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Heterogeneously Catalyzed Efficient Hydration of Alkynes to Ketones by Tin–Tungsten Mixed Oxides

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Abstract: The Sn–W mixed oxide prepared by calcination of the Sn–W mixed hydroxide precursor with a Sn/W molar ratio of 2:1 at 800 °C (SnW2-800) acts as an efficient heterogeneous catalyst for the hydration of alkynes. Structurally diverse terminal and internal alkynes, including aromatic, aliphatic, and double-bond-containing ones, can be converted into the corresponding ketones in moderate to high yields. The catalytic activity of SnW2-800 is much higher than those of previously reported heterogeneous catalysts and commonly utilized acid catalysts. The observed catalysis was truly heterogeneous, and the retrieved catalyst can be reused at least three times with retention of its high catalytic performance. The reaction rate for the SnW2-800-catalyzed hydration was decreased by addition of 2,6-lutidine and the hydration hardly proceeded in the presence of an equimolar amount of this compound with respect to that of the Brønsted acid sites in SnW2-800. Therefore, the present hydration is mainly promoted by the Brønsted acid sites in SnW2-800.

Keywords: alkynes · heterogeneous catalysis · hydration · ketones · tin–tungsten mixed oxides

Introduction

The hydration of alkynes is one of the most important and attractive C−O bond forming reactions[1] because alkynes are abundant and water is an inexpensive and environmentally friendly reagent. The hydration of alkynes possesses a long history and has classically been carried out in the presence of acidic reagents.[1] However, the acid-mediated hydration generally requires large amounts of an acidic reagent (typically ≥100 mol %) and/or highly toxic additives, such as mercury(II) oxide as well as other mercury(II) salts.[1] Several efficient catalytic hydration procedures with transition-metal salts or complexes have recently been developed.[1,2] In particular, Nolan and co-workers have very recently reported some efficient homogeneous hydration systems with $[(IPr)AuCl]/AgSbF_6$ (IPr = 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene), which show high catalytic activity at parts per million catalyst loadings.[2a] Although various kinds of alkyne can be converted into the corresponding carbonyl compounds with transition-metal salts or complexes (ketones for Markovnikov addition; aldehydes for anti-Markovnikov addition), these systems have shortcomings, particularly the recovery and reuse of (expensive) catalysts and/or the indispensable use of acidic reagents as co-catalysts, which can cause problem due to product contamination.

The development of easily recoverable and recyclable, by filtration or centrifugation, heterogeneous catalysts can solve the problems of the homogeneous systems and has received particular research interest by organic synthetic chemists.[3] To the best of our knowledge, there are only a few reports of the hydration of alkynes with mercury-free[4] heterogeneous catalysts, for example, metal-cation-exchange acidic resins (M-resins; M = Cu^{II}, Pd^{II}, or Ru^{III}),[5] Au^{I}-containing mesoporous silica (Au^{I}-MS),[6] and polystyrene-supported sulfonic acid ($PS-SO_3H$).[7] The catalytic activity of M-resins is low and very long reaction times are required to attain high yields (typically >100 h with a 2 mol % catalyst loading).[5] Although various terminal alkynes, including aromatic and aliphatic ones, can be hydrated to the corresponding ketones with Au^{I}-MS (not reported for internal alkynes), homogeneous H_2SO_4 is required as a co-catalyst (10 mol %).[6] Although the system with $PS-SO_3H$, reported by Kobayashi and co-workers, is the first example of heterogeneous hydration with a catalytic amount of a Brønsted acid (H^+: 10 mol %), the catalytic activity is low and the reported applicability is limited to reactive 4-ethynyltoluene.[7]

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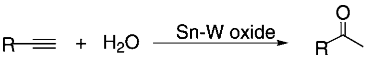
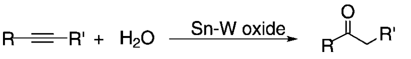
Therefore, efficient, widely applicable (to terminal as well as internal alkynes) heterogeneous hydration systems without any additives are currently unknown, and their development is a challenging subject.

Quite recently, we reported that the Sn–W mixed oxide prepared by calcination of a Sn–W hydroxide precursor with a Sn/W molar ratio of 2:1 at 800 °C (SnW2-800) acts as an effective and reusable heterogeneous acid catalyst for C–C bond-forming reactions, for example, in the cyclization of citronellal, the Diels–Alder reaction, and the cyanosilylation of carbonyl compounds with trimethylsilyl cyanide.[8] As shown for the cyclization of citronellal, the protonation of the carbonyl oxygen takes place initially, followed by cyclization via a carbocation-type transition state.[8] We have now discovered that SnW2-800 can act as an efficient heterogeneous catalyst for the hydration of various alkynes [Eqs. (1) and (2)]. The catalysis was truly heterogeneous and the retrieved Sn–W oxide catalyst can be reused at least three times without an appreciable loss of its high catalytic performance. Herein, we focus on the synthetic scope of the Sn–W oxide catalyzed hydration. In addition, a possible reaction mechanism is mentioned.



(1)



(2)

Results and Discussion

The effect of catalysts, solvents, and water: Eight different Sn–W mixed oxide catalysts were prepared by calcination of hydroxide precursors with different Sn/W ratios (see the Experimental Section). The Sn–W oxide with a Sn/W molar ratio of x prepared by calcination at T °C is designated as SnWx-T. The properties of SnWx-T catalysts are summarized in Table 1. The catalytic activity of these Sn–W oxides for the hydration of ethynylbenzene (**1a**) to acetophenone (**2a**) is largely dependent on the calcination temperature and the Sn/W molar ratio (Figure 1 a). The reaction rate with SnW2-T increased with an increase in T, reached a maximum at $T = 800$ °C, and then decreased. The reaction hardly proceeded with SnW2-1000, probably owing to the very small number of acidic sites (Table 1). The reaction rate of SnWx-800 increased with an increase in x, reached a maximum at $x = 2$, and then decreased (Figure 1 b). SnW2-800 showed the highest catalytic activity for the hydration of **1a** to **2a**. The catalytic activity of Sn–W oxides for the previously reported C–C bond-forming reactions was also dependent on the calcination temperature and Sn/W molar ratio, and SnW2-800 showed the highest catalytic activity for these reactions as well.[8] It has been revealed by various characterizations that strong Brønsted acid sites are generated on the aggregated polytungstate species in SnW2-800,[8] which can efficiently catalyze these transformations. Thus, the hydration reactions were hereafter carried out with SnW2-800.

Table 1. Properties of the Sn–W oxide catalysts.

Catalyst	Sn/W ratio	Calcination T [°C]	BET[a] [$m^2 g^{-1}$]	No. of acidic sites[b] [$\mu mol\,g^{-1}$]	Brønsted acid/Lewis acid sites[c]
SnW2-400	2	400	143	290	43:57
SnW2-600	2	600	118	189	54:46
SnW1-800	1	800	35.8	73	58:42
SnW1.5-800	1.5	800	77.4	124	66:34
SnW2-800	2	800	73.6	134	73:27
SnW5-800	5	800	68.8	78	–[d]
SnW10-800	10	800	49.4	55	–[d]
SnW2-1000	2	1000	29.5	27	–[d]

[a] From the N_2 adsorption isotherm. [b] The total number of acidic sites was determined by NH_3–TPD (TPD = temperature-programmed desorption) measurements. The values contain ≈10 % experimental errors. [c] The ratios were determined by IR spectra of pyridine adsorbed on the Sn–W oxides. [d] IR spectra of pyridine adsorbed on these Sn–W oxides could not be measured because of low transmittance (nearly 0 %).

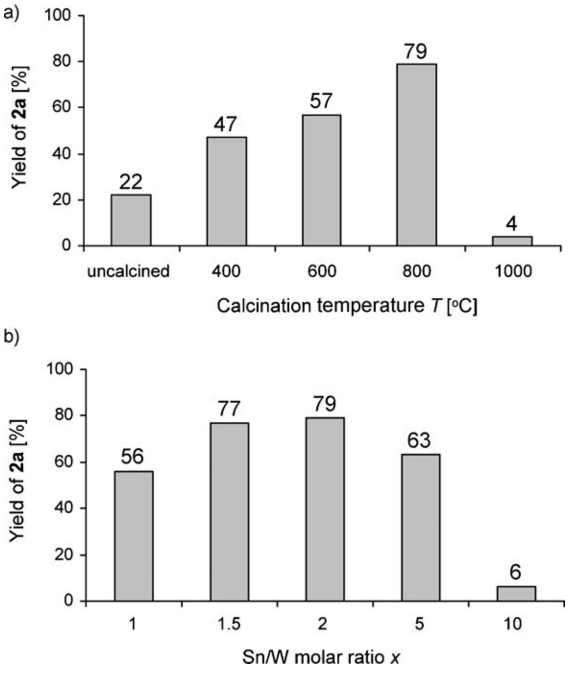


Figure 1. The hydration of **1a** to **2a** with various Sn–W oxides: a) the effect of calcination temperature (Sn–W hydroxide with a Sn/W molar ratio of 2:1 calcined at T [°C], SnW2-T) and b) the Sn/W molar ratio (Sn–W hydroxides with Sn/W molar ratio of x calcined at 800 °C, SnWx-800). Reaction conditions: catalyst (50 mg), **1a** (0.5 mmol), water (2.5 mmol), cyclooctane (2 mL), 100 °C, 15 min. Yields were determined by GC using diphenyl as an internal standard.

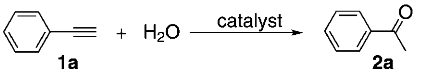
Among the solvents examined, nonpolar and nonaromatic solvents, such as cyclooctane and n-octane, selectively gave the hydration products (≥96 % selectivity; Table 2, entries 1 and 2). Although, toluene gave **2a** in 80 % yield, the Friedel–Crafts-type vinylation of toluene with **1a** occurred to

Table 2. Optimization of reaction conditions for the hydration of **1a** to **2a**.[a]

Entry	Water/**1a**	Solvent	Conversion of **1a** [%]	Yield of **2a** [%]
1	5:1	cyclooctane	98	94
2	5:1	*n*-octane	49	49
3[b]	5:1	toluene	>99	80[c]
4	5:1	ethanol	<1	n.d.
5	5:1	acetonitrile	<1	n.d.
6	5:1	1,4-dioxane	1	1
7	5:1	*N*,*N*-dimethylformanide	<1	n.d.
8	1:1	cyclooctane	98	90
9	2:1	cyclooctane	97	92
10	7:1	cyclooctane	40	38
11	10:1	cyclooctane	<1	n.d.
12	20:1	cyclooctane	<1	n.d.

[a] Reaction conditions: SnW2-800 (50 mg), **1a** (0.5 mmol), water (0.5–10 mmol), cyclooctane (2 mL), 100 °C, 30 min. Yields were determined by GC using biphenyl as an internal standard. n.d. = not detected. [b] 20 min. [c] The Friedel–Crafts-type vinylation of toluene with **1a** proceeded to some extent (≈18 %).

Table 3. Hydration of **1a** to **2a** with various catalysts.[a]



Entry	Catalyst	Conversion of **1a** [%]	Yield of **2a** [%]
1	SnW2-800	80	79
2	SnO_2	<1	n.d.
3	WO_3	<1	n.d.
4	H_2WO_4	1	n.d.
5	SnO_2+WO_3[b]	4	n.d.
6	Sn–W hydroxide[c]	22	22
7	H-mordenite	6	6
8	HY	33	12
9	SO_4^{2-}/ZrO_2	29	27
10	Nafion	6	1
11[d]	Amberlyst-15	<1	n.d.
12[d]	H_2SO_4	1	n.d.
13[d]	*p*-TsOH	2	n.d.
14[d]	$H_3PW_{12}O_{40}$	3	n.d.
15	none	<1	n.d.

[a] Reaction conditions: catalyst (50 mg), **1a** (0.5 mmol), water (2.5 mmol), cyclooctane (2 mL), 100 °C, 15 min. Yields were determined by GC using biphenyl as an internal standard. n.d. = not detected. [b] A mixture of SnO_2 (25 mg) and WO_3 (25 mg). [c] The precursor of Sn–W oxide. [d] Catalyst (H^+: 1.3 mol %) with respect to **1a**). The quantity was the same as that of the acid sites in the Sn–W oxide used in entry 1.

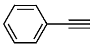
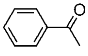
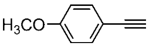
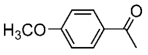
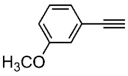
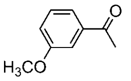
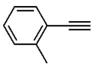
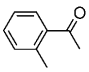
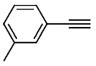
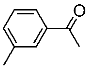
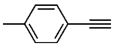
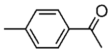
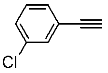
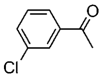
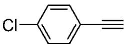
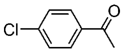
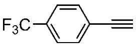
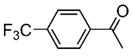
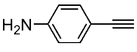
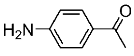
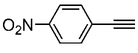
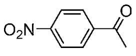
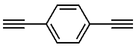
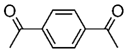
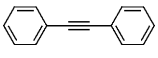
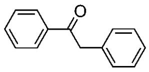
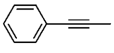
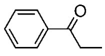
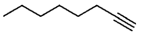
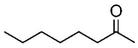
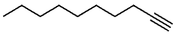
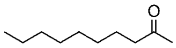
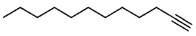
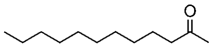
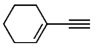
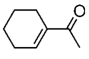
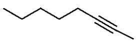
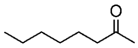
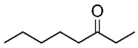
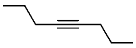
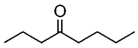
some extent (≈18 %; Table 2, entry 3). Protic and polar solvents, such as ethanol, acetonitrile, 1,4-dioxane, and *N*,*N*-dimethylformamide, were poor solvents for these reactions, likely owing to strong coordination to the active sites (Table 2, entries 4–7). The reaction rate for the hydration of **1a** was almost independent of the amount of water used, up to five equivalents, with respect to **1a** (Table 2, entries 1, 8, and 9). However, the hydration was strongly inhibited by the addition of a large amount of water (≥10 equiv with respect to **1a**; Table 2, entries 11 and 12).

Next, various acid catalysts were applied to the hydration of **1a** to **2a**. SnW2-800 showed a higher catalytic activity for the hydration of **1a** than any of the various other catalysts examined; a 79 % yield of **2a** was selectively obtained in 15 min by using 50 mg of the catalyst (number of acidic sites: only 1.3 mol % with respect to **1a**; Table 3, entry 1). In this case, the turnover frequency (TOF) reached 246 h^{-1} (based on the number of acidic sites). This value is much higher than those of previously reported mercury-free heterogeneous catalysts (M-resins, 0.12–0.36 h^{-1};[5] Au^I-MS, 4.1–6.7 h^{-1};[6] and $PS-SO_3H$, 0.17 h^{-1}).[7] Notably, the amount of catalyst can be considerably reduced; if the hydration of **1a** (0.5 mmol) was carried out at 100 °C with 5 mg of SnW2-800 (0.13 mol % acidic sites and 9.8 mass % with respect to **1a**), an 88 % yield of **2a** was obtained in 6 h (in this case, water (0.1 mmol) was added to the reaction mixture every 30 min).

No hydration of **1a** occurred in the absence of a catalyst (Table 3, entry 15). Neither were SnO_2, WO_3, H_2WO_4, or a physical mixture of SnO_2 and WO_3 effective for the hydration (Table 3, entries 2–5). The catalytic activity of SnW2-800 was higher than that of its Sn–W hydroxide precursor (Table 3, entry 6). Notably, the catalytic activity of SnW2-800 was much higher than those of commonly utilized heterogeneous acid catalysts, such as zeolites (H-mordenite and HY), SO_4^{2-}/ZrO_2, Nafion, and Amberlyst-15 (Table 3, entries 7–11). No hydration proceeded in the presence of catalytic amounts (H^+: 1.3 mol %) of H_2SO_4, *p*-toluenesulfonic acid (*p*-TsOH), or $H_3PW_{12}O_{40}$ in cyclooctane (Table 3, entries 12–14). These acid-mediated hydration reactions have typically been carried out in alcohols or cyclic ethers.[1] However, even if the hydration reactions of **1a** were carried out in ethanol at reflux or 1,4-dioxane at 100 °C by using catalytic amounts (H^+: 1.3 mol %) of H_2SO_4, *p*-TsOH, or $H_3PW_{12}O_{40}$, the corresponding ketone (**2a**) was hardly obtained.

Scope of the Sn–W oxide catalyzed hydration: The scope of the SnW2-800-catalyzed hydration of alkynes was examined next. Various structurally diverse terminal and internal alkynes, including aromatic, aliphatic, and double-bond-containing ones, can be converted into the corresponding ketones in moderate to high yields. The ketone products can easily be isolated by simple column chromatography on silica gel (see the Experimental Section), and the isolated yields are reported in Table 4 (see the values in parentheses). For all of the terminal alkynes in Table 4, ketones (Markovnikov addition) were obtained exclusively, with no formation of the corresponding aldehydes (anti-Markovnikov addition). The hydration of ethynylbenzene derivatives containing electron-donating or electron-withdrawing substituents (**1a**–**k**) efficiently proceeded to afford the corresponding acetophenone derivatives in moderate to high yields (Table 4, entries 1–11). The reaction rates for the ethynylbenzene derivatives with electron-donating substituents were larger than those with electron-withdrawing ones, suggesting an electrophilic nature of the SnW2-800-catalyzed hydration (vide infra). Reactive functional groups,

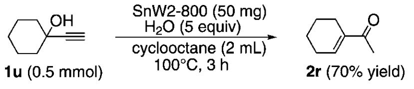
Table 4. Hydration of various alkynes.[a]

Entry	Substrate		Time [h]	Product		Yield [%]
1[b]		**1a**	0.5		**2a**	92 (91)
2		**1b**	0.3		**2b**	>99 (93)
3		**1c**	2.5		**2c**	93 (91)
4		**1d**	0.5		**2d**	>99 (88)
5		**1e**	0.6		**2e**	95 (92)
6		**1f**	0.5		**2f**	98 (95)
7		**1g**	2		**2g**	87 (80)
8		**1h**	1.5		**2h**	97 (91)
9[c,d]		**1i**	1		**2i**	88
10		**1j**	0.3		**2j**	94 (72)
11[c,d]		**1k**	24		**2k**	43
12[c,d]		**1l**	6		**2l**	>99 (83)
13		**1m**	8		**2m**	94 (79)
14		**1n**	2		**2n**	93 (85)
15[d,e]		**1o**	10.5		**2o**	88
16[d,e]		**1p**	2.5		**2p**	90 (84)
17[d,e]		**1q**	4		**2q**	76
18[f]		**1r**	1		**2r**	>99
19[c,d,e]		**1s**	17	 	**2o** **2s**	80 [g]
20[c,d,e]		**1t**	12		**2t**	82 (78)

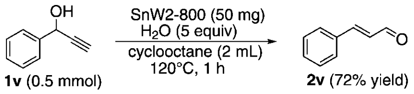
[a] Reaction conditions: SnW2-800 (50 mg), alkyne (0.5 mmol), water (2.5 mmol), cyclooctane (2 mL), 100 °C. Yields were determined by GC using biphenyl as an internal standard. The values in parentheses are the isolated yields. [b] Water (1 mmol). [c] SnW2-800 (100 mg). [d] 120 °C. [e] Water (1.5 mmol). [f] Toluene (2 mL). [g] A mixture of **2o** (41 % yield) and **2s** (39 % yield).

such as amino and nitro groups, remained intact (Table 4, entries 10 and 11). The hydration of 1,4-diethynylbenzene (**1l**) exclusively gave 1,4-diacetylbenzene (**2l**; Table 4, entry 12). The hydration of internal, aromatic alkynes (**1m** and **n**) proceeded efficiently to give the corresponding ketones (Table 4, entries 13 and 14), although these reactions required longer reaction times in comparison with those of terminal ones. Notably, methylphenylacetylene (**1n**) gave propiophenone (**2n**) exclusively, without the formation of 1-phenyl-2-propanone (Table 4, entry 14). This is likely due to the stabilization of a transient vinyl cation through conjugation with the π-electrons of the aromatic ring. Not only aromatic alkynes, but also aliphatic terminal (**1o**–**r**) and internal (**1s** and **t**) ones can be hydrated to the corresponding ketones (Table 4, entries 15–20). In the case of enyne **1r**, no hydration of the double bond occurred during the reaction (Table 4, entry 18).

In the case of the SnW2-800-catalyzed transformations of propargylic alcohols, the main products were different from those for the terminal alkynes in Table 4. For 1-ethynylcyclohexenol (**1u**), dehydration proceeded initially, followed by hydration to give **2r** as the main product [Rupe rearrangement;[9] Eq. (3)]. The transformation of 1-phenyl-2-propyn-1-ol (**1v**), which contains no C–H bonds at the β-position, mainly gave *trans*-cinnamaldehyde (**2v**), likely through the formation of an allenyl cation, followed by hydration [Meyer–Schuster rearrangement;[9] Eq. (4)].



(3)



(4)

To verify whether the observed catalysis is truly heterogeneous, the SnW2-800 catalyst was removed by hot filtration and the reaction was carried out with the filtrate under the same conditions. The hydration was completely stopped by removal of the catalyst (Figure 2). Furthermore, it was confirmed by inductively coupled plasma atomic emission spectroscopic (ICP-AES) analysis that Sn and W species are barely present in the filtrate (Sn: <0.0013 %; W: <0.0015 %). These results show that the nature of the

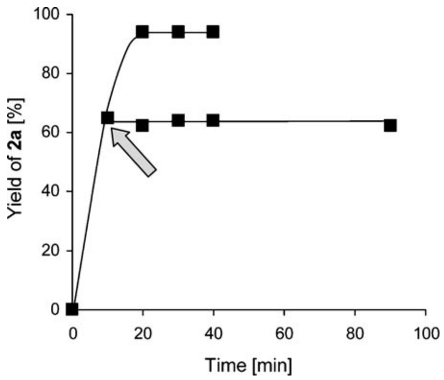


Figure 2. The effect of removal of the SnW2-800 catalyst (verification of heterogeneous catalysis). The reaction conditions were the same as those described in Table 2. The arrow indicates the removal of the catalyst by filtration.

observed catalysis is truly heterogeneous.[10] After the reaction was completed, the catalyst can be retrieved by simple filtration. The SnW2-800 catalyst can then be reused at least three times with no appreciable loss of its high catalytic performance; for the hydration of **1a** with the retrieved SnW2-800 catalyst, under the conditions described in Table 4, 92, 90, and 88 % yields of **2a** were obtained for the 1st, 2nd, and 3rd reuse experiments, respectively.

Mechanistic studies: To clarify the nature of the active sites of SnW2-800 for the hydration, the reaction of **1a** was carried out in the presence of 2,6-lutidine. It is known that 2,6-lutidine selectively interacts with Brønsted acid sites and cannot interact with Lewis acid sites due to the steric hindrance caused by its methyl groups.[11] As shown in Figure 3, the hydration of **1a** was almost completely inhibited by the presence of an equimolar amount of 2,6-lutidine with respect to that of the Brønsted acid sites. Therefore, the hydration is mainly promoted by the Brønsted acid sites in the SnW2-800 catalyst.

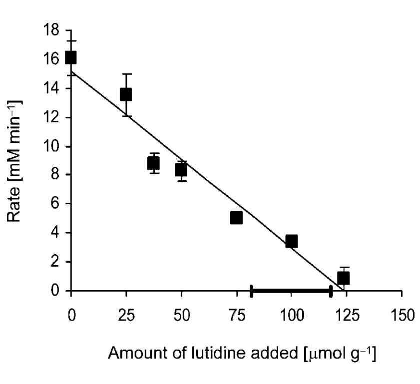
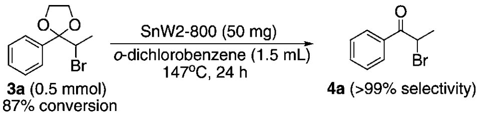


Figure 3. The dependence of the reaction rate on the amount of 2,6-lutidine added to the SnW2-800-catalyzed hydration of **1a**. The bar in the x axis indicates the number of Brønsted acid sites in the SnW2-800 catalyst (indicated with an experimental error). Reaction conditions: SnW2-800 (15 mg), **1a** (0.5 mmol), water (0.5 mmol), 2,6-lutidine, cyclooctane (2 mL), 100 °C.

It has been reported that 2-bromopropiophenone ethylene acetal (**3a**) can be converted into 2-bromopropiophenone (**4a**), 2-bromoethyl 2-phenylpropanoate, or 5-methyl-6-phenyl-2,3-dihydro-1,4-dioxin through catalysis by Brønsted acids, hard Lewis acids, or soft Lewis acids, respectively.[12] In the presence of SnW2-800, the reaction of **3a** gave **4a** exclusively and the products of Lewis acid catalysis were not formed [Eq. (5)], which also indicates that SnW2-800 is acting as a Brønsted acid catalyst.[8]



(5)

Next, the SnW2-800-catalyzed competitive hydration reactions of *para*- and *meta*-substituted ethynylbenzene derivatives were carried out. The reactivity order for ethynylbenzene derivatives is as follows: p-OCH_3 ($k_X/k_H = 85.7$) > p-CH_3 (5.9) > m-CH_3 (1.4) > p-H (1.0) > p-Cl (0.44) > m-Cl (0.11) > p-CF_3 (0.067). Figure 4 shows the relationship between $\log(k_X/k_H)$ and the Brown–Okamoto σ^+ constant for each compound.[13] A linear relationship is observed and the slope (Hammett's ρ^+ value) is -2.31.[14] This large, negative value suggests an electrophilic nature of the hydration, in which the hydration likely proceeds via a positively charged transition state, with the positive charge on the α-carbon atom adjacent to the phenyl ring, that is, a vinyl cation.[15] The correlation with the Brown–Okamoto σ^+ constants shows a better fit than that with more commonly used σ constants, in particular for electron-donating substituents, such as p-OCH_3 and p-CH_3, which also suggests that the formation of a positively charged transition state is involved in the hydration reaction pathway.[15]

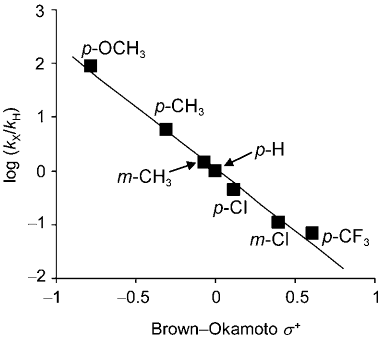
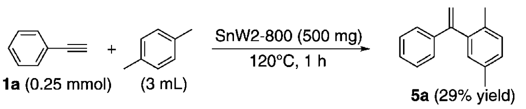


Figure 4. A Hammett plot for the competitive hydration of *para*- and *meta*-substituted ethynylbenzene derivatives ($X = p$-OCH_3, p-CH_3, m-CH_3, p-H, p-Cl, m-Cl, and p-CF_3): a $\log(k_X/k_H)$ versus Brown–Okamoto σ^+ plot. Reaction conditions: SnW2-800 (100 mg), ethynylbenzene (0.5 mmol), substituted ethynylbenzene (0.5 mmol), water (1 mmol), cyclooctane (2 mL), 100 °C. Slope (Hammett ρ^+ value) = −2.31 ($R^2 = 0.99$).

If **1a** was heated with SnW2-800 in p-xylene (in the absence of water), the Friedel–Crafts-type vinylation proceeded to afford 1,4-dimethyl-2-(1-phenylethenyl)benzene (**5a**) [Eq. (6)].[16] This also supports the formation, by the SnW2-800 catalyst, of a vinyl cation from an alkyne.



(6)

Therefore, this SnW2-800-catalyzed hydration likely proceeds through the following mechanism. Initially, protonation of an alkyne takes place to generate a vinyl cation. Then, nucleophilic attack of water[17] on the transiently formed vinyl cation proceeds to give a vinylic alcohol, followed by tautomerization to form the corresponding ketone as the final product.

Conclusion

The Sn–W mixed oxides, especially SnW2-800, act as efficient heterogeneous catalysts for the hydration of structurally diverse alkynes. Various terminal and internal alkynes, including aromatic, aliphatic, and double-bond-containing ones, can be converted into their corresponding ketones in moderate to high yields. However, with propargylic alcohols, Rupe rearrangement or Meyer–Schuster rearrangement occur instead. The catalytic activity of SnW2-800 is much higher than those of previously reported heterogeneous catalysts, including M-resins, Au^I-MS, and $PS\text{-}SO_3H$, as well as commonly utilized acid catalysts. The catalysis is truly heterogeneous and the SnW2-800 can be reused. This performance raises the prospect of using this type of simple mixed-oxide catalyst for various laboratory-scale organic syntheses, as well as practical acid-catalyzed reactions.

Experimental Section

Instruments: GC analyses were performed on a Shimadzu GC-2014 with an FID detector equipped with a DB-WAX ETR or Rtx-200 capillary column. Mass spectra were recorded on a Shimadzu GCMS-QP2010 equipped with a TC-5HT capillary column at an ionization voltage of 70 eV. Liquid-state NMR spectra were recorded on a JEOL JNM-EX-270. ^1H and ^{13}C NMR spectra were measured at 270 and 67.8 MHz, respectively. The ICP-AES analyses were performed with a Shimadzu ICPS-8100. The BET surface area was measured on a Micromeritics ASAP 2010 and calculated from the N_2 adsorption isotherm with the BET equation. The NH_3-TPD profile was measured on a BEL Japan Multitask TPD with a quadrupole mass spectrometer. The sample was pretreated (evacuated at 300 °C for 1 h) and NH_3 (20 Torr at 100 °C for 10 min) was adsorbed. After excess NH_3 was removed, He (the carrier gas) was flowed into the cell (50 mL min^{-1}). After the baseline stabilized, the temperature was linearly increased to 800 °C at a rate of 10 °C min^{-1}. The amount of desorbed NH_3 was quantified by a mass spectrometer by using the m/z 16 fragment. The IR spectrum of pyridine adsorbed on Sn–W oxides was measured on a Jasco FT/IR-460 plus spectrometer. The sample (≈50 mg) was pressed into a disk with a diameter of 20 mm. The disk was evacuated in the in situ IR cell at 300 °C for 1 h. Then, pyridine (5 Torr) was introduced into the cell, and the disk was kept at 100 °C for 30 min. After the disk was evacuated at 150 °C for 1 h, the spectrum was recorded at room temperature. The amount of pyridine adsorbed on Lewis and Brønsted acid sites was determined by using the following integrated molar extinction coefficients; 2.22 and 1.67 cm μmol^{-1} for Lewis (1451 cm^{-1}) and Brønsted acid sites (1538 cm^{-1}), respectively.[18]

Reagents: H-mordenite (JRC-Z-HM15, $SiO_2/Al_2O_3 = 14.9$) and SO_4^{2-}/ZrO_2 (JRC-SZ-1) were supplied by the Catalysis Society of Japan. HY (CBV400, $SiO_2/Al_2O_3 = 5.1$) was supplied by Zeolist. Nafion (Nafion® NR-50) and Amberlyst-15 were purchased from Wako and ORGANO, respectively. Substrates and solvents were commercially obtained from TCI, Wako, or Aldrich (reagent grade) and purified prior to use.[19]

Preparation of Sn–W mixed oxides: The Sn–W mixed oxide catalysts were prepared according to the following procedure.[8] First, the Sn–W mixed-hydroxide precursors were prepared by the following co-precipitation method.[20] The preparation of the Sn–W hydroxide with a Sn/W molar ratio of 2:1 is described here as a typical example. $Na_2WO_4\cdot 2H_2O$ (2.47 g, 7.5 mmol) was dissolved in deionized water (15 mL), followed by addition, in a single step, of $SnCl_4\cdot 5H_2O$ (5.26 g, 15 mmol). After stirring the solution for 1 h at room temperature (≈22–23 °C), more deionized water (60 mL) was added to the reaction mixture, and the colorless solution gradually became a white slurry. After stirring for 24 h at room temperature, the resulting white precipitate of Sn–W hydroxide was filtered off, washed with a large amount of deionized water (≈2.0 L), and dried in vacuo to afford the Sn–W hydroxide precursor as a white powder (4.5 g). The quantities of Sn and W were 38.3 and 33.6 wt %, respectively. Elemental analysis indicated that the Sn/W molar ratio of the hydroxide was in good agreement with that of the starting metal solution. Five kinds of Sn–W hydroxide with different Sn/W molar ratios (Sn/W = 1:1, 1.5:1, 2:1, 5:1, and 10:1) were successfully prepared by changing the molar ratio of the starting metal solutions. By calcination of the corresponding hydroxide precursor at different temperatures (400–1000 °C) for 3 h under an air atmosphere, eight different Sn–W oxide catalysts were prepared. The properties of the Sn–W oxide catalysts are summarized in Table 1.

Catalytic alkyne hydration: In this paper, the Sn–W oxide prepared by the calcination of the hydroxide precursor with a Sn/W molar ratio of 2:1 at 800 °C (SnW2-800) was generally used in the reactions. The catalytic reactions were carried out as follows. Into a Pyrex-glass screw-cap vial (volume: ≈20 mL) were successively placed the Sn–W oxide catalyst (50–100 mg), an alkyne (0.5 mmol), water (1–20 equiv with respect to the alkyne), and cyclooctane (2 mL). A Teflon-coated magnetic stir bar was added and the reaction mixture was vigorously stirred at 100–120 °C. After the reaction was completed, the catalyst was removed by filtration. Then, an internal standard (biphenyl, 15.4 mg) was added to the filtrate and the mixture was analyzed by GC. For isolation of the products (ketones), the internal standard was not added and the crude filtrate was directly subjected to column chromatography on silica gel (Silica Gel 60N (63–210 μm), Kanto Chemical, 2.5 cm, ID × 20 cm length) by initially using only n-hexane to elute cyclooctane and the alkyne and then by using n-hexane/diethyl ether (1:1 v/v) to elute the product. The isolated products were identified by comparison of their mass and ^1H and ^{13}C NMR spectra with those of authentic samples. The retrieved catalyst was washed with acetone, and dried in vacuo prior to being reused.

Acknowledgements

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