$, and H$_3$PO$_4$), organic acids (*para*-toluenesulfonic acid

(PTS) and CF$_3$COOH), benzene, formalin (27.8 mol% HCHO, 5.5 mol% methanol, and water), methyl formate (HCOOMe), formic acid, and methanol were obtained from Wako Pure Chemical Co. (Japan). Benzene and formalin were used without further purification. Sc(CF$_3$SO$_3$)$_3$ was synthesized according to the literature [24].

2.2. Catalytic reaction

A custom-designed 100 cm^3 stainless autoclave (Taiatsu Techno, Japan) was employed in this study. Benzene (40 cm^3, 450 mmol) and formalin (6.72 cm^3, 90 mmol HCHO) were used as the standard reaction solution. Following the addition of the acid catalyst, the reaction mixture was heated to the reaction temperature (140 or 160 °C), and then was vigorously stirred with a magnetic stirrer (MAG-NEO, RV-06M, Japan). Typically, the reactant solution was cooled to room temperature after a reaction time of 2 h to analyze the products; however, in some cases, the reaction times were varied. The vapor phase was analyzed using a TCD gas chromatograph (Shimadzu, 8A) equipped with an active carbon column. The benzene phase, which was clearly distinct with an obvious boundary after the reaction for all the cases, was directly analyzed using an FID gas chromatograph (Shimadzu, 14B) equipped with a 15 m capillary column of cross-linked 5% PHME siloxane (HP-5, USA). The aqueous phase was diluted with water and analyzed using the TCD gas chromatograph equipped with an APS-201 (Flusin T) column.

2.3. IR and elemental analysis

IR spectra of the fresh and spent H$_3$PW$_{12}$O$_{40}$ catalysts, as the KBr method, were obtained using an IR spectrometer (FT-IR, BIO-RAD, Japan). The carbon content for the spent H$_3$PW$_{12}$O$_{40}$ in the solid state was determined by elemental analysis.

3. Results

3.1. Time course of the reaction catalyzed by H$_3$PW$_{12}$O$_{40}$

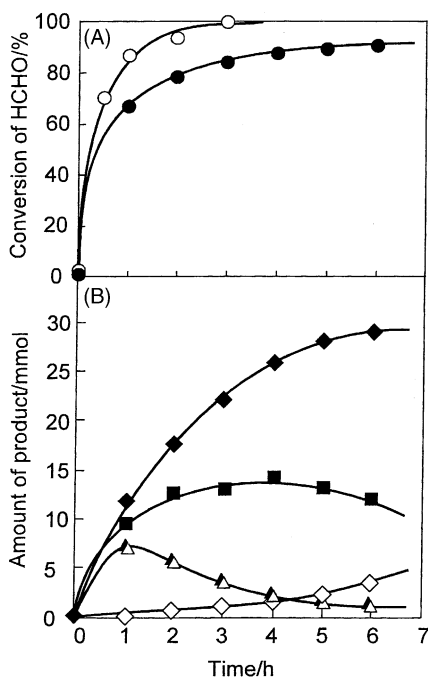The conversion of HCHO and the yields of products of the reaction between the standard mixture of

Fig. 1. Time courses of the reaction of benzene with aqueous formaldehyde using $H_3PW_{12}O_{40}$. (A) Conversion of HCHO at 140 °C (●) and 160 °C (○). (B) Amount of product at 140 °C: (◆) PhCH$_2$Ph; (■) HCOOMe; (△) HCOOH; (▲) MeOH; and (◇) (PhCH$_2$)$_2$C$_6$H$_4$. Reaction conditions: benzene, 40 cm^3 (450 mmol); $H_3PW_{12}O_{40}$, 4.2 mmol; and formalin, 6.7 cm^3 (HCHO 90 mmol, H_2O 222 mmol, and MeOH 18 mmol).

benzene (450 mmol) and aqueous HCHO (90 mmol) in the presence of $H_3PW_{12}O_{40}$ (4.2 mmol) at 140 °C and 160 °C are shown in Fig. 1. As shown in Fig. 1A, nearly 100%-conversion was attained after 3 h at 160 °C. In contrast, the reaction became slower in the latter stages of the reaction at 140 °C; changes in the product composition for the reaction at 140 °C,

as a function of the reaction time, are shown in Fig. 1B. Two competing reactions were observed: (1) condensation between HCHO and benzene to form PhCH$_2$Ph, and (2) disproportionation of HCHO to CH$_3$OH, HCOOH, and HCOOMe. The yield of PhCH$_2$Ph increased as the reaction progressed. On the other hand, amounts of HCOOH and MeOH increased initially, and then decreased slowly at the latter stages of the reaction (Fig. 1B), in which the amounts were nearly equal. It was also observed that the amount of HCOOMe increased gradually, then decreased slightly at the latter stages of the reaction.

The results of the reactions between benzene and HCOOMe or HCOOH in the presence of $H_3PW_{12}O_{40}$, along with the transformation of HCHO, are summarized in Table 1. We observed that the formation of PhCH$_2$Ph occurred only between HCHO and benzene, and not from the reactions between benzene and HCOOMe or HCOOH. In addition, HCHO was transformed to HCOOMe, CH$_3$OH, and HCOOH, when only HCHO was introduced in the presence of $H_3PW_{12}O_{40}$.

3.2. Catalytic property of liquid acids

The results for the reaction between benzene and aqueous HCHO in the presence of various liquid acids are summarized in Table 2. It should be emphasized that, among the acids listed in Table 1, only $H_3PW_{12}O_{40}$ resulted in the formation of PhCH$_2$Ph (Table 1). In each case, small amounts of methyl benzyl ether (C$_6$H$_5$CH$_2$OCH$_3$ or PhCH$_2$OMe) and dibenzylbenzene ((PhCH$_2$)$_2$C$_6$H$_4$) were formed. Furthermore, the evolution of CO in the gaseous phase was also observed. The aromatic compounds (PhCH$_2$Ph, PhCH$_2$OMe, and (PhCH$_2$)$_2$C$_6$H$_4$) were

Table 1
Reaction of benzene with formaldehyde, methylformate or formic acid in water

Runs	Reactants (mmol)					Products (mmol)						MB[a]
	Benzene	HCHO	HCOOMe	HCOOH	H_2O	PhCH$_2$Ph	HCOOMe	CH$_3$OH	HCOOH	HCHO	CO	
1	450	90	0	0	222	31.7	30.1	4.8	4.7	6.1	2.9	97.0
2	450	0	45	0	278	0.1	25.3	17.8	8.7	5.4	6.6	101.0
3	450	0	0	107	278	0	0.8	0	92.4	0	12.9	99.2
4	0	266	0	0	660	0	37.8	82.1	46.5	57.3	10.9	100.2

Reaction conditions: $H_3PW_{12}O_{40}$, 4.2 mmol, 160 °C, and 2 h.
[a] Mass balance: 100 × (total amount of products and remaining HCHO)/(the initial amount of HCHO).

Table 2

Conversion and selectivity of diphenylmethane synthesis from benzene and formalin with various liquid acids

Catalyst (mmol)	Conversion[a] (mol%)	Yield[a] (mol%)	Selectivity on the basis of HCHO[a,b] (mol%)							MB[c] (%)
			HCOOMe	MeOH	HCOOH	$PhCH_2Ph$	$(PhCH_2)_2C_6H_4$	$PhCH_2OMe$	CO	
$H_3PW_{12}O_{40}$ (4.2)	93.2	35.3	34.3	5.3	5.2	37.9	11.2	0.8	3.2	97.0
$Sc(CF_3SO_3)_3$ (2.1)	95.1	0.0	83.0	12.3	4.6	0.0	0.0	0.0	0.2	100.0
PTS[d] (12.6)	82.2	4.1	56.9	5.7	5.0	4.7	1.2	2.4	3.3	79.8[e]
CF_3COOH (14.9)	44.4	0.0	53.4	0.0	0.0	0.0	0.0	0.0	1.6	55.0[f]
HNO_3 (12.6)	24.4	0.0	90.0	0.0	0.0	0.0	0.0	0.0	10.0	100.0
H_3PO_4 (4.2)	18.7	0.0	68.8	12.0	19.0	0.0	0.0	0.0	0.2	100.0
H_2SO_4 (6.3)	33.7	0.0	92.0	4.0	4.0	0.0	0.0	0.0	0.6	101.0

Reaction conditions: benzene, $40 \, cm^3$ (450 mmol); formalin, $6.72 \, cm^3$ (HCHO, 90 mmol; H_2O, 222 mmol; methanol, 18.2 mmol); 160 °C; and 2 h.

[a] On the basis of HCHO.

[b] $PhCH_2Ph$, diphenylmethane; $(PhCH_2)_2C_6H_4$, biphenyl-benzene; $PhCH_2OMe$, methyl benzyl ether.

[c] Mass balance: $100 \times$ (total amount of products and remaining HCHO)/(the initial amount of HCHO).

[d] *para*-Toluenesulfonic acid.

[e] Toluene was detected.

[f] Unknown product was detected.

detected exclusively in the benzene phase, whereas $H_3PW_{12}O_{40}$ and HCOOH were concentrated in the aqueous phase.

Under conditions as described in Table 2, the conversion of HCHO was greater than 93% over both $H_3PW_{12}O_{40}$ and $Sc(CF_3SO_3)_3$. $Sc(CF_3SO_3)_3$ gave HCOOMe selectively, and no $PhCH_2Ph$. Similarly, PTS, CF_3COOH, and mineral acids, such as H_2SO_4, HNO_3, and H_3PO_4, showed activities towards the disproportionation of HCHO, but not towards the formation of $PhCH_2Ph$. As shown in Table 3, various heteropolyacids, such as $H_4SiW_{12}O_{40}$, $H_3PMo_{12}O_{40}$, $H_6P_2W_{18}O_{62}$, and $H_4SiMo_{12}O_{40}$, have shown catalytic activities towards the synthesis of $PhCH_2Ph$. The pH values of the aqueous solutions contain-

ing heteropolyacids were 0.10, 0.58, 0.61, 0.79, and 0.96 for $H_3PW_{12}O_{40}$, $H_4SiW_{12}O_{40}$, $H_3PMo_{12}O_{40}$, $H_6P_2W_{18}O_{62}$, and $H_4SiMo_{12}O_{40}$, respectively, and for the aqueous solutions containing H_2SO_4, H_3PO_4, HNO_3, and $Sc(CF_3SO_3)_3$ were 0.19, 1.25, 0.65, and 0.90, respectively.

3.3. Effects of the concentration of $H_3PW_{12}O_{40}$

Fig. 2 shows the relationship between the concentrations of $H_3PW_{12}O_{40}$ and the yields of the products. Whereas the conversion of HCHO increased in a reasonable manner proportionally to the amount of $H_3PW_{12}O_{40}$, the yield of $PhCH_2Ph$ was on an S-shape curve against the amount of $H_3PW_{12}O_{40}$. In

Table 3

Conversion and selectivity of diphenylmethane synthesis from benzene and formalin with heteropoly acids

Catalyst (mmol)	Conversion (mol%)	Yield (mol%)	Selectivity (mol%) on the basis of HCHO							MB[b] (%)
			HCOOMe	CH_3OH	HCOOH	$PhCH_2Ph$[a]	$(PhCH_2)_2C_6H_4$	$PhCH_2OMe$	CO	
$H_3PW_{12}O_{40}$ (4.2)	93.2	35.3	34.3	5.3	5.2	37.9 (79.9)	9.2	0.8	3.2	97.0
$H_4SiW_{12}O_{40}$ (4.2)	92.8	25.4	43.6	5.0	4.8	27.4 (79.7)	4.8	4.1	4.7	99.3
$H_3PMo_{12}O_{40}$ (4.2)	93.5	23.4	54.8	0.0	0.0	25.1 (71.1)	9.5	1.4	4.1	100.0
$H_6P_2W_{18}O_{62}$ (2.1)	72.4	9.2	68.8	5.8	5.6	12.7 (76.1)	1.7	1.5	2.0	98.2
$H_4SiMo_{12}O_{40}$ (4.2)	92.0	3.6	77.1	1.6	8.1	3.9 (33.9)	1.2	6.4	2.1	99.7

Reaction conditions and the legend are the same as the footnotes of Table 2.

[a] The figures in the parentheses are the selectivity of $PhCH_2Ph$ among the aromatic compounds.

[b] Mass balance: $100 \times$ (total amount of products and remaining HCHO)/(the initial amount of HCHO).
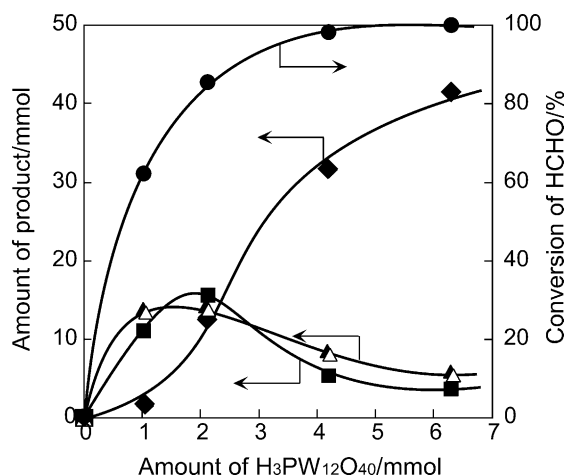
Fig. 2. Effects of amount of $H_3PW_{12}O_{40}$ on amount of product for diphenylmethane synthesis: (●) conversion of HCHO; (◆) PhCH₂Ph; (■) HCOOMe; (△) HCOOH; and (▲) MeOH. Reaction conditions: benzene, $40\,cm^3$ (450 mmol); paraformaldehyde, 2.7 g (90 mmol); and H_2O, 5.0 g (278 mmol). The reaction was performed at 160 °C for 2 h.

contrast, the disproportionation of HCHO took place readily, even at low concentrations of $H_3PW_{12}O_{40}$; however, the disproportionation products diminished as the amount of $H_3PW_{12}O_{40}$ was increased (Fig. 2).

As shown in Fig. 3, at low concentrations of HCHO, the yields of PhCH₂Ph increased proportionally to the amounts of HCHO. In contrast, yields of the disproportionation products followed a second-order increase with respect to the concentration of HCHO.

To investigate the influence of water in the reaction solution, paraformaldehyde was used as the source of HCHO in order to maintain constant amounts of HCHO and benzene. As shown in Fig. 4, increases in the amounts of water resulted in significant decreases in the conversion of HCHO and in the amounts of PhCH₂Ph formed. Complex influences of water on the amounts of the disproportionation products were observed.

3.4. Influence of the concentrations of proton and $PW_{12}O_{40}^{3-}$

In order to investigate the influences of the concentration of proton in the aqueous solution, while
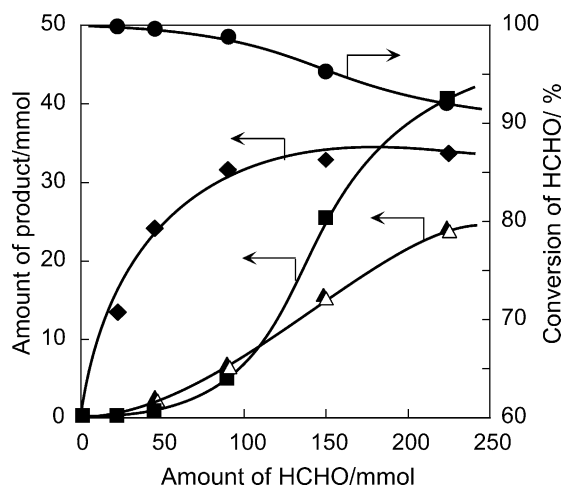

Fig. 3. Effects of amount of HCHO on amount of product diphenylmethane synthesis using $H_3PW_{12}O_{40}$: (●) conversion of HCHO; (◆) PhCH₂Ph; (■) HCOOMe; (△) HCOOH and (▲) MeOH. Reaction conditions: benzene, $40\,cm^3$ (450 mmol); H_2O, 278 mmol; $H_3PW_{12}O_{40}$, 4.2 mmol; and paraformaldehyde. The reaction was performed at 160 °C for 2 h.

maintaining a constant $PW_{12}O_{40}^{3-}$ concentration, the reaction solution was neutralized with NaOH. As shown in Fig. 5, the neutralization (addition of NaOH) of the reaction solution, which initially contained
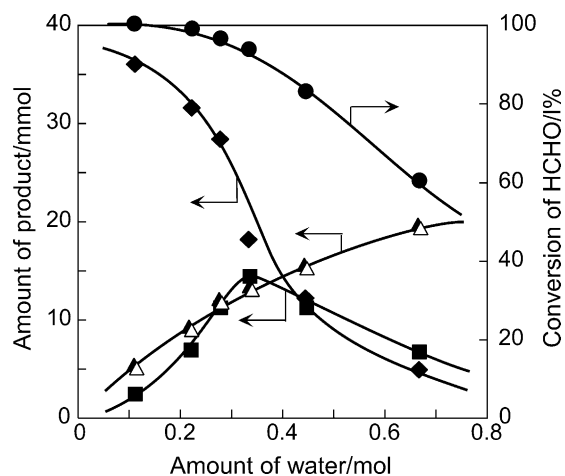

Fig. 4. Effects of water on amount of product for diphenylmethane synthesis using $H_3PW_{12}O_{40}$: (●) conversion of HCHO; (◆) PhCH₂Ph; (■) HCOOMe; (△) HCOOH; and (▲) MeOH. Reaction conditions: benzene, $40\,cm^3$ (450 mmol); paraformaldehyde, 2.7 g (90 mmol); and $H_3PW_{12}O_{40}$, 4.2 mmol. The reaction was performed at 160 °C for 2 h.

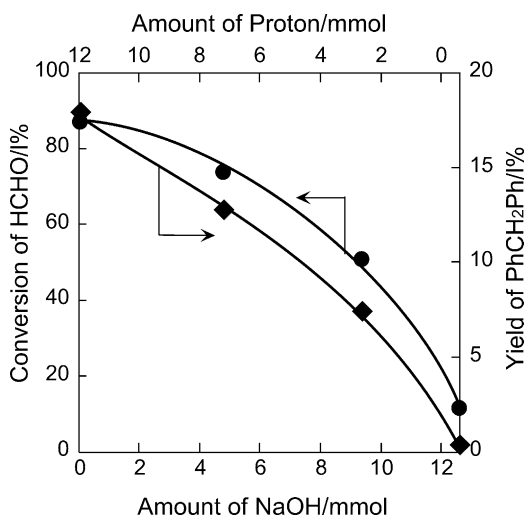Fig. 5. Effects of neutralization of $H_3PW_{12}O_{40}$ with on conversion and yield of $PhCH_2Ph$: (●) conversion of HCHO and (◆) yield of $PhCH_2Ph$. Reaction conditions: benzene, $40\,cm^3$ (450 mmol); paraformaldehyde, 90 mmol; H_2O, 389 mmol; and $H_3PW_{12}O_{40}$, 4.2 mmol. The reaction was performed at 160 °C for 2 h.

4.2 mmol $H_3PW_{12}O_{40}$, resulted in decrease in the conversions of HCHO and lower yields of $PhCH_2Ph$.

Fig. 6 shows the effect of $PW_{12}O_{40}^{3-}$ concentration on the conversion of HCHO and on the yield of
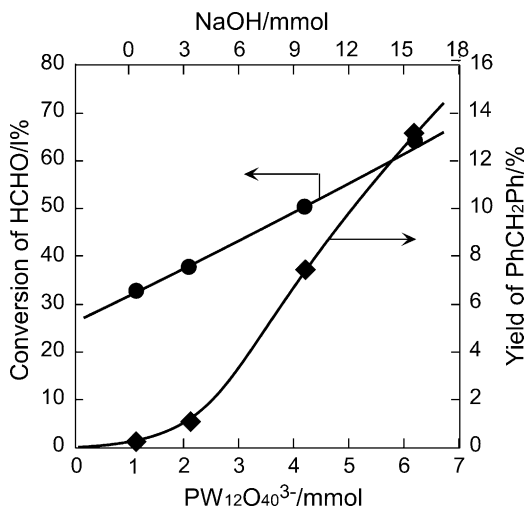
Fig. 6. Effects of the amount of $PW_{12}O_{40}^{3-}$ on conversion of HCHO and yield of $PhCH_2Ph$: (●) conversion of HCHO and (◆) yield of $PhCH_2Ph$. Reaction conditions: benzene, $40\,cm^3$ (450 mmol); paraformaldehyde, 90 mmol; H_2O, 278 mmol; $H_3PW_{12}O_{40}$; and NaOH. The reaction was performed at 160 °C for 2 h.

$PhCH_2Ph$. The apparent amount of proton was adjusted to 3 mmol by neutralization with NaOH. Our studies showed that, at amounts greater than 2 mmol, the concentration of $PW_{12}O_{40}^{3-}$ resulted in a linear increase in the yield of $PhCH_2Ph$. Assuming that the yield of $PhCH_2Ph$ is proportional to the reaction rate, the rate for formation of $PhCH_2Ph$ can be expressed as:

$$Rate(PhCH_2Ph) = k[H^+][PW_{12}O_{40}^{3-}][HCHO] \quad (2)$$

3.5. Activities of recycled $H_3PW_{12}O_{40}$

The activities of spent $H_3PW_{12}O_{40}$ are summarized in Table 4. When the reaction was repeated using recovered $H_3PW_{12}O_{40}$ (by drying the used aqueous solution at room temperature overnight), the conversion of HCHO and the total yield of aromatic products were slightly lower, which remained at a constant level after five successive runs. As shown in Fig. 7, the IR spectra of $H_3PW_{12}O_{40}$ recovered after the fifth runs at 160 °C revealed that the Keggin structure was completely retained. The decreases in the conversions and yields are probably attributable to the residual carbonaceous species on the $H_3PW_{12}O_{40}$ molecules. Accordingly, elemental analysis showed that the amount of carbon on the spent $H_3PW_{12}O_{40}$, after five runs was 2.1%, which corresponds to 0.4 mol of $PhCH_2Ph$ per one heteropolyacid.
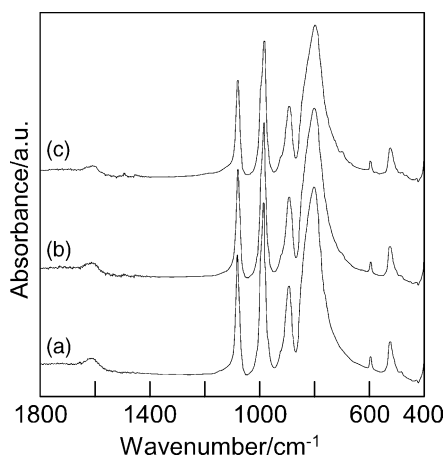

Fig. 7. IR spectra of $H_3PW_{12}O_{40}$ before and after the reaction. (a) Before the reaction; (b) after the reaction at 140 °C; (c) after the reaction of 5th run at 160 °C.

Table 4
Recycled $H_3PW_{12}O_{40}$[a]

Run	Conversion[b] (%)	Total yield of aromatics[c]/(mmol)	Selectivity of aromatic products (%)		
			$PhCH_2Ph$	$(PhCH_2)_2C_6H_4$	$PhCH_2OMe$
1	83.5	31.4	79.1	18.9	2.0
2	74.7	23.8 (75.6%)	76.2	15.6	8.2
3	72.2	21.1 (68.4%)	73.4	14.9	11.7
4	64.1	17.8 (56.7%)	70.6	14.1	15.3
5	63.1	17.6 (56.1%)	66.7	14.0	19.4

Reaction conditions: benzene, $40 \, cm^3$ (450 mmol); formalin, $6.72 \, cm^3$ (HCHO, 90 mmol; H_2O, 222 mmol; methanol, 18.2 mmol); 160 °C; and 30 min.

[a] Between the runs, the aqueous phase of $H_3PW_{12}O_{40}$ was dried in the ambient atmosphere. The recovered solid $H_3PW_{12}O_{40}$ was used again without any treatment.

[b] On the basis of HCHO.

[c] Total yields of $PhCH_2Ph$, $(PhCH_2)_2C_6H_4$, and $PhCH_2OMe$. The figures in the parentheses are the percentages of the yield to that of the first run.

4. Discussion

As mentioned above, $PhCH_2Ph$ is an important chemical in various synthetic methods, and therefore, the development of the novel and environmentally friendly catalytic synthesis of $PhCH_2Ph$ from benzene and aqueous HCHO is highly desirable. It has been reported that the reactions between methyl-substituted benzenes and paraformaldehyde (anhydrous HCHO oligomers) can be readily accelerated by mineral acids; however, the selectivity of the reaction to afford the desired products were low, along with the generation of large amounts of waste acids [25–27]. For example, Kawai and Yamazaki [26] showed that the reaction between 1,2,4-trimethylbenzene and paraformaldehyde at 100 °C was accelerated in the presence of organic acids such as PTS.

Izumi et al. [28] have reported on the reaction between phenol and paraformaldehyde catalyzed by heteropolyacid that was supported on silica. We have reported that polymer-resins that are supported on silica such as Nafion–SiO_2 and Aciplex–SiO_2 showed activities on the reaction of benzene with paraformaldehyde [12]. However, when formalin (aqueous HCHO) was used as the source of HCHO, these catalysts were significantly less active due to the strong poisoning effects of water. Studies of the reaction between toluene and formalin using various mineral acids, undertaken by Machida et al. [29] have shown that H_2SO_4 and $HClO_4$ accelerated the reaction, but

only when excess amounts of acid (H^+/HCHO molar ratio = 4) were used. Since the reactivity of benzene is lower than those of alkylbenzenes for this reaction, the condensation reaction between benzene and aqueous HCHO can be described as a "highly difficult reaction".

Previously, we demonstrated the catalytic activity of $H_3PW_{12}O_{40}$ to afford $PhCH_2Ph$ in a biphasic reaction system, one of which contained the aqueous of solution $H_3PW_{12}O_{40}$ [30]. The present results have demonstrated the novel and excellent catalytic activity of aqueous heteropolyacids for this highly difficult reaction, through the direct use of formalin as a clean synthetic methodology.

4.1. Catalytic features of heteropolyacids

The results in Fig. 5, in which the yields of $PhCH_2Ph$ correlate with the apparent amounts of proton, support the argument that the reaction is acid-catalyzed. In this biphasic system, the liquid acids (with the exception of PTS) existed in the aqueous phase, exclusively. These strong acids should be completely dissociated in the aqueous phase, and therefore, significant differences should not exist between the heteropolyacids and the mineral acids. As an indication of the amount of proton dissociated in the aqueous phase, the pH values of these aqueous phases ranged from 0.1 to about 1. Therefore, it is reasonable to consider that the exceptionally

high activity of $H_3PW_{12}O_{40}$, as shown in Table 2, is due to the critical characteristic of the polyanion, and not to its acid strength. Inherent catalytic activities of the heteropolyacids are also demonstrated in Table 3.

As shown in Fig. 6, the influence of the heteropoly anion on the yield is remarkable. With the concentration of proton constant, the yields of $PhCH_2Ph$ were enhanced as the concentration of $PW_{12}O_{40}^{3-}$ increased. Therefore, it can be concluded that the heteropoly anion, in addition to the pH, is critical for the acceleration of the reaction. The apparent second-order dependence of the yield of $PhCH_2Ph$ on the amount of $H_3PW_{12}O_{40}$ (Fig. 2) can be understood as the effects of both heteropoly anion and proton.

4.2. Reaction pathways over heteropolyacid catalysts

As mentioned above, two competing reaction of HCHO were observed: (1) condensation with benzene, and (2) disproportionation to HCOOH/MeOH (Cannizzaro-type reaction) and HCOOMe [31,32]. For these two types of reactions, the different relationships between the yields and the concentration of $H_3PW_{12}O_{40}$ were observed (Fig. 2).

The proposed reaction paths to $PhCH_2Ph$, involving the condensation of benzene and HCHO, are shown in Scheme 1. It is noted that the amount of $PhCH_2Ph$ was proportional to the concentrations of proton, $PW_{12}O_{40}^{3-}$, and HCHO. Considering the acid-catalyzed reaction and the important role of heteropoly anion, the reaction pathways for $PhCH_2Ph$ consisting of (a) through (c) in Scheme 1 can be proposed. In the first step [Scheme 1(a)], HCHO is activated by a proton to form H_2^+COH, which then attacks benzene to form a benzyl cation through benzyl alcohol [Scheme 1(b)]. The benzyl cation reacts further with benzene to produce $PhCH_2Ph$ [Scheme 1(c)]. The fact that a small amount of $PhCH_2OMe$ was detected (Table 2) supports the formation of benzyl alcohol [Scheme 1(b)]. Assuming that the steps in Scheme 1(a) and (b) are in equilibrium, and that the step of Scheme 1(c) is slow, the dependence shown by Eq. (2) can be derived.

Furthermore, the effect of the heteropoly anion on the acceleration of the formation of $PhCH_2Ph$ can be
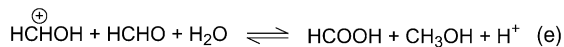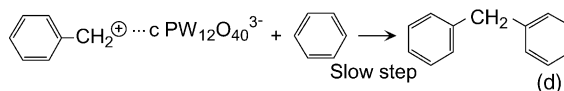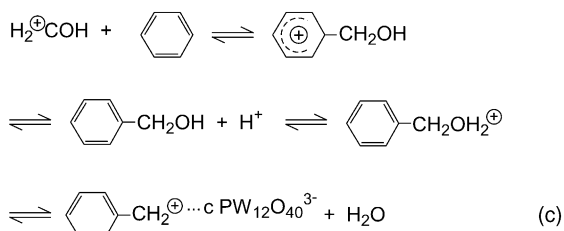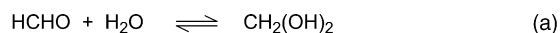
Scheme 1.

reasonably understood in terms of the stabilization of the carbocation by the heteropoly anion. This concept has been previously proposed by Izumi et al. [33]. Furthermore, they have suggested on the basis of kinetics that heteropoly anions play a critical role in the hydration of isobutylene, in which the intermediate, *tert*-butyl cation, is stabilized by the heteropoly anion through its soft-basicity. Although, to date, there is no evidence supporting the active role of the heteropoly anions, the exceptional activities of heteropolyacids in this reaction would be attributed to the characteristic of heteropolyacid. It is reasonable to assume that, although the rate constant of the reaction step of *tert*-butyl cation is large, the overall rate is slow because of the low concentration of *tert*-butyl cation. The presence of the heteropoly anion should enhance the concentration by stabilization, resulting in the acceleration of the reaction.

In the case of the disproportionation side-reaction, the relative independence of the disproportionation reaction on the $H_3PW_{12}O_{40}$ concentration was unexpected since the two reactions, condensation and disproportionation, were considered as parallel reactions.

We can assume that the disproportionation reaction occurs between the protonated and neutral HCHO molecules, and that therefore, the balance of the concentrations of protonated and neutral HCHO is critical for the rate. If HCHO forms protonated clusters such as $(HCHO)_nH^+$ the effect of the concentration will become negative, even at $n = 3$. The small dependence of the rate of disproportionation on the concentration of $H_3PW_{12}O_{40}$ (Fig. 2) is expected in this case.

Two reaction paths to HCOOMe and $CH_3OH/HCOOH$ are possible: (1) disproportionation of HCHO with H_2O to form CH_3OH and HCOOH, followed by esterification to afford HCOOMe, and (2) dimerization–isomerization of two HCHO molecules to form HCOOMe, which can undergo hydrolysis to afford CH_3OH and HCOOH [28,29]. As shown in Fig. 1, CH_3OH and HCOOH were formed in large quantities at the initial stage, whereas HCOOMe increased at latter stages, which indicates that reaction path (1), disproportionation–esterification, occurs in this system. The dependence of the reaction rate for disproportionation on the concentration of HCHO (nearly second-order) can be reasonably explained by Scheme 1(d). An analogous reaction, the formation of methyl glycerol from HCHO and HCOOH catalyzed by a heteropolyacid, was recently reported by He et al. [34].

5. Conclusion

Among the various liquid acids, heteropolyacids such as $H_3PW_{12}O_{40}$ have exhibited significantly high activities for the condensation between benzene and aqueous HCHO to afford diphenylmethane in biphasic reaction systems. The yield of diphenylmethane was proportional to the concentrations of proton, $PW_{12}O_{40}^{3-}$, and HCHO. The reaction path for the formation of diphenylmethane was presumed to be the protonation of HCHO to form H_2^+COH, which attacks benzene to form a benzyl cation, which in turn reacts with benzene to afford diphenylmethane. It is reasonable to suggest the heteropoly anion played a critical role in stabilizing the benzyl cation. Furthermore, it was confirmed that $H_3PW_{12}O_{40}$ could be reused at least five times by only drying at room temperature overnight without significant decreases in the activity.

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