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Solvent-free hydration of alkynes over a heterogeneous silver exchanged silicotungstic acid catalyst

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Silver exchanged silicotungstic acid (AgSTA) catalysts were prepared and characterized by X-ray diffraction, FT-IR spectroscopy, laser Raman, temperature programmed desorption of ammonia, FT-IR pyridine adsorption and X-ray photo electron spectroscopy. The activity of the catalysts was evaluated for the hydration of non-activated alkynes to corresponding carbonyl compounds without addition of any acid co-catalyst under solvent-free conditions. The highest catalytic activity was obtained for the catalyst with partially silver exchanged STA. This catalytic system provides one of the most straight forward syntheses of carbonyl compounds from terminal alkynes with Markovnikov-type regioselectivity. The catalyst can be recovered by simple filtration and is reusable without loss of activity and selectivity. A plausible reaction mechanism for the AgSTA catalyzed hydration of alkynes is proposed.

Introduction

The catalytic addition of O-H bonds to alkynes, leading to the formation of carbonyl compounds is of major interest, allowing for the wide availability of alkynyl substrates and the fundamental importance of carbonyl compounds in modern organic synthesis.¹ The reaction proceeds by the addition of water to the metal π -alkyne complex, according to Markovnikov's rule, to form the corresponding ketone compound. This reaction has long been catalyzed by mercury(II) sulfate in aqueous sulfuric acid solution in which the mercury ion acts as a Lewis acid.² This catalyst has disadvantages, such as the toxicity of mercury and the requirement of strong acidic conditions. Therefore, various transition metals including Pt,³ Ir,⁴ Pd,⁵ Fe⁶ and Brønsted acids⁷ have been examined for the hydration of alkynes. On the other hand anti-Markovnikov's hydration of alkynes to aldehydes was achieved with Ru complexes.^{8,9} Recently, gold complexes^{10,11} were reported as efficient catalysts for the hydration of alkynes. In previous studies silver salts are used as a co-catalyst to enhance the catalytic activity of the gold metal species in the hydration of alkynes.¹² However, the role of silver as co-catalyst was not disclosed clearly. Recently, AgSbF₆ catalyzed hydration of alkynes has been reported by M. Bui et al. 13 The authors studied the ability of this catalyst to promote the hydration of a variety of non-activated terminal alkynes. Despite the advantage of converting various kinds of alkynes into carbonyl compounds these systems have certain drawbacks, predominantly the recovery and reuse of catalysts and the indispensible use of acid co-catalysts, which can cause problems due to product contamination.

In contrast, heterogeneous catalysts have been receiving more attention over homogeneous catalysts because of their advantage in easy recovery and recyclability. In view of this, Kobayashi and co-workers first reported the hydration of 4-ethynyltoluene over heterogeneous polystyrene supported sulfonic acid using a catalytic amount of Brønsted acid (10 mol%).¹⁴ Nevertheless the catalytic activity is low and the scope of this catalyst is limited to 4-ethynyltoluene only. Recently, Au^I-containing mesoporous silica catalyzed hydrations of alkynes, including aromatic and aliphatic alkynes, have been well documented.¹⁵ Although, this catalyst showed high efficiency, it requires a catalytic amount of a homogeneous H₂SO₄ co-catalyst. Later Mizuno and coworkers ¹⁶ reported a heterogeneous Sn-W mixed oxide catalyst for the efficient hydration of a variety of terminal and internal alkynes. Despite the advantage of this catalyst, one critical limitation associated is that of using organic solvent as reaction medium. Hydration of alkynes could be performed in solventfree conditions using a solid heterogeneous catalyst without the addition of a metal salt or mineral acid co-catalyst, the process would be safer, cheaper and greener than many of the processes in use today.

Solvent-free reactions lead to new environmentally benign procedures that save resources and energy. Solvent-free reactions possess some advantages over traditional reactions in organic solvents, as they are not only reducing the burden of organic solvent disposal, but also enhance the rate of many organic reactions. To the best of our knowledge, there is only one report on the solvent-free hydration of alkynes using a heterogeneous Au nanoparticle–acid catalyst (Au–HS/SO₃H-PMO(Et)).¹⁷ The high cost of preparation of this catalyst constitutes a limitation of this protocol. Therefore, the development of an inexpensive, more efficient and environmentally benign heterogeneous catalyst, without any additives, for the hydration of alkynes is highly desirable.

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Heteropoly acids (HPAs) are known to be strong acid and oxidation catalysts. These have a wide range of applications, especially in fine chemical synthesis.¹⁸ Nevertheless, its applications are limited in the bulk form as they are soluble in polar solvents, possess low surface areas and low thermal stabilities.¹⁹ In order to overcome these difficulties HPAs could be modified at a molecular level. Modification of heteropoly acids, especially the Keggin-type, can be done in three ways, *i.e.*, by converting them into salts or the incorporation of various other transition metal ions like V into the Keggin frame work, or by supporting them on various solid supports.²⁰

In continuation of our interest to develop modified Keggintypes of heteropoly acid catalysts for various organic transformations under solvent-free conditions,^{21,22} in the present work silver exchanged silicotungstic acid (STA), as a solid acid catalyst, for the hydration of alkynes under solvent-free conditions is reported. The catalysts characteristics are derived from different spectroscopy techniques and correlated with observed alkyne hydration activity.

Experimental

Preparation of Ag_xH_{4-x}SiW₁₂O₄₀ catalysts

Silver exchanged silicotungstic acid catalysts with variations of silver in the secondary structure of STA were prepared according to the reported procedure.²³ Silicotungstic acid (5 g, 1.73 mmol) was dissolved in 20 mL of deionized water and stirred vigorously at room temperature. Then, the required amount of aqueous solution of AgNO₃ was added drop wise to the former solution. The silver content, *x* in Ag_xH_{4-x}SiW₁₂O₄₀ (*x* = 1 to 4) was adjusted using the required amount of silver. The resultant mixture was aged overnight at room temperature and the excess water removed on a rotavapor. The solid mass obtained was dried at 120 °C for 12 h and calcined at 350 °C for 3 h. In that way the catalysts were prepared with varying Ag content in Ag_xH_{4-x}SiW₁₂O₄₀ (*x* = 1, 2, 3, 4). These catalysts are denoted as Ag₁STA, Ag₂STA, Ag₃STA and Ag₄STA. Where the number indicates the number of Ag ions exchanged.

FT-IR spectra of catalysts were taken on a DIGILAB (USA) IR spectrometer by using the KBr disc method. Powder X-ray diffraction (XRD) patterns of the catalysts were recorded on a Rigaku Miniflex (Rigaku Corporation, Japan) X-ray diffractometer using Ni filtered Cu K α radiation ($\lambda = 1.5406$ Å) with a scan speed of 2° min⁻¹ and a scan range of 10–80° at 30 kV and 15 mA.

The Raman spectra of the samples were collected with a Horiba–Jobin Yvon LabRam-HR spectrometer equipped with a confocal microscope, 2400/900 grooves mm^{-1} gratings, and a notch filter. The visible laser excitation at 532 nm (visible/green) was used. The scattered photons were directed and focused onto a single-stage monochromator and measured with a UV-sensitive LN₂-cooled CCD detector.

XPS measurements were conducted on a KRATOS AXIS 165 with a dual anode (Mg and Al) apparatus using Mg K α anode. The non-monochromatized Al K α X-ray source (*hv*) 1486.6 eV) was operated at 12.5 kV and 16 mA. Before acquisition of the data, the sample was out gassed for about 3 h at 100 °C under a vacuum of 1.0×10^{-7} torr to minimize surface contamination.

The XPS instrument was calibrated using Au as standard. For energy calibration, the carbon 1s photoelectron line was used. The carbon 1s binding energy was taken as 285 eV. A charge neutralization of 2 eV was used to balance the charge up of the sample. The spectra were deconvoluted using a Sun Solaris based Vision-2 curve resolver. The location and the full-width at half-maximum (FWHM) value for the species were first determined using the spectrum of the pure sample. Symmetric Gaussian shapes were used in all cases.

Temperature programmed desorption of ammonia (TPD) was carried out on a laboratory-built apparatus. In a typical experiment about 0.1 g of the sample was pretreated at 300 °C for 1 h by passing helium (99.9%, 50 mL min⁻¹). After pretreatment, the sample was saturated with anhydrous ammonia (10% NH₃ balance He) at 100 °C for 1 h and subsequently flushed with He at the same temperature to remove physisorbed ammonia. Then the TPD analysis was carried out from ambient temperature to 800 °C at a heating rate of 10 °C min⁻¹ and the desorbed NH₃ was measured using a gas chromatography equipped with thermal conductivity detector.

General reaction procedure. A 5 mL round bottom flask equipped with magnetic stir bar was charged with phenyl acetylene (204 mg, 2 mmol), water (108 mg, 6 mmol) and Ag₃STA catalyst (50 mg). Then, the reaction mixture was heated at 100 °C for 6 h. The progress of the reaction was monitored by TLC. After completion of the reaction the reaction mixture was cooled to room temperature and extracted with ethyl acetate (3 × 10 mL). The organic phase was dried with anhydrous Na₂SO₄, concentrated at reduced pressure, and purified by column chromatography. The products were identified by GC-MS and their identity was confirmed by ¹H NMR.

Results and discussion

The prepared AgSTA catalysts were tested for the hydration of alkynes to the corresponding carbonyl compounds at atmospheric pressure. Initially, phenyl acetylene was chosen as a model substrate for the hydration of alkynes with water. Parent STA and the catalysts with varying Ag content in STA are studied for this reaction. The activity results are presented in Table 1. In Keggin heteropoly acids STA is one of the Brønsted acid exhibited moderate activity for this reaction. Although, STA showed activity, this catalyst was not a heterogeneous one, as it is highly soluble in polar solvents and reactants. The silver salts

 Table 1
 Hydration of phenyl acetylene over different heteropoly tungstate catalysts

Catalyst	Acidity (mmol g^{-1})	B/L ratio	Conversion ^a (%)	Selectivity ^a (%)
STA	1.20		52	100
Ag ₁ STA	1.44	0.938	67	100
Ag ₂ STA	1.46	1.006	83	100
Ag ₃ STA	1.55	1.014	98	100
Ag ₄ STA	1.49	0.918	79	100

Reaction conditions: Alkyne (2 mmol), H_2O (6 mmol), catalyst (50 mg), 100 °C, 6 h. ^{*a*} Conversion and selectivity based on GC-MS.

of STA which are insoluble showed very good catalytic activity as compared to pure STA.

The hydration of phenyl acetylene increased with an increase of the silver content in the secondary structure of STA, where the catalyst Ag_3STA showed the highest activity. In order to understand the difference in activity with varying Ag content, these catalysts are characterized by different spectroscopic techniques.

Fig. 1 shows the FT-IR patterns of silver salts of silicotungstic acid catalysts. For the sake of comparison the parent STA spectra is also shown in the inset of the figure. The pure STA exhibited characteristic infrared frequencies at 1020 cm⁻¹ (Si–O, oxygen



Fig. 1 FT–IR pattern of (a) Ag_1STA , (b) Ag_2STA , (c) Ag_3STA , (d) Ag_4STA , (e) Ag_3STA (used).

in central SiO₄ tetrahedron), 979 cm⁻¹ (W=O, terminal oxygen bonding to W), 877 cm⁻¹ (W–O–W, inter-octahedral) and 778 cm⁻¹ (W–O–W, intra-octahedral). These characteristic bands are found in the spectra of all silver exchanged STA catalysts. A similar type of observation was made by S. Borghese *et al.*²³ The presence of characteristic IR spectra of Keggin ions for the AgSTA catalysts indicates that the Keggin structure is intact during the exchange of protons in the secondary structure of STA with silver ions.

Fig. 2 illustrates the XRD pattern of STA and AgSTA catalysts. For pure STA, three main diffraction peaks appeared at 10.3°, 25.5° and 34.7° which are assigned to the characteristic peaks of body centred cubic secondary structure of the Keggin ion.²⁴ In the case of silver exchanged STA catalysts $(Ag_{x}H_{4-x}SiW_{12}O_{40}, x = 1 \text{ to } 4)$ the same diffraction pattern is observed with a marginal shift towards higher 2θ values. This shift is particularly observed at a 2θ value of 25.5° for the catalyst with increases in Ag content in the secondary structure of STA. According to earlier reports silver salts of heteropoly acids possess the same cubic crystalline structure as that of pure HPAs but with a contracted unit cell.²⁵ Therefore, the reflexes assigned to the Keggin salts were shifted in the case of AgSTA compared to those of pure STA towards higher angles. Zieba et al. observed that for the silver doped tungstophosphoric $(Ag_{r}H_{3-r}PW_{12}O_{40})$ acid, where the silver content x < 1, the XRD pattern showed both crystalline phases of the Ag salt and pure $H_3PW_{12}O_{40}$. Whereas an increase in silver content (with x > 1) showed only one phase of crystalline Ag salts of TPA.²⁶ The same behavior is noticed in the present silver exchanged STA catalysts.

Raman spectra of STA and its silver exchanged catalysts are shown in Fig. 3. Pure STA showed characteristic sharp Raman



Fig. 2 XRD patterns of (a) STA, (b) Ag₁STA, (c) Ag₂STA, (c) Ag₃STA, (d) Ag₄STA, (e) Ag₃STA (used).



Fig. 3 Raman spectra of (a) STA, (b) Ag_1STA , (c) Ag_2STA , (c) Ag_3STA , (d) Ag_4STA , (e) Ag_3STA (used).



Fig. 4 FT–IR pyridine adsorption studies of (a) Ag₁STA, (b) Ag₂STA, (c) Ag₃STA, (d) Ag₄STA.

bands at 997 and 970 cm⁻¹. The band at 997 cm⁻¹ with a distant shoulder at 970 cm⁻¹ can be ascribed to symmetric and asymmetric stretching modes of $v_{(W=O)}$. In addition, another band was observed at 875 cm⁻¹, which is assigned to the asymmetric stretching mode of $v_{(W=O-W)}$.²⁷ The strong band at 243 cm⁻¹ corresponds to the W–O–W bending mode of intact Keggin. All these characteristic Raman bands are observed in the case of the silver salts of STA, which indicates that the Keggin structure of STA was not affected, even after exchange of protons with silver. The results drawn from the Raman spectroscopy are in support of the observations made from FT-IR and XRD.

Pyridine is the probe molecule to identify or differentiate the Lewis and Brønsted acidic sites presented on the catalyst surface. FT-IR pyridine adsorbed STA and silver salts of STA catalysts are shown in Fig. 4. The IR band observed at 1536 cm⁻¹ is assigned to characteristic protonation of the pyridine molecule



Fig. 5 NH₃-TPD studies of (a) STA, (b) Ag₁STA, (c) Ag₂STA, (d) Ag₃STA, (e) Ag₄STA.

onto Brønsted acidic sites, while the IR band at 1438 cm⁻¹ is characteristic of chemisorbed pyridine onto Lewis acidic sites.²⁸ The strong band at 1486 cm⁻¹ is attributed to pyridine adsorbed onto both Brønsted and Lewis acidic sites. The intensity of Brønsted (B) and Lewis acid (L) sites obtained from the absorbance at 1534 and 1438 cm⁻¹, respectively, are used to calculate B/L ratios and are presented in Table 1. The B/L ratio increased with the increase of silver content in the secondary structure of STA and maximum ratio obtained for Ag₃STA. The partially exchanged Ag₃STA catalyst exhibits higher proton mobility and results in stronger Brønsted acidity than the fully exchanged Ag₄STA.²⁹ The fully exchanged Ag₄STA catalyst showed the presence of a greater number of Lewis acidic sites.

The acidity of the catalysts were measured by the temperature programmed desorption of ammonia. The TPD pattern of STA and its silver exchanged catalysts are shown in Fig. 5. The acidity of the catalysts are calculated and presented in Table 1. In the case of pure STA one desorption peak at a higher temperature around 550-750 °C was observed. This could be attributed to the presence of strong acidic sites. In the case of Ag₁STA, two well resolved desorption peaks were observed. The first one originating around 200-300 °C, and the second peak at 550-700 °C. The low temperature desorption peak corresponds to weak acidic sites associated due to the presence of silver. The high temperature desorption peak attributed to the strong acidic sites are shifted to lower temperatures with respect to pure STA. An increase in silver content in the secondary structure of STA (Ag₂STA) causes a decrease in the strong acidic sites, whereas an increase in the weak and moderate acidic sites was observed. Further increase of silver content, as in the case of Ag₃STA, and in addition to the weak and strong acidic sites, causes a new desorption peak to appear at around 300-500 °C, which corresponds to the moderate acidic sites. On the other hand, Ag₄STA catalyst exhibited two types of desorption peaks with increase in intensity at low and intermediate temperature corresponds to weak and moderate acidic sites. The absence of NH₃ desorption peak at higher temperature in case of Ag₄STA catalyst reveals the complete exchange of STA protons with silver ion. In overall Ag₃STA exhibited high acidity in contrast to the half or fully



Fig. 6 XPS spectra of (a) fresh and (b) used Ag₃STA catalyst.

exchanged catalysts. The acidity of these catalysts can be correlated to activity data and Ag_3STA showed the highest catalytic activity in short reaction times. The high activity of Ag_3STA is due to the presence of strong acidic sites compared to other catalysts. The variation in hydration of phenyl acetylene is related to the amount of acidity, which in turn depends on Ag substitution to STA.

XPS is a good tool to investigate the surface elemental composition and to identify the metal oxidation states of a solid inorganic material. The XPS spectra of the fresh and used Ag₃STA catalysts are shown in Fig. 6(a) and (b), respectively. The BE of Si $2p_{3/2}$ observed at 102.2 eV can be assigned to silica in the form of silicates.³⁰ The BE of Ag 3d resolved into four peaks at 368.8, 369.9, 374.7 and 375.9 eV. The BE peaks around 368.2 and 374.4 eV, which are readily assigned to core-level Ag 3d_{5/2}, Ag 3d_{3/2} photoemissions, respectively. The peak with BE 368.8 eV could be ascribed to Ag⁺ ions.³¹ The BE of 369.3 eV is high to be assigned simply to metallic silver. This BE might be related to the nano Ag species formed with strong interactions with Keggin ion. The standard binding energy for silver in metallic form is equal to $368.0 \text{ eV}^{32,33}$ which is slightly less than silver in its oxidation state. It suggests that the silver species is responsible for the main peak is located in more electropositive surroundings than the atoms in metallic silver.³⁰

The observed binding energy of W 4f showed two photo electron peaks at 35.8, and 37.8 eV. The XPS peak at 35.8 eV corresponds to W $4f_{7/2}$. The observed binding energy at 35.8 eV can be assigned to W⁶⁺.³⁴ The O1s spectrum resolved into two peaks and the first peak at 530.1 eV corresponds to the oxygen in the Keggin structure of the W–O–W unit.³⁵ The higher binding energy at 531.5 eV is attributed to the presence of adsorbed water. The XPS spectra of the used catalyst also showed similar spectra as that of the fresh catalysts. These results suggest stability of the catalyst during the reaction. The

XPS results are in support of the observations made from FT-IR, XRD and Raman for fresh and used catalysts.

The observed catalytic activity can be explained based on the observed characteristics of the catalysts. The acidity of the catalysts can be directly correlated to activity data. TPD of ammonia and FT-IR pyridine absorption techniques confirm that Ag₃STA contains both Brønsted and Lewis acidic sites and these are responsible for high catalytic activity. The importance of Lewis acidic sites is supported by the less activity of bulk STA (without Ag) which showed only 52% conversion of phenyl acetylene (Table 1). Whereas in the presence of AgNO₃ (Table 2, entry 1) alone the reaction proceeded very slow and obtained low conversion (15%). On the other hand the hydration of phenyl acetylene with AgNO₃ in combination of mineral acid H₂SO₄ as co-catalyst improved the catalytic activity (Table 2, entry 2). H₂SO₄ itself is also active and gave 27% conversion (Table 2, entry 3). The variation in hydration of phenyl acetylene is related to the amount of both Brønsted and Lewis acidity, which in turn depends on Ag substitution in STA. These results clearly demonstrate that both Brønsted and Lewis acid sites facilitate this reaction. The generation of Lewis acidity and the increase in Brønsted acidity is related to the presence of the intact Keggin ions of STA even after the exchange of Ag with its protons. The XRD, IR, Raman and XPS results clearly suggest the existence of the Keggin ion structure of the Ag salts of STA.

Further, the effect of metal ions in secondary structure of silicotungstic acid was studied and the results are presented in Table 2. Copper, iron and tin salts of STA were examined and none of those are effective as that of Ag_3STA (Table 2, entries 4–7). In addition to acetophenone a trace amount of 1,4-dipheylbuta-1,3-diyne a glacer coupling product was observed with the copper exchanged STA catalyst.

The activity of the present Ag_3STA catalyst was compared with various other heterogeneous solid acid catalysts. The results are presented in Table 2. It is noticed that the catalytic activity of Ag_3STA was much higher than the commonly exploited heterogeneous catalysts such as Amberlyst-15, SO_4/ZrO_2 , WO_3/ZrO_2 and WO_3/TiO_2 . Mizuno and co-workers reported tin-tungsten mixed oxide catalyzed hydration of alkynes which gave high conversion and selectivity towards carbonyl compounds in the presence of organic solvent.¹² However, under solvent-free

Table 2 Comparison of different catalysts with Ag₃STA

Entry	Catalyst	Conversion ^a (%)	Selectivity ^a (%)
1	AgNO2	15	100
2	$AgNO_2^b$	51	100
3	H ₂ SO ₄ ^b	27	100
4	Cu ₁₅ HSiW ₁₂ O ₄₀	85	87
5	Fe HSiW ₁₂ O ₄₀	71	100
6	$Sn_{1.5}HSiW_{12}O_{40}$	83	100
7	Ag ₃ STA	98	100
8	Amberlyst-15	53	100
9	WO_3/ZrO_2	66	100
10	WO ₃ /TiO ₂	59	100
11	Sn-WO ₃	86	100

Reaction conditions: Alkyne (2 mmol), H_2O (6 mmol), catalyst (50 mg), 100 °C, 6 h. ^{*a*} Conversion and selectivity based on GC-MS. ^{*b*} 0.25 mmol of H_2SO_4 .

conditions the activity of this catalyst is comparatively low with the present Ag₃STA catalyst.

Subsequently, the scope of the present catalyst with various aromatic and aliphatic alkynes was examined. All the substrates are efficiently converted into corresponding carbonyl compounds in moderate to high yields. The results are summarized in Table 3. All the products were identified by GC-MS and their identity was confirmed by ¹H NMR. Substrates with various electron donating or withdrawing groups at para or meta position on aromatic ring underwent reaction smoothly to corresponding carbonyl compounds in moderate to high yields (Table 3, entries 2-8). Heteroaromatic alkyne 2-ethynylpyridine is also reactive and gave 88% yield (Table 3, entry 9). In the case of 1-ethynylcyclohexanol, it first underwent dehydration followed by hydration of the alkyne to give the Rupe rearrangement product (Table 3, entry 10). 4-Phenyl-butyne reacted smoothly and gave corresponding carbonyl compound with excellent yield (Table 3, entry 11). Aliphatic terminal alkynes are also reactive but require prolonged reaction times to obtain corresponding ketones with good yields (Table 3, entries 12-14). Hydrations of internal alkynes are also studied. Diphenylacetylene is unreactive under the present reaction conditions whereas 1-phenyl-1-butyne gave a 20% yield (Table 3, entry 16).

The recycling of catalyst was carried out by performing the reaction with phenyl acetylene under the same experimental conditions. After completion of the reaction the reaction mixture was cooled to room temperature and then ethyl acetate was added. The catalyst was separated by simple filtration and washed three to four times with ethyl acetate. The retrieved catalyst was dried in an oven at 100 °C for 2 h and was used for next cycle. These recycling results are shown in Fig. 7. The catalytic activity is consistent even after fourth cycle. A separate experiment is carried to investigate the possible leaching of active component of the catalyst during the reaction. The catalyst is filtered in hot conditions, at the reaction temperature, to avoid readsorption of any leached metal ions as proposed by Lempers and Sheldon.36 After removing the catalyst from the reaction mixture, the reaction was continued further. It is not observed any conversion thereafter. This result suggests that there is no leaching of any active component during the reaction.

The retention of catalytic activity of the reused catalyst might be due to the stability of the Ag_3STA catalyst. The used catalyst was characterized by XRD, FT-IR, Raman spectroscopy and XPS to see is there were any changes in its structural characteristics. These characterization results are shown along with those of the fresh catalyst in the respective figures. All these characterization techniques divulge that the Keggin structure of Ag_3STA remains intact.

The plausible reaction mechanism for this catalyst is shown in Scheme 1. The mechanism is assumed to proceed in the same pathway as R. Casado *et al.* proposed for the gold(Π) complex catalyzed hydration of phenyl acetylene.¹¹ First, phenyl acetylene coordinates with the silver salt of STA to form intermediate **1**. Then intermediate **1** reacts with H₂O to give **2** by nucleophilic attack of ⁻OH. The nucleophile ⁻OH attacked at the carbon bearing phenyl group to generate the more stable carbocation. Consequently intermediate **2** undergoes keto–enol tautomerism to produce **3** that would generate the product, acetophenone **4**,

 Table 3
 Hydration of various alkynes over Ag₃STA catalyst

Entry	Alkyne	Ketone	Yield ^a (%)
1		0	96
2	F		97
3			91
4	осн ₃	OCH3	93
5		CI	85
6		°, CI	92
7	Br	Br	94
8	F	F O C C C C	78
9			88
10	OH		81
11			89
12 ^c	C ₆ H ₁₃ ==	0 C ₆ H ₁₃ -Ü-CH ₃	79 ^b
13 ^c	C ₇ H ₁₅	О С ₇ Н ₁₅ -С-СН ₃	82 ^b
14 ^c	C ₈ H ₁₇	0 C ₈ H ₁₇ -C-CH ₃	81 ^b

Fable 3	(Contd.)



Reaction conditions: Alkyne (2 mmol), H₂O (6 mmol), catalyst (50 mg), 100 °C, 6 h. a Isolated yield. b GC-MS yield. c 10 h. d 14 h.



Fig. 7 Recycling results of Ag₃STA catalyst.



Scheme 1 Plausible reaction mechanism.

and regenerate the catalyst by reacting with $H^{\!+}$ which is present in the reaction mixture.

Conclusions

In summary, a simple silver salt of heteropoly tungstate is developed as a highly efficient heterogeneous catalyst for the hydration of various structural derivatives of alkynes. The advantage of the present catalyst is that it works well in the absence of organic solvent and mineral acid co-catalyst. The activity of the catalyst mainly depends upon acidity and the amount of Brønsted and Lewis acid sites. The preparation of the catalyst is simple, environmentally benign, recyclable, and suitable for practical applications. One of the author KTVR thanks to Council of Scientific and Industrial Research (CSIR), New Delhi for the award of Senior Research Fellowship.

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