Efficient Ketones Synthesis via Catalytic Hydration over Hydrophobic Zeolites

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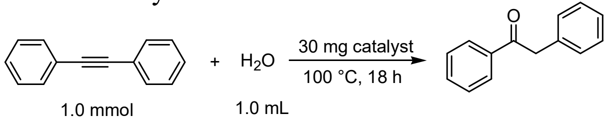
Catalytic hydration of alkynes is of particular importance in organic synthetic chemistry because the resulting carbonyl compounds are useful in bulk and fine chemical industries. Conventional catalysis in industrial processes use Hg(II) salts together with large amount of acids such as H_2SO_4. However, these catalytic systems suffer from the high toxicity of Hg. Although various catalytic systems have been reported for the reaction, systems having both high activity and reusability are still rare [1].

We report herein that a HBEA zeolite with a moderate Si/Al ratio (Si/Al =75), HBEA-75, serves as an effective and reusable catalyst for hydration of alkynes. In the initial phase of this study, hydration of diphenylacetylene was utilized as a model reaction to screen various acid catalysts (Table 1). The reaction was carried out at 100 °C by using diphenyl-acetylene (1.0 mmol), water (1.0 ml), catalyst (30 mg) and *n*-dodecane (0.2 mmol) as an internal standard. HBEA-75 gave 98% yield of the corresponding ketone after the reaction time of 18 h. As demonstrated in Table 1, HBEA zeolites lead to higher yield than those observed over HZSM-5 zeolites. This result could be because of the large pore size of the BEA structure compared to the MFI structure. It was also demonstrated that a moderate Si/Al ratio gave high reaction rate as shown in Fig .1. This fact suggests that both hydrophobicity and the number of acid sites play important roles for the progression of the reaction as in the case with our previous study describing catalytic hydrolysis of hydrophobic esters over HBEA zeolites [2]. As a result, HBEA-75 having large pore size and a moderate Si/Al ratio was found to be the most effective catalyst for hydration of diphenylacetylene. It was also confirmed that the HBEA-75 zeolite showed a broad range of substrate scope under the same condition.

Table 1. Hydration of diphenylacetylene over various catalysts.[a]



Entry	Catalyst	Conv. (%)[b]	Yield (%)[b]
1	HBEA-12.5	46	44
2	HBEA-20	53	51
3	HBEA-75	100	98
4	HBEA-255	12	10
5	HZSM-5-11	3	2
6	HZSM-5-22.5	5	3
7	HZSM-5-75	12	11
8	HZSM-5-150	16	15
9	SiO_2	18	16
10	ZrO_2	3	2
11	TiO_2	8	6
12	SnO_2	5	4
13	CeO_2	2	1
14	Nb_2O_5	6	5
15	H_2SO_4	6	5

[a] 30 mg catalyst, 1.0 mmol diphenylacetylene, 1.0 mL water, 100 °C, 18 h. [b] Conversions and yields were determined by GC analyses.

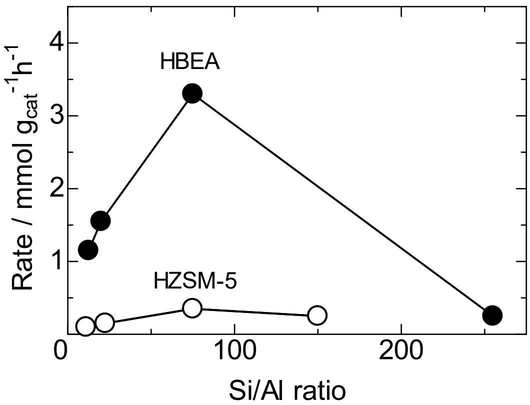


Fig.1 Initial rates for hydration of diphenyl acetylene versus the Si/Al rations in the HBEA and HZSM-5 catalysts.

REFERENCE

[1] N. Mameda, et al., Appl. Catal. A, 505 (2015) 213.

[2] S.M.A.H. Siddiki, et al., J. Catal., 341 (2016) 744.