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Supporting Information

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A Tungsten-Tin Mixed Hydroxide as an Efficient Heterogeneous Catalyst for Dehydration of Aldoximes to Nitriles

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Full Experimental Section

General: GC analyses were performed on Shimadzu GC-2014 with a FID detector equipped with a TC-1 or TC-5 capillary column. Mass spectra were recorded on Shimadzu GCMS-QP2010 at an ionization voltage of 70 eV. Liquid-state NMR spectra were recorded on JEOL JNM-EX-270. ^{1}H and ^{13}C NMR spectra were measured at 270 and 67.8 MHz, respectively, in chloroform-d_1 with TMS as an internal standard. XPS measurements were carried out on JEOL JPS-90 using monochromated Al Kα radiation (hn = 1486.6 eV). The X-ray anode was run at 200 W and the voltage was kept at 10 kV. The pass energy was fixed at 10.0 eV to ensure sufficient resolution to determine peak positions accurately. The binding energies were calibrated by using the C 1s signal at 285.0 eV. The NH_3-TPD profile was measured using a glass equipment with vacuum pumps. The sample was pretreated (W-Sn hydroxide, evac. at 100 °C for 1 h; zeolite, evac. at 500 °C for 1 h) and 13.3 kPa of NH_3 was adsorbed at 100 °C. After excess NH_3 was purged off, He (carrier gas) was allowed to flow into the cell

(50 mL·min^{-1}). After the baseline was stabilized, the temperature was increased linearly at a rate of 10 ^{o}C·min^{-1} from 100 ^{o}C to 800 ^{o}C (Figure S3). The desorbed NH_3 was quantified by a mass spectrometer with the fragment of $m/z = 16$.[24] The IR spectrum of pyridine adsorbed on the W-Sn hydroxide was measured as follows. The W-Sn hydroxide was pressed into the disk with a radius of 10 mm (45 mg). The sample was pretreated in the *in situ* IR cell under under reduced pressure (<0.13 Pa) at 150 ^{o}C for 3 h. The sample was cooled to room temperature and the spectrum was recorded. Then, pyridine (6.7×10^2 Pa) was introduced into the cell and contacted with the sample at 100 ^{o}C for 30 min. After the gas phase and physically adsorbed pyridine on the W-Sn hydroxide were removed under reduced pressure (<0.13 Pa) at 150 ^{o}C, the spectrum was recorded at room temperature. The difference spectrum (Figure S2) was obtained by substracting the spectrum of the W-Sn hydroxide from that after pyridine adsorption. The amounts of pyridine adsorbed on Lewis and Brønsted acid sites were determined by using the following integrated molar extinction coefficients; 2.22 and 1.67 cm·μmol^{-1} for Lewis (1452 cm^{-1}) and Brønsted acid sites (1540 cm^{-1}), respectively.[25]

$Na_2WO_4·2H_2O$, $SnCl_4·5H_2O$, and H_2WO_4 were obtained from Wako (reagent grade) and used as received. Montmorillonite KSF was purchased from Alfa Aesar. KF/Al_2O_3 was purchased from Aldrich (40 wt% KF on Al_2O_3). H-Y (JRC-Z-HY5.5, $SiO_2/Al_2O_3 = 5.7$,

Na_2O 3.8 wt%, H^+ >90%) and H-mordenite (JRC-Z-HM10, SiO_2/Al_2O_3 = 9.9, Na_2O 0.12 wt% or JRC-Z-HM15, SiO_2/Al_2O_3 = 14.9, Na_2O 0.06 wt%) were supplied from the Catalysis Society of Japan and TOSHO. SO_4^{2-}/ZrO_2, WO_3/ZrO_2 (W: 20 wt%), and WO_3/SnO_2 (W: 5 wt%) were prepared according to the ref. 20. $[RuCl_2(p\text{-cymene})]_2/C$ was prepared according to ref. 11. $Sn(OH)_4$ was prepared by the base treatment (NH_3 aq.) of $SnCl_4\cdot 5H_2O$. Aldehydes and solvents were obtained from Tokyo Kasei or Aldrich (reagent grade) and purified prior to the use.[26]

Synthesis of Aldoximes: Aldoximes were synthesized by the dehydrative condensation of the corresponding aldehydes with $NH_2OH\cdot HCl$.[27] A typical procedure was as follows: Into a glass flask were successively placed an aldehyde (10 mmol), $NH_2OH\cdot HCl$ (2–3 equiv. with respect to an aldehyde), ethanol (10 mL), and pyridine (1 mL). The reaction mixture was stirred at room temperature. After complete the reaction, ethanol was removed under reduced pressure on a rotary evaporator. Then, deionized water (10 mL) was added to the residue and the mixture was cooled in an ice-bath until the aldoxime crystallized out. The aldoxime was filtered, washed with deionized water (ca. 100 mL), dried, and recrystallized from ethanol. All aldoximes were confirmed by the comparison of their GC retention time, mass, and ^1H and ^{13}C NMR spectroscopy with those of authentic samples.[27] The configuration of aldoximes were *E* (>90%) except for entry 11 (*E*/*Z* = 59/41), entry 12 (*E*/*Z* = 58/42), entry 13 (*E*/*Z* = 54/46), entry 15 (*E*/*Z* = 36/64), entry 17 (*E*/*Z* = 64/36), and entry 18 (*E*/*Z* = 53/47) in Table 2.

Dehydration of Aldoximes: A typical procedure for the dehydration of aldoximes was as follows: Into a glass vial were successively placed W-Sn hydroxide (0.1 g), benzaldoxime (1 mmol), and *o*-xylene (3 mL). The reaction mixture was stirred (800 rpm with magnetic stirrer bar) at 149 ^{o}C under 1 atm of Ar. The conversion and product selectivity were periodically determined by GC analysis. After the reaction was finished, the spent catalyst was separated by the filtration, washed with acetone, and dried in vacuo prior to being recycled. The products were isolated by a column chromatography using *n*-pentane/ether as an eluent. All products were known and available. The products were confirmed by the comparison of their GC retention time, mass, and ^{1}H and ^{13}C NMR spectroscopy with those of authentic samples.

A Larger Scale Dehydration: Into a glass reactor with a Dean-Stark apparatus were successively placed W-Sn hydroxide (1 g), *p*-methoxybenzaldoxime (7.56 g, 50 mmol), and *o*-xylene (100 mL). The reaction mixture was stirred (800 rpm with magnetic stirrer bar) under reflux conditions (bath temp. 170 °C) and the conversion and product selectivity were periodically determined by GC analysis. After the reaction was finished (6 h), the catalyst was separated by filtration. Then, the filtrate was evaporated in vacuo to give the corresponding nitrile in 97% yield.

One-Pot Synthesis: A typical procedure for the one-pot synthesis of nitriles was as follows: Into a glass vial were successively placed W-Sn hydroxide (0.1 g), benzaldehyde (1 mmol), $NH_2OH{\cdot}HCl$ (2 equiv. with respect to benzaldehyde), and *o*-xylene (3 mL). The reaction mixture was stirred (800 rpm with magnetic stirrer bar) at 133 °C under 1 atm of Ar. The conversion and product selectivity were periodically determined by GC analysis. After the reaction was finished, the spent catalyst was separated by the filtration, washed with and acetone, and dried in vacuo prior to being recycled. All products were known and available. The products were isolated by a column chromatography using *n*-pentane/ether as an eluent. The products were confirmed by the comparison of their GC retention time, mass, and ^{1}H and ^{13}C NMR spectroscopy with those of authentic samples.

One-Pot Synthesis with Zeolites: Although this tandem one-pot synthesis of nitriles is a very useful transformation and a topic of current interest in organic synthesis, stoichiometric reagents such as triethylamine sulfur dioxide, sulphuryl chloride fluoride, methanesulfonyl chloride/dry-Al_2O_3, and KF/Al_2O_3 have been utilized for the transformation even at present.[21,22] Das and co-workers reported that H-Y zeolites are used as heterogeneous catalysts for the direct one-pot synthesis of nitriles from aldehydes and hydroxylamine under reflux conditions in toluene or under microwave irradiation. As far as we know, this is only the example of heterogeneously catalyzed one-pot synthesis of nitriles from aldehydes and hydroxylamine. We carried out the one-pot synthesis of benzonitrile from benzaldehyde and hydroxylamine according to the procedures described in ref. 22. We used well-authorized and –characterized H-Y, Na-Y, H-mordenite, and H-ZSM-5 zeolites with different SiO_2/Al_2O_3 ratios. All operations were performed using Schlenk techniques under Ar atmosphere and benzaldehyde and solvent were carefully purified. The zeolites were pretreated under three different conditions before use. The reaction conditions were the same as those in ref. 22; zeolite (60 mg), benzaldehyde (3 mmol), $NH_2OH\cdot HCl$ (4 mmol), and toluene (25 mL) were charged into the reaction vessel and the reaction mixture was refluxed for 7 h (bath temp. 135 ^oC). The results are summarized in Table S3. No benzonitrile was obtained in the presence of Na-Y, H-mordenite, and H-ZSM-5 zeolites. Although the H-Y zeolites were active for the reaction, the amounts of benzonitrile formation (0.09–0.54 mmol) were comparable to those of the acidic sites in H-Y zeolites (0.14–0.3 mmol, calculated with the amounts of Al^{3+} sites).

References

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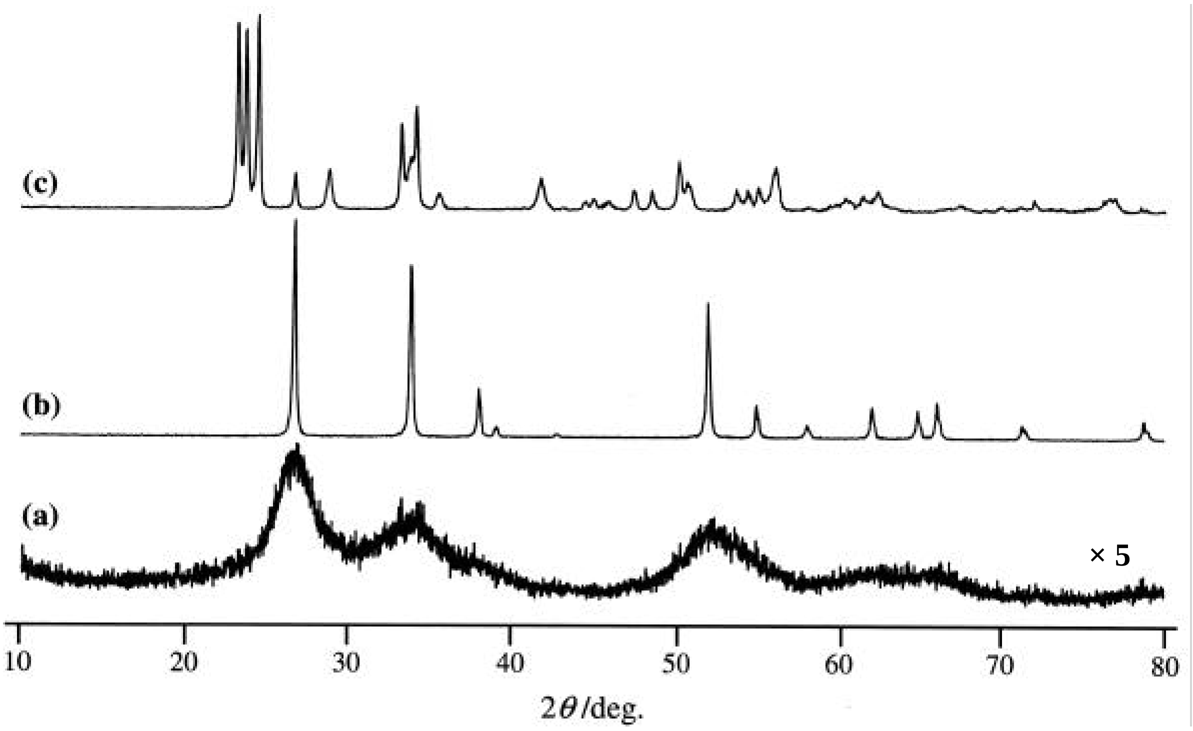


Figure S1. XRD patterns of (a) W-Sn hydroxide, (b) SnO_2, and (c) WO_3.

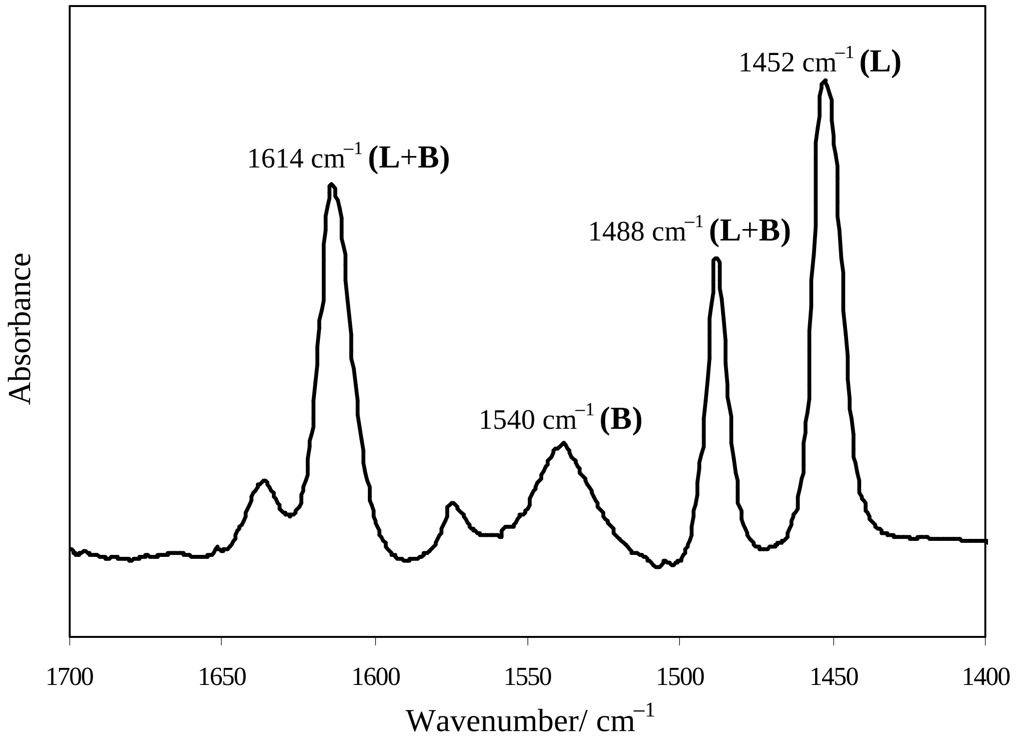


Figure S2. IR spectrum of pyridine adsorbed on the W-Sn hydroxide: L = pyridine adsorbed on Lewis acidic sites, B = pyridine adsorbed on Brønsted acidic sites.

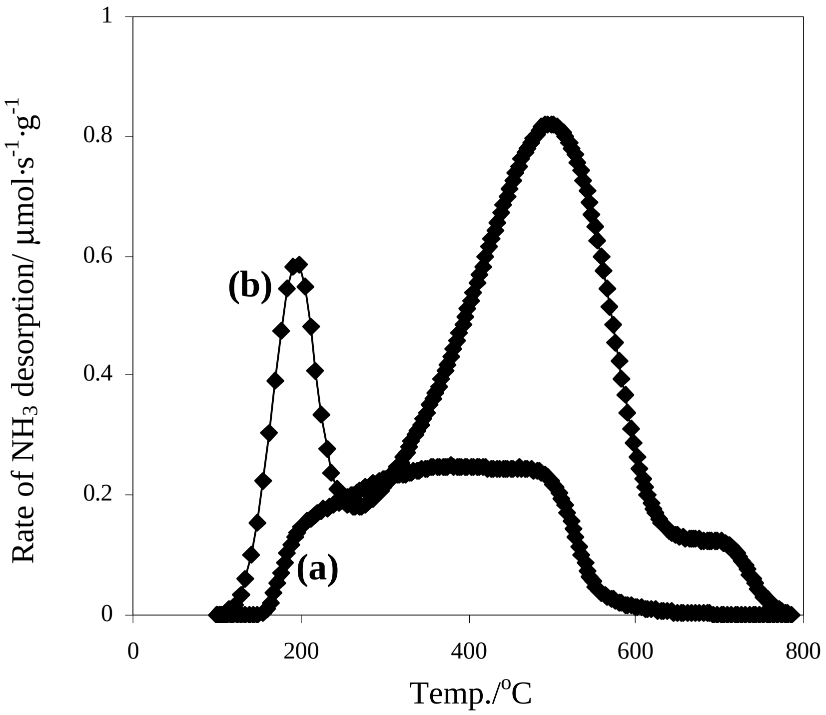


Figure S3. NH_3-TPD profiles of (a) W-Sn hydroxide and (b) H-mordenite (JRC-Z-HM15, SiO_2/Al_2O_3 = 14.9; Na_2O, 0.06 wt%).

Table S1: Dehydration of aldoximes to nitriles with solid materials.

Catalyst	Amount	Substrate	Solvent	Temp. [°C]	Yield [%]	Ref.
W-Sn mixed hydroxide	**13 mass%**	***p*-methoxy benzaldoxime**	***o*-xylene**	**reflux**	**97**	**this work**
mont KSF	500 mass%	benzaldoxime	toluene	100	70	12
KF/Al_2O_3	4800 mass% (KF: 5000 mol%)	*p*-methoxy benzaldoxime	DMF	85	90	15
$[RuCl_2(p\text{-cymene})]/C$ + MS4A[a]	Ru: 4.4 mol% MS4A: 200 mass%	*p*-methoxy benzaldoxime	CH_3CN	80	85	11
H_2SO_4/SiO_2	400 mass%	benzaldoxime	no solvent	MW[b] (275 W)	76	14

[a] In the absence of MA4A, the dehydration hardly proceeded.

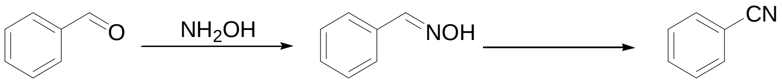
[b] MW = microwave irradiation.

Table S2: One-pot synthesis of nitriles from aldehydes and hydroxylamine with solid materials.

Catalyst	Amount	Substrate	Solvent	Temp. [^{o}C]	Yield [%]	Ref.
W-Sn mixed hydroxide	**74 mass%**	***o*-methoxy benzaldehyde**	***o*-xylene**	**133**	**91**	**this work**
KF/Al_2O_3	5300 mass% (KF: 5000 mol%)	*o*-methoxy benzaldoxime	DMF	100	87	21d
H-Y zeolite	20 mass%	benzaldehyde	toluene	reflux	74	22
H-Y zeolite	24 mass%	benzaldehyde	no solvent	MW[a] (466 W)	94	22

[a] MW = microwave irradiation

Table S3: One-pot synthesis of benzonitrile from benzaldehyde and hydroxylamine with various zeolites (in our hand)[a]



benzaldoxime **benzonitrile**

Entry	Zeolite	Pretreatment of zeolite	Conv. of aldehyde [%]	Yield (%)	
				Benzaldoxime	Benzonitrile
1[b]	H-Y	not reported	not reported	not reported	74 isolated yield
2	H-Y[c]	without	71	41	18(22)
3	H-Y[c]	150 °C for 1 h under reduced pressure ($<10^{-2}$ torr)	72	35	16(19)
4	H-Y[c]	300 °C for 1 h under reduced pressure ($<10^{-2}$ torr)	45	15	11
5	H-Y[c]	Reuse experiment. The recovered catalyst was washed with solvents before reuse.	58	47	trace
5	H-Y[d]	without	42	30	3
7	Na-Y[e]	without	98	86	trace
8	Na-Y[e]	300 °C for 1 h under reduced pressure ($<10^{-2}$ torr)	93	84	trace
9	H-mordenite[f]	150 °C for 1 h under reduced pressure ($<10^{-2}$ torr)	52	31	trace
10	H-ZSM5[g]	150 °C for 1 h under reduced pressure ($<10^{-2}$ torr)	42	27	trace

[a] Reaction conditions: Benzaldehyde (3 mmol), $NH_2OH \cdot HCl$ (4 mmol), catalyst (60 mg), toluene (25 mL), reflux (bath temperature 135 °C) for 7 h under N_2 atmosphere. The reaction conditions were the same as those for the conditions in ref. 22 (B. Das *et al.*, *Synlett* **2002**, 625). Yields were determined by GC analysis with diphenyl as an internal standard. Values in the parentheses were yields after 24 h [b] The data was taken from ref. 22. [c] Obtained from Catalysis Society of Japan (JRC-Z-HY5.5, SiO_2/Al_2O_3 = 5.7). [d] Obtained from TOSHO (SiO_2/Al_2O_3 = 12). [e] Obtained from Catalysis Society of Japan (JRC-Z-Y4.8, SiO_2/Al_2O_3 = 4.8). [f] Obtained from Catalysis Society of Japan (JRC-Z-HM10, SiO_2/Al_2O_3 = 9.9). [g] Obtained from Catalysis Society of Japan (JRC-Z5-H25, SiO_2/Al_2O_3 = 25).