

## Hydration of $\alpha$ -Pinene in a Triphasic System Consisting of $\alpha$ -Pinene, Water, and $\text{Cs}_{2.5}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}\text{-SiO}_2$ Composite

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$\text{Cs}_{2.5}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}\text{-SiO}_2$  composite combined with (3-aminopropyl)triethoxysilane exhibited greater activity and selectivity for hydration of  $\alpha$ -pinene at 333 K in a triphasic system ( $\alpha$ -pinene/water/solid acid) compared to previously reported water-tolerant catalysts such as zeolites, polymer-resins (Amberlyst 15 and Nafion-H), oxides, and liquid acids such as  $\text{H}_3\text{PW}_{12}\text{O}_{40}$  and  $\text{H}_2\text{SO}_4$ . The selectivity toward alcohols, including mono- and dialcohols, was approximately 80% over  $\text{Cs}_{2.5}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}\text{-SiO}_2$  composite.

Terpenic alcohols, such as  $\alpha$ -terpineol, 1,8-terpin, and their derivatives, have applications in perfume and pharmaceutical industries and have drawn attention as a raw material for electronic and optical materials. Currently, the practical synthesis of terpenic alcohols involves hydration of  $\alpha$ -pinene using  $\text{H}_2\text{SO}_4$  as a catalyst. However, replacement of  $\text{H}_2\text{SO}_4$  with a solid acid is desirable from an environmental point of view. Although hydration of  $\alpha$ -pinene over solid acids such as H- $\beta$  zeolite,<sup>1</sup> polymeric membrane containing heteropolyacid,<sup>2</sup> and supported heteropolyacid<sup>3</sup> have been conducted in a biphasic system, consisting of a solid acid and homogeneous solution including  $\alpha$ -pinene, water, and cosolvent, the activity and selectivity toward alcohols were unsatisfactory.

Few solid acids possess acceptable activity for hydrolysis, hydration, or esterification, in which water participates as either a reactant or product.<sup>4-8</sup> However, an acidic Cs salt of 12-tungstophosphoric acid,  $\text{Cs}_{2.5}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}$  (Cs2.5), is highly active

in acid-catalyzed reactions, even in the presence of a large excess of water,<sup>9</sup> while a  $\text{Cs}_{2.5}\text{-SiO}_2$  composite combined with (3-aminopropyl)triethoxysilane (APS) is an insoluble and sedimentable water-tolerant solid acid.<sup>10</sup> Here, we demonstrate the high activity and selectivity of the  $\text{Cs}_{2.5}\text{-SiO}_2$  composite for the hydration of  $\alpha$ -pinene in a triphasic system ( $\alpha$ -pinene/water/solid acid), which is a desirable system for easy separation of the product (oil phase) from an oil-water biphasic system.<sup>11</sup> The  $\text{Cs}_{2.5}\text{-SiO}_2$  composite is a more efficient catalyst than other water-tolerant solid acids, including high-silica zeolite (H-ZSM-5, H- $\beta$ , and H-mordenite), ion-exchange resins (Amberlyst 15 and Nafion-H), and liquid acids ( $\text{H}_3\text{PW}_{12}\text{O}_{40}$  and  $\text{H}_2\text{SO}_4$ ).

$\text{Cs}_{2.5}\text{-SiO}_2$  composites<sup>10</sup> were prepared using  $\text{SiO}_2$  [Aerosil 50 (A-50),  $48\text{ m}^2\text{ g}^{-1}$ ; and CARiACT Q-30 (Q-30),  $126\text{ m}^2\text{ g}^{-1}$ ], APS (Merck), and Cs2.5. The  $\text{SiO}_2$  (1.3 g) was added to a toluene solution of APS (85.6 mmol;  $200\text{ cm}^3$ ) at room temperature under  $\text{N}_2$ . After mixing the suspension for 2 h at room temperature, the solid was separated by filtration. The solid recovered was dispersed in water ( $26\text{ cm}^3$ ) acidified with 6% HCl ( $6\text{ cm}^3$ ), then separated, and dried at 373 K ( $\text{SiO}_2\text{-APS}$ ). To an aqueous suspension of  $\text{SiO}_2\text{-APS}$ , a colloidal aqueous solution of Cs2.5, prepared in advance,<sup>9</sup> was added to obtain the  $\text{Cs}_{2.5}\text{-SiO}_2$  composite, with 14 wt % of  $\text{SiO}_2\text{-APS}$ .

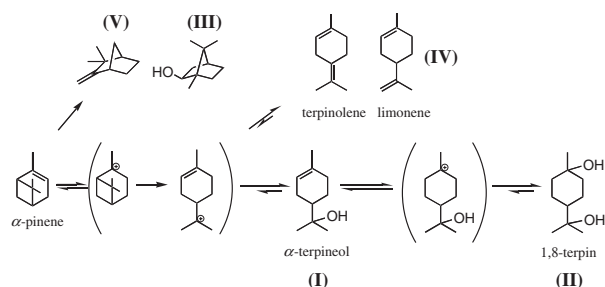
Hydration of  $\alpha$ -pinene was performed in a batch reactor (Pyrex,  $15\text{ cm}^3$ ) at 333 K with 0.64 mmol of  $\alpha$ -pinene,  $6\text{ cm}^3$  of water, and 40 mg of catalyst. The products were analyzed by FID-GC equipped with a capillary column (NB-1,  $0.25\text{ mm} \times 60\text{ m}$ ).

**Table 1.** Catalytic data for hydration of  $\alpha$ -pinene over solid and liquid acids<sup>a</sup>

Entry	Catalyst	Conv. /%	Selectivity <sup>b</sup> /%					Acid amount /mmol g <sup>-1</sup>	$k^c \times 10^2$ /h <sup>-1</sup>	TOF <sup>d</sup> /h <sup>-1</sup>
			I + II + III	I	II	III	IV + V			
<i>Solid acid</i>										
1	Cs2.5-(SiO <sub>2</sub> (A-50)-APS)	86	75	30	41	4	25	0.08 <sup>f</sup>	4.3	8.8
2	Cs2.5-(SiO <sub>2</sub> (A-50)-APS) <sup>e</sup>	62	67	60	2	5	33	0.08 <sup>f</sup>	2.0	4.1
3	Cs2.5-(SiO <sub>2</sub> (Q-30)-APS)	40	79	45	29	5	21	0.08 <sup>f</sup>	1.0	2.0
4	H- $\beta$ (Si/Al = 25)	69	50	13	19	18	50	0.72	2.4	0.5
5	H-ZSM-5 (Si/Al = 30)	3	0	0	0	0	100	0.80	0.1	<0.1
6	H-mordenite (Si/Al = 20)	0	—	—	—	—	—	0.71	—	—
7	SiO <sub>2</sub> -Al <sub>2</sub> O <sub>3</sub>	0	—	—	—	—	—	0.48	—	—
8	Amberlyst 15	44	51	26	19	6	49	4.70	1.2	<0.1
9	Nafion-H	16	43	18	21	5	57	0.80	0.4	<0.1
<i>Liquid acid</i>										
10	H <sub>3</sub> PW <sub>12</sub> O <sub>40</sub>	40	77	39	35	3	23	1.04	1.1	0.2
11	H <sub>2</sub> SO <sub>4</sub>	73	75	31	38	6	25	20.1	0.5	<0.1

<sup>a</sup>Reaction conditions:  $\alpha$ -pinene 0.64 mmol, water  $6\text{ cm}^3$ , catalyst 40 mg, temperature 333 K, and reaction time 48 h. <sup>b</sup>I monocyclic terpenic monoalcohols, II monocyclic terpenic dialcohols, III bicyclic terpenic monoalcohols, IV monocyclic terpenes, and V bicyclic terpenes (see Scheme 1). <sup>c</sup>First-order rate constant. <sup>d</sup>Turnover frequency ( $\text{h}^{-1}$ ) = initial reaction rate ( $\text{mmol g}^{-1}\text{ h}^{-1}$ )/acid amount ( $\text{mmol g}^{-1}$ ). <sup>e</sup>Reaction was conducted in a mixture of water ( $3\text{ cm}^3$ ) and 1,4-dioxane ( $3\text{ cm}^3$ ), instead of water ( $6\text{ cm}^3$ ).

<sup>f</sup>Estimated by temperature programmed desorption of benzonitrile.



**Scheme 1.** Reaction pathway for the hydration of  $\alpha$ -pinene.

Table 1 summarizes the conversion, selectivity (for 48 h), first-order rate constant ( $k$ ), turnover frequency (TOF) for the hydration of  $\alpha$ -pinene and acid amount of the catalyst. The products included monocyclic terpenic monoalcohols (**I**), mainly  $\alpha$ -terpineol, monocyclic terpenic dialcohols (**II**), mainly 1,8-terpine, bicyclic terpenic monoalcohols (**III**), monocyclic terpenes (**IV**), mainly limonene and terpinolene, and bicyclic terpenes (**V**) (see Scheme 1). While Cs2.5 showed high conversion (92%) but lower sedimentation, heteropoly species leached into the reaction mixture (data not shown). As shown in Table 1, Cs2.5-(SiO<sub>2</sub>(A-50)-APS) was highly active (Entry 1), entirely insoluble as confirmed by ICP analysis of the reaction mixture, and easily underwent sedimentation. Furthermore, the alcohols (**I** + **II** + **III**) were selectively formed (75% selectivity). The activity of Cs2.5-(SiO<sub>2</sub>(Q-30)-APS) was lower than that of Cs2.5-(SiO<sub>2</sub>(A-50)-APS), but selectivity toward alcohols (**I** + **II** + **III**) reached about 80% (Entry 3). Note that reaction in the biphasic system consisting of Cs2.5-(SiO<sub>2</sub>(A-50)-APS) and a homogeneous solution of  $\alpha$ -pinene, water, and 1,4-dioxane yielded predominantly monocyclic terpenic monoalcohols (**I**) (Entry 2), a conversion slightly lower than that in the triphasic system.

In zeolites and amorphous SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> (Entries 4–7), only H- $\beta$  zeolite (Si/Al = 25) showed decent activity, but selectivity toward alcohols was moderate (50%). Nb<sub>2</sub>O<sub>5</sub>, Al<sub>2</sub>O<sub>3</sub>, and SO<sub>4</sub><sup>2-</sup>/ZrO<sub>2</sub> were essentially inactive (data not shown). While previous reports demonstrate that ion-exchange resins such as Amberlyst 15 and Nafion-H are much effective for water-concerning reactions,<sup>12</sup> it should be emphasized that Cs2.5-(SiO<sub>2</sub>(A-50)-APS) possessed greater activity. Liquid acids, H<sub>3</sub>PW<sub>12</sub>O<sub>40</sub>, and H<sub>2</sub>SO<sub>4</sub> (Entries 10 and 11), were less active than Cs2.5-(SiO<sub>2</sub>(A-50)-APS), while both showed selectivity toward alcohols comparable to Cs2.5-(SiO<sub>2</sub>(A-50)-APS).

As summarized in Table 1, specific activity per acidic site (TOF), which was calculated by dividing the initial reaction rate by the acid amount, for Cs2.5-(SiO<sub>2</sub>(A-50)-APS) was dramatically larger than that for other solid and liquid acids. This suggests that the protons on Cs2.5-(SiO<sub>2</sub>(A-50)-APS) probably are shielded from poisoning by water owing to the hydrophobic nature of the surface.<sup>9</sup> As Table 1 demonstrates, the Cs2.5-SiO<sub>2</sub> composites were much selective toward alcohols than H- $\beta$  as well as Amberlyst 15 and Nafion-H. It is known that the acid strength of Cs2.5 is greater than those of H- $\beta$ , Amberlyst 15, and Nafion-H, as evaluated by NH<sub>3</sub>-TPD<sup>13,14</sup> and titration.<sup>13,15</sup> Thus, the cation intermediate formed from  $\alpha$ -pinene on the Cs2.5-SiO<sub>2</sub> composite is much exposed to nucleophilic attack by water than that on H- $\beta$  as well as ion-exchange resins, resulting in high selectivity toward alcohols during the hydration of

**Table 2.** Hydration of  $\alpha$ -terpineol and limonene over Cs2.5-(SiO<sub>2</sub>(A-50)-APS) composite<sup>a</sup>

Substrate	Composition				
	I	II	III	IV	V
$\alpha$ -terpineol ( <b>I</b> )	39	45	0	16	0
limonene ( <b>IV</b> )	7	8	0	85	0

<sup>a</sup>Reaction conditions: substrate 0.64 mmol, water 6 cm<sup>3</sup>, catalyst 40 mg, temperature 333 K, and reaction time 48 h.

$\alpha$ -pinene.

The time course of the conversion and selectivity in the hydration of  $\alpha$ -pinene over Cs2.5-(SiO<sub>2</sub>(A-50)-APS) showed that the selectivity toward alcohols was about 75%, which was independent of the conversion. The changes in selectivity toward monocyclic terpenic monoalcohols (**I**) and that toward dialcohols (**II**) indicated that **II** were formed by consecutive reaction through **I**, as shown in Scheme 1. In fact, hydration of  $\alpha$ -terpineol over Cs2.5-(SiO<sub>2</sub>(A-50)-APS) under the same reaction conditions as that of  $\alpha$ -pinene showed high selectivity to dialcohols (**II**) (Table 2) and was comparable in activity to that of  $\alpha$ -pinene. Thus, the selective formation of alcohols in the hydration of  $\alpha$ -pinene is due to high selectivity for the both steps in the consequent reaction. In contrast, Cs2.5-(SiO<sub>2</sub>(A-50)-APS) was less active for hydration of limonene. In the present reaction system, the solubilities of products were greatly different; the solubility of limonene (**IV**, 0.15 mmol dm<sup>-3</sup>) is only eightieth part of that of  $\alpha$ -terpineol (**I**, 12.3 mmol dm<sup>-3</sup>).<sup>16</sup> The low solubility of limonene probably accounts for the low activity in the hydration of this over Cs2.5-(SiO<sub>2</sub>(A-50)-APS).

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