Hydration of α-Pinene in a Triphasic System Consisting of α-Pinene, Water, and $Cs_{2.5}H_{0.5}PW_{12}O_{40}$–$SiO_2$ Composite

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$Cs_{2.5}H_{0.5}PW_{12}O_{40}$–$SiO_2$ composite combined with (3-aminopropyl)triethoxysilane exhibited greater activity and selectivity for hydration of α-pinene at 333 K in a triphasic system (α-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 $H_3PW_{12}O_{40}$ and H_2SO_4. The selectivity toward alcohols, including mono- and dialcohols, was approximately 80% over $Cs_{2.5}H_{0.5}PW_{12}O_{40}$–$SiO_2$ composite.

Terpenic alcohols, such as α-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 α-pinene using H_2SO_4 as a catalyst. However, replacement of H_2SO_4 with a solid acid is desirable from an environmental point of view. Although hydration of α-pinene over solid acids such as H-β zeolite,[1] polymeric membrane containing heteropolyacid,[2] and supported heteropolyacid[3] have been conducted in a biphasic system, consisting of a solid acid and homogeneous solution including α-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.[4–8] However, an acidic Cs salt of 12-tungstophosphoric acid, $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ (Cs2.5), is highly active in acid-catalyzed reactions, even in the presence of a large excess of water,[9] while a Cs2.5–SiO_2 composite combined with (3-aminopropyl)triethoxysilane (APS) is an insoluble and sedimentable water–tolerant solid acid.[10] Here, we demonstrate the high activity and selectivity of the Cs2.5–SiO_2 composite for the hydration of α-pinene in a triphasic system (α-pinene/water/solid acid), which is a desirable system for easy separation of the product (oil phase) from an oil–water biphase.[11] The Cs2.5–SiO_2 composite is a more efficient catalyst than other water–tolerant solid acids, including high-silica zeolite (H-ZSM-5, H-β, and H-mordenite), ion-exchange resins (Amberlyst 15 and Nafion-H), and liquid acids ($H_3PW_{12}O_{40}$ and H_2SO_4).

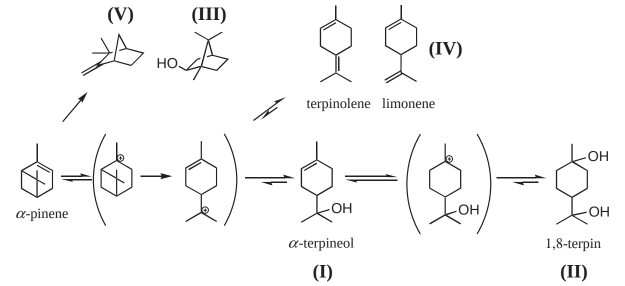
Cs2.5–SiO_2 composites[10] were prepared using SiO_2 [Aerosil 50 (A-50), 48 $m^2\,g^{-1}$; and CARiACT Q-30 (Q-30), 126 $m^2\,g^{-1}$], APS (Merck), and Cs2.5. The SiO_2 (1.3 g) was added to a toluene solution of APS (85.6 mmol; 200 cm^3) at room temperature under N_2. After mixing the suspension for 2 h at room temperature, the solid was separated by filtration. The solid recovered was dispersed in water (26 cm^3) acidified with 6% HCl (6 cm^3), then separated, and dried at 373 K (SiO_2–APS). To an aqueous suspension of SiO_2–APS, a colloidal aqueous solution of Cs2.5, prepared in advance,[9] was added to obtain the Cs2.5–SiO_2 composite, with 14 wt % of SiO_2–APS.

Hydration of α-pinene was performed in a batch reactor (Pyrex, 15 cm^3) at 333 K with 0.64 mmol of α-pinene, 6 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 mm × 60 m).

Table 1. Catalytic data for hydration of α-pinene over solid and liquid acids[a]

Entry	Catalyst	Conv. /%	Selectivity[b]/% I + II + III	I	II	III	IV + V	Acid amount /mmol g^{-1}	$k^c \times 10^2$ /h^{-1}	TOF[d] /h^{-1}
Solid acid										
1	Cs2.5–(SiO_2(A-50)–APS)	86	75	30	41	4	25	0.08[f]	4.3	8.8
2	Cs2.5–(SiO_2(A-50)–APS)[e]	62	67	60	2	5	33	0.08[f]	2.0	4.1
3	Cs2.5–(SiO_2(Q-30)–APS)	40	79	45	29	5	21	0.08[f]	1.0	2.0
4	H-β (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_2–Al_2O_3	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
Liquid acid										
10	$H_3PW_{12}O_{40}$	40	77	39	35	3	23	1.04	1.1	0.2
11	H_2SO_4	73	75	31	38	6	25	20.1	0.5	<0.1

[a] Reaction conditions: α-pinene 0.64 mmol, water 6 cm^3, catalyst 40 mg, temperature 333 K, and reaction time 48 h. [b] **I** monocyclic terpenic monoalcohols, **II** monocyclic terpenic dialcohols, **III** bicyclic terpenic monoalcohols, **IV** monocyclic terpens, and **V** bicyclic terpenes (see Scheme 1). [c] First-order rate constant. [d] Turnover frequency (h^{-1}) = initial reaction rate (mmol $g^{-1}\,h^{-1}$)/acid amount (mmol g^{-1}). [e] Reaction was conducted in a mixture of water (3 cm^3) and 1,4-dioxiane (3 cm^3), instead of water (6 cm^3). [f] Estimated by temperature programmed desorption of benzonitrile.



Scheme 1. Reaction pathway for the hydration of α-pinene.

Table 1 summarizes the conversion, selectivity (for 48 h), first-order rate constant (k), turnover frequency (TOF) for the hydration of α-pinene and acid amount of the catalyst. The products included monocyclic terpenic monoalcohols (**I**), mainly α-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_2(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_2(Q-30)–APS) was lower than that of Cs2.5–(SiO_2(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_2(A-50)–APS) and a homogeneous solution of α-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_2–Al_2O_3 (Entries 4–7), only H-β zeolite (Si/Al = 25) showed decent activity, but selectivity toward alcohols was moderate (50%). Nb_2O_5, Al_2O_3, and $SO_4{}^{2-}/ZrO_2$ 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,[12] it should be emphasized that Cs2.5–(SiO_2(A-50)–APS) possessed greater activity. Liquid acids, $H_3PW_{12}O_{40}$, and H_2SO_4 (Entries 10 and 11), were less active than Cs2.5–(SiO_2(A-50)–APS), while both showed selectivity toward alcohols comparable to Cs2.5–(SiO_2(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_2(A-50)–APS) was dramatically larger than that for other solid and liquid acids. This suggests that the protons on Cs2.5–(SiO_2(A-50)–APS) probably are shielded from poisoning by water owing to the hydrophobic nature of the surface.[9] As Table 1 demonstrates, the Cs2.5–SiO_2 composites were much selective toward alcohols than H-β as well as Amberlyst 15 and Nafion-H. It is known that the acid strength of Cs2.5 is greater than those of H-β, Amberlyst 15, and Nafion-H, as evaluated by NH_3–TPD[13,14] and titration.[13,15] Thus, the cation intermediate formed from α-pinene on the Cs2.5–SiO_2 composite is much exposed to nucleophilic attack by water than that on H-β as well as ion-exchange resins, resulting in high selectivity toward alcohols during the hydration of α-pinene.

Table 2. Hydration of α-terpineol and limonene over Cs2.5–(SiO_2(A-50)–APS) composite[a]

Substrate	Composition				
	I	**II**	**III**	**IV**	**V**
α-terpineol (**I**)	39	45	0	16	0
limonene (**IV**)	7	8	0	85	0

[a]Reaction conditions: substrate 0.64 mmol, water 6 cm^3, catalyst 40 mg, temperature 333 K, and reaction time 48 h.

The time course of the conversion and selectivity in the hydration of α-pinene over Cs2.5–(SiO_2(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 α-terpineol over Cs2.5–(SiO_2(A-50)–APS) under the same reaction conditions as that of α-pinene showed high selectivity to dialcohols (**II**) (Table 2) and was comparable in activity to that of α-pinene. Thus, the selective formation of alcohols in the hydration of α-pinene is due to high selectivity for the both steps in the consequent reaction. In contrast, Cs2.5–(SiO_2(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^{-3}) is only eightieth part of that of α-terpineol (**I**, 12.3 mmol dm^{-3}).[16] The low solubility of limonene probably accounts for the low activity in the hydration of this over Cs2.5–(SiO_2(A-50)–APS).

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