Preparation of Brønsted acid gel catalysts with highly hydrophobic surface and their application to acid-catalyzed reactions

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Abstract: Highly hydrophobic Brønsted acid catalysts based on siloxane gel with sulfo and methyl groups were synthesized. Control of hydrophobicity on the surface of gel catalysts was achieved by changing their ratio of S and methyl groups. The effect of surface hydrophobicity of the gel catalyst on their activity for hydrolysis of dodecyl acetate was investigated, and the hydrophobic gel catalysts were found to show higher activity than conventional solid acid catalysts. Kinetic study revealed that rate-determining step of hydrolysis of dodecyl acetate over hydrophobic gel catalysts is nucleophilic attack of H_2O to protonated esters.

Keywords: Solid acid catalyst, Hydrophobicity, Siloxane gel, Hydrolysis of ester.

1. Introduction

Solid acid catalysts are of great importance from the perspective of chemical industry and green chemistry. However, the conventional solid acid catalysts work less effectively in the reactions involving water as reactant such as hydrolysis because of severe poisoning of the acid sites by water. Therefore, control of hydrophobicity on the surface of solid acid is one of the important factors[1]. In this study, hydrophobic Brønsted acid catalysts based on siloxane gel with sulfo and methyl groups were prepared, and the effect of surface hydrophobicity of gel catalyst on their activity for hydrolysis of hydrophobic substrates investigated.

2. Experimental

Siloxane gels were prepared through hydrolytic condensation of alkoxysilanes containing mercaptopropyl and methyl groups[2]. Then, oxidation SH group, followed by protonation gave sulfo-functionalized gel catalysts. A series of gel catalysts with different ratio of S and methyl groups (S/Me) was prepared. Surface hydrophobicity of gel catalysts was evaluated by water contact angle. Hydrolysis of dodecyl acetate was carried out by gel catalysts with various S/Me ratio, and kinetic study was conducted by changing the amount of dodecyl acetate and H_2O.

3. Results and discussion

Figure 1 shows the relationship between water contact angle of gel catalysts and their catalytic activities toward hydrolysis of dodecyl acetate. Water contact angle was gradually decreased with increasing S/Me ratio up to 0.9, then sharply decreased around S/Me=1.0. This result indicates that surface hydrophobicity of gel catalysts was successfully controlled by changing their S/Me ratio, and gel catalysts with low S/Me ratio possessed hydrophobic surface. Gel catalysts with low S/Me ratio showed high initial formation rate of dodecanol, and then the gel catalyst with S/Me=0.26 showed the highest activity among the gel catalysts tested. Additionally, the gel catalyst with S/Me=0.26 showed higher activity than HCl, H_2SO_4, Amberlyst-15, Nafion-NR50 and Zeolites (Table 1). There is no correlation between acid amount and catalytic activity, suggesting that hydrophobicity around acid sites is important factor for hydrolysis of dodecyl acetate.

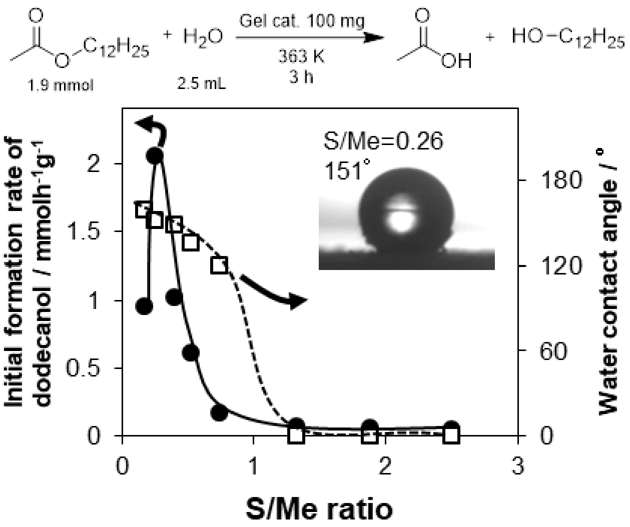

Figure 1. Relationship between surface hydrophobicity and catalytic activity toward hydrolysis of dodecyl acetate.

Table 1. Hydrolysis of dodecyl acetate by solid acid catalysts

entry	catalysts	Acid amount /mmol	Initial formation rate / mmolh^{-1}g^{-1}
1	Gel cat. (S/Me=0.26)	0.04	2.05
2	Amberlyst-15	0.47[b]	0
3	Nafion-NR50	0.08[b]	0
4	H-ZSM-5(90[a])	0.03[c]	0.26
5	H-β(150[a])	0.02[c]	0.33
6	1M H_2SO_4	8.00	0
7	1M HCl	4.00	0
8	*p*-Toluene sulfonic acid	0.04	0
9	Siloxane gel (S/Me=0.26) without oxidation		0

[a] SiO_2/Al_2O_3 ratio of zeolites
[b] T. Okuhara et al. *Appl. Catal. A*, **1997**, *167*, 227
[c] Calculated on the SiO_2/Al_2O_3 ratio.

To evaluate the effect of surface hydrophobicity of gel catalysts on hydrolysis of ester, kinetic study was carried out by changing the amount of dodecyl acetate and H_2O. Hydrophobic gel catalyst(S/Me=0.26) was diffused in organic phase (Figure 2(a)). Initial formation rate of dodecanol did not depend on the amount of dodecyl acetate (Figure 2(b)). On the other hand, higher reaction rate of hydrolysis was observed on the reaction with amount of H_2O (Figure 2(c)). These facts indicate that the rate-determining step of hydrolysis of dodecyl acetate over hydrophobic gel catalyst is nucleophilic attack of H_2O to ester. In constant, the other conventional acid catalysts diffused in aqueous phase, suggesting that the unique surface property of hydrophobic gel catalyst promotes hydrolysis of dodecyl acetate.

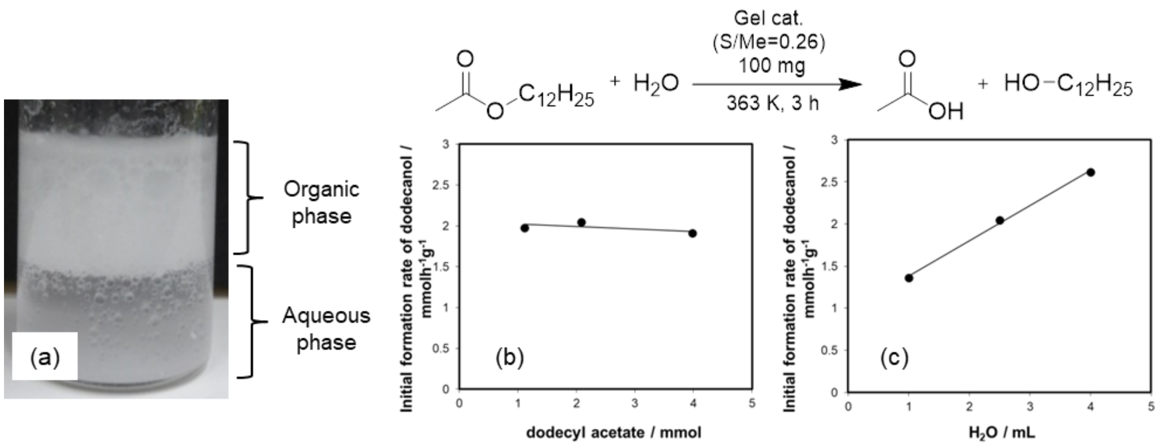

Figure 2. Image of two phase system with gel catalyst(S/Me=0.26) (a), and dependence of initial formation rate on amount of dodecyl acetate (b) and H_2O (c)

4. Conclusions

Siloxane gel catalysts with different surface hydrophobicity were successfully prepared. Hydrophobic gel catalyst showed higher activity for hydrolysis of dodecyl acetate than conventional solid acid catalysts. Hydrophobicity around acid sites was found to be important factor for hydrolysis of dodecyl acetate.

References

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