Acetalization of glycerol with ketones and aldehydes catalyzed by high silica Hβ zeolite

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ABSTRACT

In this work, proton-exchanged *BEA zeolite with a high Si/Al ratio of 75 (Hβ-75), was demonstrated as an effective catalyst for the acetalization of glycerol with carbonyl compounds. This catalyst system was applicable to various substrates and reusable for at least 4 times with slight decrease in activity. The turnover frequency, based on acid site concentration, increased as a function of Hβ Si/Al ratio, indicating the importance of the zeolite hydrophobic surface properties. The origin of the high efficiency exhibited by Hβ-75 is quantitatively discussed based on kinetic studies, hydrophobicity, and acid site concentration.

1. Introduction

Glycerol is considered as a common renewable biomass material, which is the main by-product in natural triglyceride methanolysis for biodiesel production [1]. Increased glycerol production, together with a concomitant decreasing commodity price, has resulted in glycerol becoming a promising substrate in numerous chemical processes across a broad range of industrial sectors, such as personal care products, soaps, pharmaceuticals and foods. However, the glycerol demand in the aforementioned sectors is not able to consume all the glycerol produced from the biodiesel industries. New opportunities for the conversion of glycerol into value-added chemicals have emerged in recent years. In this context, catalysts play an important role in realizing the selective transformation of glycerol. Various catalytic transformations have, hitherto, been developed to obtain valuable chemicals, such as acrolein, glycidol carbonate, syngas, propanediols, and epichlorohydrin [2–10].

Among the developed catalytic processes, the condensation of glycerol with carbonyl compounds to synthesize acetals (acetalization) has attracted significant attention because valuable cyclic acetals for diesel fuels and flavor compounds are obtained with the formation of H_2O as a non-toxic co-product [11–38]. Additionally, this reaction offers a sustainable alternative to the present acetal technology in organic synthesis. Homogeneous acid catalysts, including *p*-toluene-sulfonic acid (PTSA), HCl, H_3PO_4, and metal complex catalysts [11–13] have been utilized for the acetalization of glycerol with carbonyl compounds. However, after the reaction using these catalytic systems,

neutralization or tedious separation of homogeneous catalysts are required, which results in both environmental issues and poor techno-economics. To circumvent these issues, various heterogeneous catalyst systems, for example, transition metal catalysts [14–19], heteropoly acids [20–22], transition metal-oxides or phosphates [23–26], sulfonic acid-functionalized carbon materials [27–31], metal-organic frameworks [32,33], and aluminosilicate zeolites [34–38] have been developed. Among them, proton-exchanged aluminosilicate zeolites are promising materials as durable and practical heterogeneous catalysts, owing to their all-inorganic frameworks and commercial availabilities, as well as the absence of transition metal species [39]. For example, Mota et al. compared the activities of several proton-exchanged zeolites with Amberlyst-15 toward the acetalization of glycerol with acetone and formaldehyde [34]. In their experiments, Amberlyst-15 afforded the highest reaction yield in the presence of acetone, while higher yields were obtained in the presence of formaldehyde using proton-exchanged *BEA zeolite (Hβ), with a Si/Al ratio of 16, compared with Amberlyst-15 as well as ZSM5 and Y zeolites. Dealuminated and desilicated Hβs were synthesized and then applied to the acetalization of glycerol by Venkatesha et al. [35] and Bokade et al. [36], respectively. Both groups concluded that the enhanced catalytic performances were as a result of the increased pore volumes by dealumination or desilication. Very recently, Corma et al. demonstrated the acetalization of glycerol with 5-(alkyloxymethyl)furfural for the one-pot synthesis of biomass-derived surfactants using various Hβ zeolites and observed that the Hβ with a high Si/Al ratio of 100 exhibited high activity [37].

The aforementioned studies demonstrate the high potential of Hβ for the acetalization of glycerol with carbonyl compounds. However, quantitative studies, which focus on the effects of surface properties/acidity and substrate scope for carbonyl compounds, have not been reported, hitherto. Such studies would help elucidate zeolite catalysis including Hβ.

Our research group has previously developed efficient heterogeneous catalyst systems using Hβ zeolites for ester hydrolysis [40] and the hydration of alkynes/epoxides [41]. Furthermore, we have also quantitatively reported how this type of catalysis is influenced by acid site concentration and the catalyst surface hydrophobic/hydrophilic properties based on various adsorption experiments and kinetic studies. In this work, we investigated the glycerol acetalization efficiency of Hβ as a function of Si/Al ratio by comparing with other heterogeneous and homogeneous catalysts, and observed that Hβ, with relatively high Si/Al ratio of 75 (Hβ-75), showed the highest efficiency. The substrate scope for carbonyl compounds and the reusability of Hβ-75 were also examined. Furthermore, the effect of hydrophobicity and acid site concentration on the acetalization efficiency is discussed to provide insight into the high efficiency of Hβ-75.

2. Experimental

2.1. General

Commercial compounds (Tokyo Chemical Industry or Kanto Chemical Company) were used without further purification. GC–MS (Shimadzu GCMS-QP2010) analyses were performed using an Ultra ALLOY^{+}-1 capillary column (Frontier Laboratories Ltd.) with N_2 and He as the carrier gases. ^{1}H NMR analyses were performed using a JEOL-ECX 600 spectrometer operating at 600.17 MHz.
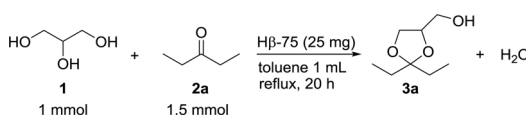
2.2. Catalyst preparation

Hβ-75 (JRC-Z-HB150, originally supplied from Clariant), Hβ-12.5 (JRC-Z-HB25), HMOR-45 (JRC-Z-HM90, originally supplied from Clariant), TiO_2 (JRC-TIO-4), CeO_2 (JRC-CEO-3), and amorphous SiO_2-Al_2O_3 (JRC-SAL-2) were provided by the Catalysis Society of Japan. Hβ-20 (HSZ-940HOA), Hβ-255 (HSZ-980HOA), HZSM5-20 (HSZ-840HOA) and HY-50 (HSZ-385HUA) were purchased from Tosoh Co. As-synthesized Hβ-5 (HSZ-940HOA), based on a previous report [42], was supplied from UniZeo Co., Ltd. HZSM5-11 was obtained by calcination of NH_4-ZSM5 having a Si/Al ratio of 11 (HSZ-820NHA, purchased from Tosoh Co.), at 550 °C for 3 h. HZSM5-75 and HZSM5-150 were obtained from N.E. CHEMCAT Co. Niobic acid ($Nb_2O_5 \cdot n H_2O$, HY-340) was kindly provided by CBMM. Nb_2O_5 was synthesized by calcination of the niobic acid (500 °C for 3 h). SiO_2 (Q-10) was provided by Fuji Silysia Chemical Ltd. ZrO_2 and SnO_2 were obtained by calcination of $ZrO_2 \cdot n H_2O$ and H_2SnO_3 (Kojundo Chemical Laboratory Co., Ltd.), at 500 °C for 3 h. Sulfonic acid-functionalized resin (Amberlyst-15) was commercially purchased from Sigma-Aldrich.

2.3. Catalytic tests

For a typical catalytic reaction, glycerol (1 mmol) was subjected to acetalization with aldehydes or ketones (1.5 mmol) in the presence of a catalyst (25 mg) and toluene (1 mL). The reaction mixture was added to a reaction tube (cylindrical Pyrex glass tube, 17 cm³), containing a magnetic stirrer bar and placed in a heated reactor, at reflux conditions, under a nitrogen atmosphere with stirring at 400 rpm. After completion of the reaction, methanol (2 mL) was added and catalyst was removed by filtration. The solvent was evaporated from the reaction mixture, and the acetal/ketal product yield and glycerol conversion in the crude mixture determined by ^{1}H NMR analysis (JEOL-ECX 600 spectrometer operating at 600.17 MHz, solvent CD_3OD) using mesitylene as an internal standard.

Table 1
Catalyst screening for the acetalization of glycerol (**1**) with 3-pentanone (**2a**).

Entry	Catalyst	Yield (%)[a]
1	none	0
2	Hβ-12.5	44
3	Hβ-20	48
4	Hβ-75	96
5	Hβ-255	77
6	HZSM5-11	43
7	HZSM5-20	46
8	HZSM5-75	68
9	HZSM5-150	62
10	HY-50	58
11	HMOR-45	61
12	Al_2O_3	48
13	ZrO_2	61
14	TiO_2	43
15	SnO_2	67
16	Nb_2O_5	54
17	$Nb_2O_5 \cdot n H_2O$	65
18	SiO_2	16
19	CeO_2	13
20	$Cs_{2.5}H_{0.5}PW_{12}O_{40}$	62
21	Amberlyst-15	2
22	Montmorillonite K10	56
23[b]	H_2SO_4	25
24	PTSA	44
25	$Sc(OTf)_3$	28

[a] Yields of **3a** were determined by ^{1}H NMR spectroscopy.
[b] 40 wt.% aqueous solution.

3. Results and discussion

3.1. Comparison of Hβ zeolites with various acid catalysts

Initially, the acetalization of glycerol (**1**) with 3-pentanone (**2a**) was investigated using a wide matrix of 24 heterogeneous and homogenous catalyst types, by refluxing in toluene for 20 h. The results are summarized in Table 1. Under these conditions, the reaction does not proceed in the absence of any catalyst (entry 1). Among the catalysts tested, Hβ-75 afforded the highest yield (96%) of the five-membered cyclic acetal (**3a**) (entry 4), without the formation of the corresponding six-membered cyclic acetal. The Si/Al ratio of Hβ is observed to influence the **3a** yield, which increased as a function of increased Si/Al ratio from 12.5 to 75 (entries 2–4), while the use of Hβ-255 resulted in a lower yield compared with Hβ-75 (entry 5). A similar dependency on the Si/Al ratio was observed using a series of proton-exchanged ZSM5 (HZSM5) zeolites having Si/Al ratios between 11 and 150 (entries 6–9). HZSM5-75 exhibited a higher yield compared with the other HZSM5 catalysts (entry 8), although HZSM5-75 was inferior to Hβ-75. The zeolites possessing a relatively high Si/Al ratio of 75 exhibited high catalytic performance. The performance of Hβ-75 with other heterogeneous acid catalysts was compared, including other proton-exchanged zeolites (HY-50 and HMOR-45), metal oxides (Al_2O_3, ZrO_2, TiO_2, SnO_2, Nb_2O_5, $Nb_2O_5 \cdot n H_2O$, SiO_2, and CeO_2), a heteropoly acid ($Cs_{2.5}H_{0.5}PW_{12}O_{40}$), and commercially-available solid acid catalysts (Amberlyst-15 and Montmorillonite K10). Moderate-to-good yields (43–67%) of **3a** were obtained in the presence of Al_2O_3, ZrO_2, TiO_2, SnO_2, and Nb_2O_5 (entries 12–16). $Nb_2O_5 \cdot n H_2O$, known as a water-tolerant solid acid [43], also exhibited an acceptable yield of 65% (entry 17). However, all **3a** yields were lower when compared with the yield for Hβ-75. Conversely, the yields for SiO_2 and CeO_2 were significantly lower (entries 18 and 19). $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ and montmorillonite K10 exhibited moderate activity, forming **3a** in 62% and 56% yields (entries

20 and 22), respectively, while the use of Amberlyst-15 resulted in a poor yield (entry 21). In the previous work [34], the authors compared the catalytic activity between Amberlyst-15 and the Hβ with Si/Al = 16 in acetalization of glycerol with acetone (as reactant and solvent). One of the main reasons for higher activity of Hβ-75 than Amberlyst-15 in this work might be its hydrophobic nature, as discussed in 3.4 Relationship between activity and hydrophobicity/acidity (vide infra). Furthermore, typical homogeneous catalysts, such as H_2SO_4, PTSA, and $Sc(OTf)_3$, were applied to this reaction, however, the resultant yields of 3a were low (25%, 44%, and 28%, respectively). The low activities of homogenous acids for acetalization were reported in the previous paper [44]. Besides, metal triflates and mineral acid (H_2SO_4) are potential in dimerization of glycerol to give the corresponding ether [45]. The low yield of the acetalization product using homogeneous catalysts are ascribed to the low reactivity and formation of the dimerization product of glycerol. From the above results, Hβ-75 is deemed the most effective catalyst for the acetalization of glycerol with ketone **2a**.

3.2. Optimization of reaction conditions

Using the most effective catalyst, Hβ-75, the optimal reaction conditions were determined for the acetalization of **1** with **2a** (Table 2). In the presence of **1** (1 mmol), **2a** (1 mmol), and toluene (1 mL), the use of Hβ-75 (25 mg) afforded the highest yield (entries 1–5). The influence of ketone **2a** content was studied (0.5–1.5 mmol) using Hβ-75 (25 mg) and **1** (1 mmol) in toluene (entries 5–8). Although the use of an equimolar amount of **2a** gave **3a** in 85% yield (entry 5), **2a** in slight excess (1.25–1.5 mmol) is required to achieve > 90% yield (entries 7 and 8). Furthermore, the influence of the solvent was examined through a series of experiments comprising **1** (1 mmol), **2a** (1.5 mmol), and Hβ-75 (25 mg) for 20 h (entries 8–12). The aromatic solvents, such as toluene, *o*-xylene, and mesitylene, were effective (entries 8–10), with toluene being observed to be the most efficient solvent studied (entry 8). The use of 1,4-dioxane resulted in a significantly lower yield of **3a** (entry 11). Conversely, acetalization did not proceed using H_2O as a solvent (entry 12). Furthermore, time-on-stream was also investigated, as shown in Fig. 1. Glycerol was not observed after 10 h, while the yield of **3a** reached the highest value of 96% after 20 h. Based on these results, the optimized reaction conditions were determined as follows: **1** (1 mmol), **2a** (1.5 mmol), Hβ-75 (25 mg), and toluene (1 mL) under reflux for 20 h.

3.3. Substrate scope and reusability of Hβ-75

After establishing the optimized reaction conditions, the substrate

Table 2
Optimization of the acetalization reaction conditions using Hβ-75 catalyst.

Entry	Hβ-75 (mg)	1 (p mmol)	2a (q mmol)	Solvent	Yield (%)[a]
1	5	1	1	toluene	42
2	10	1	1	toluene	51
3	15	1	1	toluene	73
4	20	1	1	toluene	81
5	25	1	1	toluene	85
6	25	1	0.5	toluene	41
7	25	1	1.25	toluene	91
8	25	1	1.5	toluene	96
9	25	1	1.5	*o*-xylene	88
10	25	1	1.5	mesitylene	83
11	25	1	1.5	1,4-dioxane	23
12	25	1	1.5	H_2O	0

[a] Yields of **3a** were determined by ^1H NMR spectroscopy.
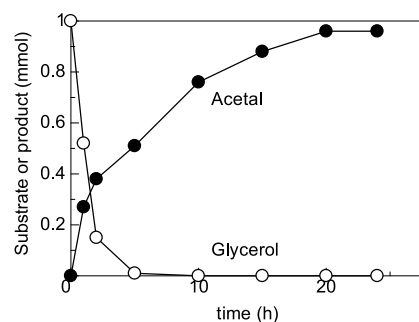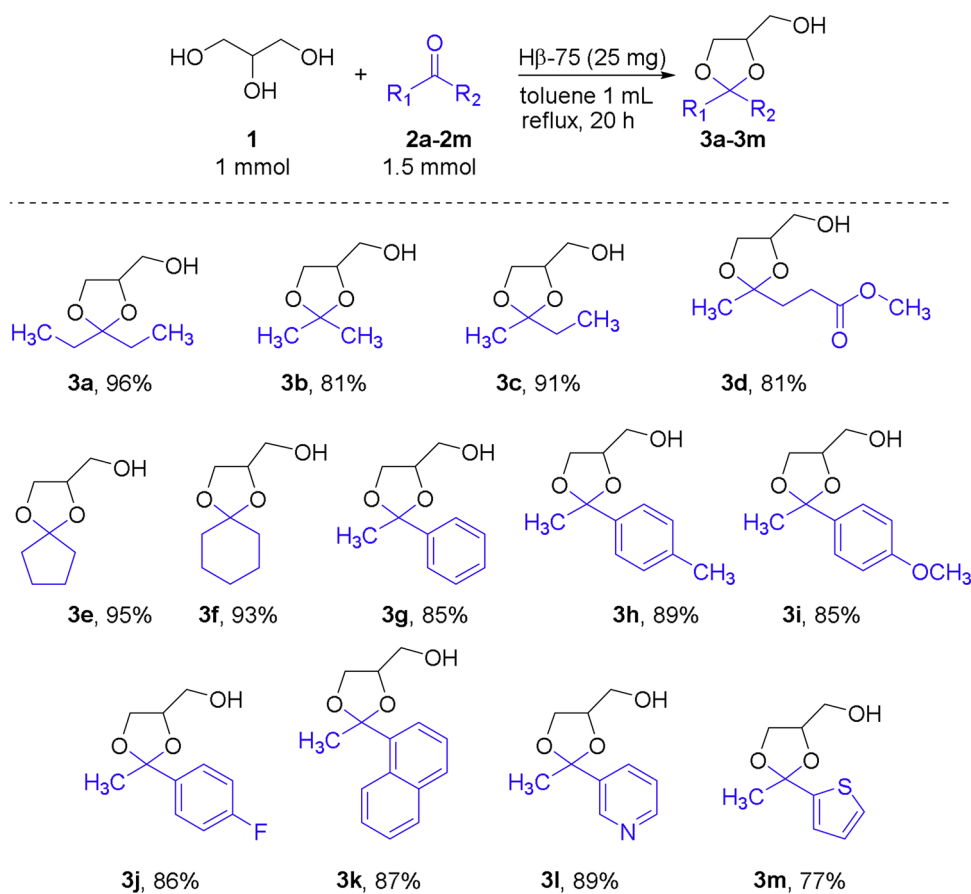

Fig. 1. Acetalization of glycerol (**1**) with 3-pentanone (**2a**) to the corresponding acetal (**3a**) as a function of time-on-stream. Reaction conditions: Hβ-75 (25 mg), **1** (1 mmol), **2a** (1.5 mmol), toluene (1 mL), refluxed under a N_2 atmosphere for 0–24 h.

scope toward ketones amenable to the Hβ-75-catalyzed acetalization with glycerol **1** was studied. The products **3a**–**3m**, together with their respective yields, are summarized in Scheme 1. Various acyclic (**2a**–**2d**) and cyclic (**2e**, **2f**) ketones reacted efficiently with **1** to give the corresponding ketals **3a**–**3f** in 81%–96% yield. Acetophenone (**2g**) and its derivatives, possessing either electron-donating (**2h** and **2i**) or electron-withdrawing groups (**2j**), were also amenable to acetalization with glycerol. During the acetalization, the ester and methoxy moieties in the products (**3d** and **3i**) were retained. Furthermore, Hβ-75 promoted the acetalization of ketones having a bulky naphthalene ring (**2k**) as well as heterocycles (**2l** and **2m**), affording the desired products in good yields. Additionally, the substrate scope toward aldehydes in the present catalyst system was also studied (Scheme 2). The reaction of formaldehyde (**4a**) with **1** efficiently occurred, giving 1,3-dioxolane-4-methanol (**5a**) in 91% yield. The aldehydes incorporating furan (**4b** and **4c**) or phenyl rings (**4d**, **4e**) underwent acetalization with **1** to form the corresponding products **5b**–**5e** in 82%–93% yields. During the acetalization of cinnamaldehyde (**4e**), the olefinic moiety was tolerant. Overall, Hβ-75 efficiently promoted the acetalization of various ketones and aldehydes possessing numerous functional groups. The applicability of Hβ-75 to the reaction of bulky substrates is ascribed to its large pore size; the minimum cross-section diameters of products, **3d** and **3k**, are 7.2 Å × 7.8 Å and 7.5 Å × 8.4 Å, respectively, which are comparable to the Hβ pore size (7.6 Å × 7.3 Å). All the substrates and products can be considered to diffuse within the pores of Hβ.
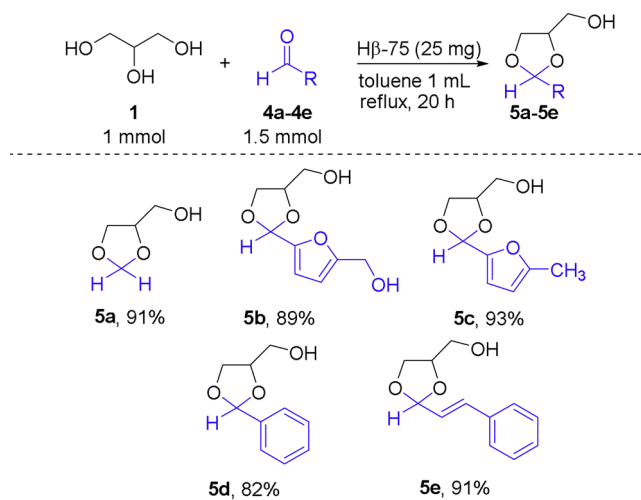
After the acetalization of glycerol and ketone **2a**, Hβ-75 was easily separated from the reaction mixture by centrifugation. The recovered catalyst was washed with acetone, dried at 90 °C for 3 h, and then reused for another reaction. Although product yields decreased slightly, Hβ-75 was recyclable in at least four reuse experiments (Fig. 2). Furthermore, acetalization reactions of glycerol with **2a**, **2g**, **4c**, and **4d** were performed on a 5 mmol scale. As summarized in Scheme 3, the desired products (**3a**, **3g**, **5c**, and **5d**) were successfully obtained in 79%–91% yield. These results demonstrate the promising potential of Hβ-75 for practical applications in the acetalization of glycerol.

3.4. Relationship between activity and hydrophobicity/acidity

Previously, we determined the hydrophobicity/hydrophilicity of Hβ as a function of Si/Al ratio (Si/Al = 12.5–255) by *n*-dodecane/H_2O adsorption experiments and revealed that hydrophobicity monotonically increases with increased Si/Al ratio (Fig. 3C) [41]. A similar dependency of hydrophobicity on the Si/Al ratio was reported by Fukuoka et al. [46] and Yokoi et al. [47]. The quantitative determination of acid sites was also studied by NH_3 adsorption experiments using IR spectroscopy [41,48]. The acid sties in Hβ (Si/Al = 12.5–255) comprised principally of Brønsted acid sites, and the Brønsted acid site concentration decreases with increasing Si/Al ratio (Fig. 3D) [41]. Based on such adsorption experiments and kinetic studies, we further

Scheme 1. Acetalization of glycerol with different ketones. Ketal yields were determined by ^{1}H NMR spectroscopy.

Scheme 2. Acetalization of glycerol with different aldehydes. Acetal yields were determined by ^{1}H NMR spectroscopy.

Fig. 2. Catalyst reusability for the Hβ-75-catalyzed acetalization of glycerol (**1**) with 3-pentanone (**2a**). Reaction conditions: Hβ-75 (25 mg), **1** (1 mmol), **2a** (1.5 mmol), toluene (1 mL), refluxed under a N_2 atmosphere for 20 h.

reported the influence of hydrophobicity/acidity on the hydration catalysis [41].

During the acetalization of glycerol with ketone **2a**, as shown in Table 1, Hβ-75, with relatively high Si/Al ratio, is observed to be the most effective catalyst among the Hβ zeolites having Si/Al ratios ranging from 12.5 to 255 (entries 2–5). Similar phenomena were observed in the experiments using HZSM5 having a broad range of Si/Al ratios (entries 6–9). To elucidate the origin of the high efficiency observed for Hβ-75, the initial reaction rates (V_{init}) of a series of Hβ catalysts were
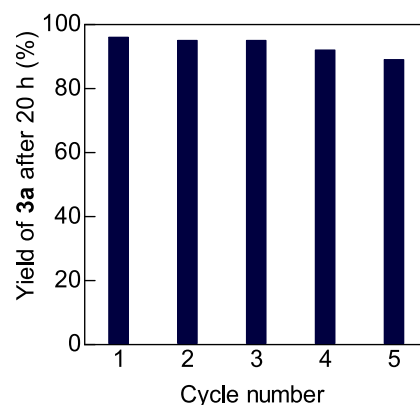
measured at below 20% conversion. It is noted that we focused on proton-type zeolites having mainly Brønsted acid sites but not metal oxides for this discussion because of difficulty in generalizing the activity difference between proton-type zeolites and metal oxide catalysts generally having both Brønsted and Lewis acid sites [32,43]. The reaction rate exhibited a volcano-type dependency on the Si/Al ratio (Fig. 3A), with Hβ-75 exhibiting the highest V_{init} value (11.3 mmol $h^{-1}g_{cat}^{-1}$). Conversely, the turnover frequency value, determined based on the Brønsted acid site concentration [34], monotonically increased with increasing Si/Al ratio (Fig. 3B), which is similar to the dependency of hydrophobicity on the Si/Al ratio (Fig. 3C). Based on these results obtained by kinetic studies and adsorption experiments,
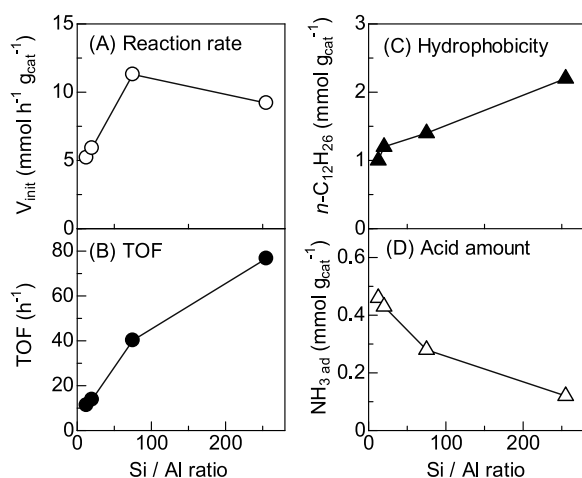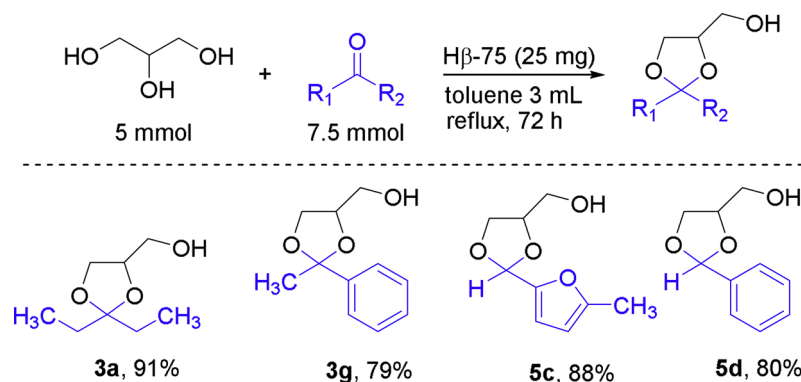
Scheme 3. 5 mmol-scale acetalization of glycerol catalyzed by Hβ-75.

Fig. 3. Results of the kinetic studies and adsorption experiments. (A) Initial reaction rate and (B) turnover frequencies (TOF), normalized to Brønsted acid site concentration, versus Hβ Si/Al ratio, for the acetalization of glycerol (**1**) with 3-pentanone (**2a**). (C) Hydrophobicity, as estimated by *n*-dodecane adsorption [41] and (D) total Hβ Brønsted acid site concentration [41] as a function of Si/Al ratio.

the hydrophobic nature of the Hβ catalysts is suggested to accelerate the acetalization effectively. On the hydrophobic inner pore surface, the generated H_2O molecule, as a co-product, easily desorbs, thus accelerating the acetalization reaction. Hβ-75 is tailored to possess both a suitable hydrophobic nature and a sufficient acid site concentration in the pores, which promotes acetalization. The higher efficiency observed for Hβ-75, compared with HZSM5-75, is interpreted by a difference of pore size. The Hβ pore size (7.6 Å × 7.3 Å) is larger than HZSM5 (5.6 Å × 5.3 Å). As a consequence, the product **3a**, having the minimum cross-section diameter of 6.2 Å × 7.6 Å (See Supporting Information), can more effectively ingress and diffuse within the larger pores of Hβ, resulting in enhanced catalytic performance of Hβ-75, compared with HZSM5-75 [40].

4. Conclusions

Hβ-75 exhibited the highest catalytic performance toward acetalization using glycerol among 21 various types of heterogenous acid catalysts. The present catalyst system was amenable to the acetalization of numerous ketones and aldehydes to afford the corresponding products in good yields. The catalyst was also observed to be easily separated from the catalytic process and recyclable without demonstrating a significant loss in activity. The wide substrate scope and high recyclability of Hβ-75 offer advantages from a practical viewpoint. The kinetic studies and adsorption experiments using Hβ, as a function of Si/Al ratio, indicated that the acid sites present at the hydrophobic pore

surface promoted acetalization more efficiently. The data provide a platform to develop further efficient acid catalysts for acetalization. The high activity of Hβ-75 is realized by the tailored hydrophobic nature of the catalyst surface, a sufficient number of accessible acid sites and in having a larger pore size compared with HZSM5.

Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:https://doi.org/10.1016/j.mcat.2019.110608.

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