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Solvent-free hydration of alkynes over Hβ zeolite

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ABSTRACT

An efficient and environmentally benign catalytic system has been successfully developed for highly Markovnikov selective hydration of various alkynes over heterogeneous catalyst (Hβ zeolite) in solvent-free conditions. The catalyst (Hβ zeolite) is commercial available, recyclable and exhibits excellent catalytic activity towards the hydration of alkynes to ketones. Moreover, the propargylic aryl carbinols undergo Meyer–Schuster rearrangement to give α,β-unsaturated carbonyl compounds in excellent yields.

1. Introduction

Catalytic hydration of CC triple bond is one of the most straightforward and environmentally benign method to form C—O bond. In this respect, Markovnikov hydration of alkynes is a convenient and efficient method for the production of ketones and the reaction involves the simple addition of a water molecule to the alkyne with 100% atom efficiency [1,2]. Ketones are unambiguously important motifs in modern organic synthesis. Mercury (II) salts combined with acids, such as HgO/H_2SO_4 and HgO/BF_3, are reliable catalysts for the hydration of alkynes and these catalysts were extensively used in high-scale industrial processes until the discovery of the toxicity of mercury salts [3,4]. Alternative metallic catalysts have been searched over the years, mainly transition metal based catalysts, such as Pt [5,6], Fe [7,8], Pd [9], Ir [10], Ag [11,12], Os [13] and Au [14,15]. Whereas, most of these metal catalysts have shortcomings, such as lower reactivity, recovery and reuse of (expensive) catalysts and prohibit their frequent use for laboratory as well as industrial purpose. In addition, use of concentrated solution of strong acids (H_2SO_4 [16], CF_3SO_3H [17] and PTSA [18]) is known to promote the alkyne hydration process. Nevertheless, it not always fruitful for large scale preparations.

In recent years, green and economical considerations have raised strong attention to redesign commercially important processes to avoid the use of harmful reagents and the generation of toxic waste. In this respect, the development of easily recyclable and recoverable heterogeneous catalysts can solve the problems of the homogeneous systems and has received particular research interest by synthetic organic chemists [19]. In view of this, the hydration of 4-ethynyltoluene over heterogeneous polystyrene supported sulfonic acid using a catalytic amount of triflic acid was reported by Kobayashi et al. [20]. But applicability of this method is limited to only 4-ethynyltoluene. Hexing Li and coworkers reported the Au^I-modified mesoporous silica for the hydration of alkynes [21]. Although, this catalyst showed high efficiency, mineral acid (H_2SO_4) is required as a co-catalyst (10 mol%). Later Mizuno and coworkers [22] reported an efficient hydration of various alkynes using heterogeneous Sn–W mixed oxide catalyst. However, main drawback associated with this method is the need of organic solvent as reaction medium.

For reasons of economy and pollution prevention, solvent-free methods [23,24] are used to revise classical procedures by making them cleaner, safer and easier to perform. To the best of our knowledge, there are only two reports on the solvent-free hydration of alkynes using heterogeneous catalysts, for example, Au nanoparticle-acid catalyst (Au–HS/SO_3H-PMO(Et) [25] and silver

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exchanged silicotungstic acid (AgSTA) [26]. However, the preparation of Au–HS/SO_3H-PMO(Et) catalyst is very expensive [25] and the catalytic activity of AgSTA is low towards internal alkynes [26]. Therefore, the development of an inexpensive, more efficient, solvent-free and eco-friendly heterogeneous hydration systems without any additives is highly desirable.

Catalysts based on zeolites possess major importance both in petroleum and fine chemical industries [27,28]. This is mainly due to the fact that zeolites have uniform channel size and unique molecular shape selectivity, as well as strong acidity and good thermal/ hydrothermal stability. The BEA-type of zeolite consists of an intergrowth of two or more polymorphs comprised of a three dimensional system of 12-membered ring channels [29]. The BEA framework topology attracts much attention because of the large available micro-pore volume, large-pore channel system and the presence of active sites (Bronsted acid sites in the micropores and on the external surface and Lewis acid sites predominantly at the internal surface due to the local defects) in different concentrations. In continuation of our efforts toward the development of novel and eco-friendly synthetic protocols using zeolites [30–32], herein we report a simple, efficient and environmentally benign approach for the hydration of alkynes using zeolite under solvent-free conditions.

2. Experimental

2.1. General information

Alkynes were purchased from Sigma–Aldrich. Hβ (Si/Al = 15) zeolite was obtained from Alfa Aesar, England. All chemicals used were reagent grade and used as received without further purification. All the samples were systematically characterized by different spectroscopic techniques. The XRD patterns of the samples were obtained on a Regaku miniflux X-ray Diffractometer using Ni filtered CuKα radiation at $2\theta = 2\ 80^\circ$ with a scanning rate of 2° min^{-1} and the beam voltage and currents of 30 kV and 15 mA, respectively. ^{1}H NMR spectra were recorded by using Bruker VX NMR FT-300 or Varian Unity 500 and ^{13}C NMR spectra were recorded by using Bruker VX NMR FT-75 MHz spectrometers instrument in $CDCl_3$. The chemical shifts (δ) are reported in ppm units relative to TMS as an internal standard for ^{1}H NMR and $CDCl_3$ for ^{13}C NMR spectra. Coupling constants (J) are reported in hertz (Hz) and multiplicities are indicated as follows: s (singlet), d (doublet), dd (doublet–doublet), t (triplet), q (quartet), m (multiplet). Column chromatography was carried out using silica gel (100–200 mesh).

2.2. General procedure for hydration of alkynes

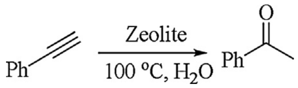
Reactions were performed in a magnetically stirred round bottomed flask fitted with a condenser and placed in a temperature controlled oil bath. Zeolite (Hβ) (100 mg) was added to the well stirred solution of alkyne (2 mmol) and H_2O (8 mmol) and the reaction mixture was allowed to stir at 100 °C. After disappearance of the alkyne (monitored by TLC) or after an appropriate time, the reaction mixture was cooled to room temperature, diluted with ethyl acetate. The catalyst was separated by filtration and the removal of solvent in vacuo yielded residue. and it was further purified by column chromatography using silica gel (100–200 mesh) to afford pure products. All the products were identified on the basis of H^{1}and C^{13} NMR spectral data.

3. Results and discussion

3.1. Catalyst screening

In the initial investigation, phenylacetylene was selected as a model substrate for alkyne hydration to find out the best reaction conditions (Table 1). In order to choose the best catalyst first, the reaction was carried out over various zeolites and other catalysts at 100 °C for 3 h and the results are presented in Table 1 (entries 1–12). Among the catalysts examined, Hβ zeolite showed a higher catalytic activity and furnished the corresponding methyl ketone in excellent yield (Table 1, entry 1). Under the similar reaction conditions, H-mordenite, HZSM-5 (40) and montmorillonite K10 provided the corresponding methyl ketones in < 60% yield (Table 1, entries 2–5). NaY and MCM-41delivered virtually no conversion of starting material (Table 1, entries 6–7). When the acidic resins, homogeneous Bronsted acids and heterogeneous Lewis acid catalysts were investigated under similar reaction conditions, the hydration product was obtained in up to 33% yield (Table 1, entries 8–12). Once Hβ catalyst was found as the best catalyst for hydration of phenylacetylene, the influence of a catalyst amount was studied. By varying the catalyst amount from 50 to 100 mg, a gradual improvement in yield (25–98%) was observed and any further increase of amount did not have accountable effect on the yield (Table 1, entries 1 and 13–14). In the absence of catalyst no hydration of phenylacetylene was observed, thus confirming the role of the catalyst in the reaction (Table 1, entry 15).

Table 1
Optimization of reaction conditions for the hydration of phenylacetylene.[a]

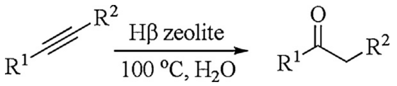


Entry	Water (mmol)	Catalyst	Temperature (°C)	Yield[b] (%)
1	8	Hβ	100	98
2	8	H-mordenite	100	60
3	8	HZSM-5 (40)	100	58
4	8	Montmorillonate K10	100	27
5	8	HY	100	50
6	8	NaY	100	00
7	8	MCM-41	100	00
8	8	Amberlyst-15	100	8
9	8	Amberlite	100	12
10	8	H_2SO_4[c]	100	33
11	8	HCl[c]	100	31
12	8	$Nb_2O_5.nH_2O$	100	00
13	8	Hβ	100	25[d]
14	8	Hβ	100	56[e]
15	8	N/A[f]	100	00
16	8	Hβ	RT	00
17	8	Hβ	60	07
18	8	Hβ	80	58
19	N/A[f]	Hβ	100	30
20	4	Hβ	100	57
21	6	Hβ	100	85

[a] Reaction conditions: phenylacetylene (2 mmol), H_2O (8 mmol), Catalyst (100 mg), 100 °C, 3 h.
[b] Isolated yields.
[c] 0.25 mmol of catalyst.
[d] Catalyst (50 mg).
[e] Catalyst (75 mg).
[f] N/A refers to not applicable.

The reaction was remarkably accelerated by varying the reaction temperature from room temperature to 100 °C (Table 1, entries 1 and 16–18) and yield improved progressively from 0 to 98%. The mole ratio of phenyl acetylene to H_2O also had a significant influence on the product yield. When increasing the mole ratio of phenyl acetylene to H_2O (1:0–1:4), the yield of the desired product was increased from 30 to 98% (Table 1, entries 1 and 19–21). As can be seen from the above obtained results, the optimized reaction conditions to get the highest yield for this hydration reaction are 1:4 mole ratio of phenylacetylene to H_2O at 100 °C over Hβ catalyst (100 mg).

Table 2
Hydration of alkynes over Hβ zeolite.[a]



Entry	R^1	R^2	Time (h)	Yield[b] (%)
1	Ph	H	3	98
2	4-MePh	H	4	98
3	4-C_5H_{11}Ph	H	4	96
4	4-FPh	H	2	97
5	3KClPh	H	3	95
6	C_5H_4N	H	24	00
7	6-MeO-$C_{10}H_7$	H	4	98
8	n-C_8H_{14}	H	24	80
9	n-$C_{10}H_{22}$	H	24	78
10	Ph	CH_3	20	90
11	Ph	C_2H_5	22	93
12	Ph	C_4H_9	24	83
13	Ph	Ph	24	65

[a] Reaction conditions: Alkyne (2 mmol), H_2O (8 mmol), Hβ (100 mg), 100 °C.
[b] Isolated yields.

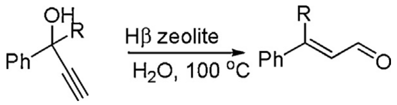
3.2. Hydration of alkynes

To demonstrate the generality of the Hβ-catalyzed alkyne hydration reaction, we probed different substrates with significant structural variation under optimized conditions. All the substrates were efficiently converted into corresponding ketones in good to excellent yields. The results are depicted in Table 3. For all of the terminal alkynes in Table 2, ketones (Markovnikov addition) were obtained exclusively, without the formation of respective aldehydes (anti-Markovnikov addition). Phenylacetylene substituted with either activating (alkyl) (Table 2, entries 2–3) or deactivating groups (halide) (Table 2, entries 4–5), reacted smoothly and furnished the corresponding methyl ketones in excellent yields under these reaction conditions. Unfortunately, hydration of electron-poor heteroaryl alkyne, i.e., 2-ethynylpyridine failed to give any product under similar conditions even after prolonged reaction time (Table 2, entry 6). 2-Ethynyl-6-methoxynaphthalene also reacted easily and gave the corresponding ketone in 98% yield (Table 2, entry 7). Simple aliphatic alkynes, such as 1-octyne and 1-decyne were efficiently converted into 2-octanone and 2-decenone in 80% and 78% yields, respectively (Table 2, entries 8 and 9), but require longer reaction times compared to aromatic terminal alkynes.

Next, we investigated the efficiency of the method with internal alkynes (Table 2, entries 10–13). The hydration of asymmetrically substituted aryl-alkyl alkynes, proceeded smoothly under standard conditions to give the corresponding phenyl alkyl ketones in high yields with excellent regioselectivity (Table 2, entries 10–12). The exclusive Markovnikov regioselectivity is likely due to the stabilization of a transient vinyl cation through conjugation with the pi-electrons of the aromatic ring. In the case of symmetrical internal alkyne i.e., diphenylacetylene, the desired product was obtained in slightly lower yield than aryl-alkyl alkynes probably because of steric hindrance (Table 2, entry 13). In case of incomplete conversions, the starting materials were recovered along with the desired hydration products (Table 2, entries 8–13).

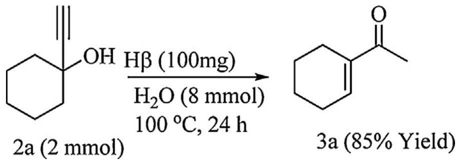
Finally, we studied the hydration of propargylic alcohols under similar reaction conditions (Table 3 and Scheme 1). Interestingly, the propargylic alcohols did not afford the expected methyl ketones, but underwent the Meyer-Schuster rearrangement or Rupe-rearrangement [33]. For example, 1-Phenylprop-2-yn-1-ol and 1,1-diphenyl-2-propyn-1-ol provided the Meyer-schuster rearrangement products in 90% and 93 % yields, respectively (Table 3, entries 1–2), whereas 2-phenyl-3-butyn-2-ol gave a mixture of *E* and *Z* stereoisomers of corresponding Meyer-schuster product (Table 3, entry 3). Notably, in the case of 1-ethynylcyclohexanol (**2a**), the Rupe-rearrangement product (**3a**) was obtained in 85% yield (Scheme 1).). There was no leaching of aluminium or silicon from zeolite (Hβ) and confirmed by elemental analysis.

Table 3
Meyer–Schuster rearrangement of propargylic aryl carbinols over Hβ zeolite.[a]



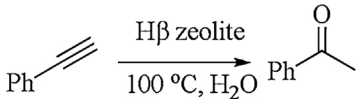
Entry	R	Time (h)	Yield[b] (%)
1	H	10	90
2	Ph	15	93
3	CH_3	15	98[c]

[a] Reaction conditions: propargylic aryl carbinol (2 mmol), H_2O (8 mmol), Hβ (100 mg), 100 °C.
[b] Isolated yields.
[c] *E*/*Z* = 58:40.



Scheme 1. Rupe-rearrangement of 1-ethynylcyclohexanol over Hβ zeolite.

Table 4
Hydration of phenylacetylene - reusability of the catalyst.[a]



Entry	Cycle	Yield[b] (%)
1	First	98
2	Second	97
3	Third	95

[a] Reaction conditions: Phenylacetylene (2 mmol), H_2O (8 mmol), Hβ (100 mg), 100 °C.
[b] Isolated yields.

The plausible reaction mechanism for the hydration of alkyne over Hβ zeolite is illustrated in Scheme 2

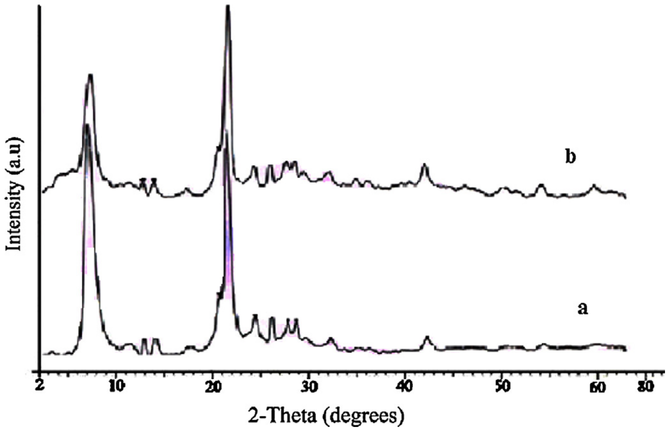
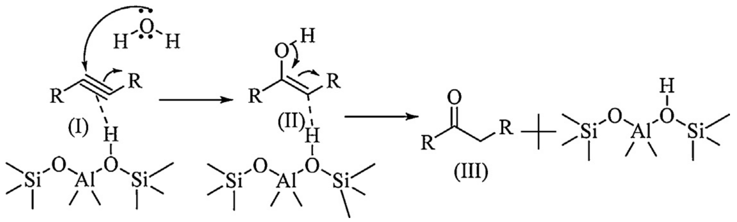


Fig. 1. XRD patterns of Hβ zeolite: (a) Before reaction (b) After reaction.



Scheme 2. Plausible reaction mechanism for the hydration of alkynes.

3.3. *Reusability of catalyst*

The reusability of the catalyst is one of the most significant property for the industrial applications and environmental considerations. The catalyst (zeolite) was easily separated from the reaction mixture by simple filtration. Further, recycling of catalyst was carried out by performing the reaction with phenyl acetylene under standard reaction conditions and the reused catalyst showed consistent activity even after third reuse (Table 4). The catalyst was highly crystalline before and after the reaction, which was confirmed by XRD (Fig. 1. Based on the literature report [34], it is assumed that the alkyne (**I**) adsorbs on the Bronsted acid sites of zeolite. Subsequently, nucleophilic attack of H_2O on the triple bond of alkyne to give a vinylic alcohol (**II**), which further undergoes keto-enol tautomerism to produce the respective ketone (**III**) as the final product.

4. Conclusion

In summary, an effective and green protocol for the transformation of various alkynes to ketones using zeolite (Hβ) as a heterogeneous catalyst under solvent-free conditions has been successfully developed. Notable advantages offered by this strategy are absence of organic solvent, broad substrate scope, high atom economy, use of non-hazardous and reusable catalysts, higher yields of the desired products, simple work-up procedure and mild reaction conditions, which make it an attractive and useful alternative to the existing methods.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.apcata.2015.07.038

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