Green Chemistry



View Article Online

PAPER



Cite this: DOI: 10.1039/c5gc02806j

Hydrodeoxygenation of sulfoxides to sulfides by a Pt and MoO_x co-loaded TiO₂ catalyst[†]

Abeda Sultana Touchy,^a S. M. A. Hakim Siddiki,^b Wataru Onodera,^a Kenichi Kon^a and Ken-ichi Shimizu*^{a,b}

Supported metal nanoparticle catalysts were studied for the hydrodeoxygenation of sulfoxides to sulfides under solvent-free and mild conditions (50–155 °C, 1 or 7 atm H₂). The catalytic activity for the model reaction of diphenyl sulfoxide depended on the type of metals, support materials and co-loaded oxides of transition metals (V, Nb, Mo, W, Re). Pt and MoO_x co-loaded TiO₂ (Pt–MoO_x/TiO₂) showed the highest activity. Pt–MoO_x/TiO₂ was reusable after the reaction and was effective for the reduction of various sulfoxides and showed a higher turnover number (TON) than previously reported catalysts. Using Pt–MoO_x/ TiO₂, benzylphenylsulfone was reduced by H₂ to give phenylbenzyl sulfide *via* benzylphenyl sulfoxides, which represented the first example of catalytic conversion of a sulfone to a sulfide by H₂. Characterization studies of Pt–MoO_x/TiO₂ show that the surface of TiO₂ is covered by small (or thin layer) Mo oxide species with exposed Mo cations as Lewis acid sites, and 4–5 nm sized Pt metal nanoparticles are supported on the Mo oxide-covered TiO₂.

Received 23rd November 2015, Accepted 4th January 2016 DOI: 10.1039/c5gc02806j

www.rsc.org/greenchem

Introduction

Deoxygenation of sulfoxides to the corresponding sulfides is an important transformation in organic synthesis.^{1,2} Several catalytic methods have been developed to reduce sulfoxides using stoichiometric amounts of reducing agents, including silanes,³⁻⁹ boranes,^{10,11} and phosphines,¹²⁻¹⁵ which suffer from the use of hazardous reagents and the production of by-products that are sometimes difficult to remove from the reaction media. Recently, greener catalytic methods with alcohols¹⁶⁻²⁰ as reducing agents were developed, but they also suffered from low atom-efficiency. The catalytic deoxygenation of sulfoxides by H₂, as the most atom-efficient method, is a more challenging reaction, but the previous catalytic methods²¹⁻²³ suffer from limited substrate scope, low yields, low turnover number (TON) and no reports on catalyst reuse. Recently, Mitsudome et al.²⁴ reported a heterogeneous catalytic system for the deoxygenation of various sulfoxides by 1 atm H₂ using 5 mol% of Ru/TiO₂, which exhibited a high TON (500) for hydrodeoxygenation of diphenyl sulfoxide. Further improvement in this heterogeneous hydrodeoxygenation method will lead to a greener route to sulfides from sulfoxides. Additionally, hydrodeoxygenation of sulfones to sulfides, which is unprecedented in the literature, is a challenging target in catalysis.

Recently, we found that Pt and MoO_x co-loaded TiO₂ (Pt-MoO_x/TiO₂) showed high activity for three types of hydrogenation reactions: (1) catalytic methylation of secondary amines by CO₂ and H₂,²⁵ (2) reductive amination of levulinic acid by H₂ to *N*-alkyl-5-methyl-2-pyrrolidones,²⁶ and (3) selective synthesis of primary amines by the reductive amination of ketones.²⁷ The results motivated us to study a possible application of Pt-MoO_x/TiO₂ to the reduction of S=O bonds. Considering that we have not characterized the structure of Pt-MoO_x/TiO₂ in detail, estimation of the structure of Pt-MoO_x/TiO₂ is an additional issue to be addressed.

We report herein a new catalytic system for the hydrodeoxygenation of various sulfoxides and sulfones to sulfides under mild conditions (50–155 °C, 1 or 7 atm H₂) using Pt–MoO_x/ TiO₂ as a reusable heterogeneous catalyst. The substrate scope, catalyst reuse and catalyst characterization studies are also carried out to show the structure and catalytic performance of Pt–MoO_x/TiO₂.

Experimental

General

Commercially available organic and inorganic compounds (from Tokyo Chemical Industry, WAKO Pure Chemical Industries, Kanto Chemical or Mitsuwa Chemical) were used without further purification. GC (Shimadzu GC-2014) and

^aInstitute for Catalysis, Hokkaido University, N-21, W-10, Sapporo 001-0021, Japan ^bElements Strategy Initiative for Catalysts and Batteries, Kyoto University, Katsura, Kyoto 615-8520, Japan. E-mail: kshimizu@cat.hokudai.ac.jp; Fax: +81-11-706-9163 †Electronic supplementary information (ESI) available. See DOI: 10.1039/ c5gc02806j

GCMS (Shimadzu GCMS-QP2010) analyses were carried out with an Ultra ALLOY capillary column UA^+ -1 (Frontier Laboratories Ltd) using N₂ and He as the carrier gas.

Catalyst preparation

TiO₂ (JRC-TIO-4, 50 m² g⁻¹), MgO (JRC-MGO-3), CeO₂ (JRC-CEO-3) and HBEA zeolite (JRC-Z-HB25, SiO₂/Al₂O₃ = 25 ± 5) were supplied from the Catalysis Society of Japan. SiO₂ (Q-10, 300 m² g⁻¹) was supplied from Fuji Silysia Chemical Ltd. Active carbon (C) was purchased from Kanto Chemical. γ -Al₂O₃ was prepared by calcination of γ -AlOOH (Catapal B Alumina, Sasol) for 3 h at 900 °C. Nb₂O₅ was prepared by calcination of Nb₂O₅·*n*H₂O (supplied by CBMM) at 500 °C for 3 h. ZrO₂ was prepared by hydrolysis of zirconium oxynitrate 2-hydrate by an aqueous NH₄OH solution, followed by filtration, washing with distilled water, drying at 100 °C for 12 h, and by calcination at 500 °C for 3 h.

Precursors of M^1 -MoO_x/TiO₂ (M^1 = 5 wt% Pt, Rh, Pd, Re, Ru, Ni, Cu; 7 wt% Mo) and Pt- M^2O_x/TiO_2 (5 wt% Pt; $M^2 = 7$ wt % Mo, V, Nb, W, Re) were prepared by a sequential impregnation method using M¹ source [aqueous HNO₃ solutions of Pt(NH₃)₂(NO₃)₂, Rh(NO₃)₃ or Pd(NH₃)₂(NO₃)₂, NH₄ReO₄, RuCl₃ or aqueous solution of nitrates (Ni, Cu)], M² source $[(NH_4)_6Mo_7O_{24} \cdot 4H_2O,$ NH₄VO₃, niobium oxalate, (NH₄)₁₀W₁₂O₄₁·5H₂O or NH₄ReO₄] and TiO₂. For the preparation of Pt-MoO_x/TiO₂ (5 wt% Pt, 7 wt% Mo) as an example, 5 g of TiO₂ and 0.88 mmol of (NH₄)₆Mo₇O₂₄·4H₂O were added to 50 mL of water at 50 °C, followed by evaporation to dryness at 50 °C, and by drying at 90 °C for 12 h and calcination in air at 500 °C for 3 h to obtain MoO₃-loaded TiO₂ (MoO₃/TiO₂). MoO₃/TiO₂ was added to an aqueous HNO₃ solution of Pt (NH₃)₂(NO₃)₂, followed by evaporation to dryness at 50 °C, and by drying at 90 °C for 12 h. Precursors of metal oxide-supported Pt catalysts were prepared by the impregnation method using an aqueous HNO₃ solution of $Pt(NH_3)_2(NO_3)_2$. Before each catalytic experiment, catalysts were prepared by prereduction of the precursor in a Pyrex tube under a flow of H₂ (20 cm³ min⁻¹) at 300 °C for 0.5 h.

Catalyst characterization

X-ray absorption near-edge structures (XANES) at the Pt L_3 edge were measured at the BL14B2 in the SPring-8 (Proposal No. 2012A1734) in a transmittance mode. The storage ring was operated at 8 GeV. A Si(111) double crystal monochromator was used to obtain a monochromatic X-ray beam. Pt–MoOX/ TiO₂ pre-reduced in 100% H₂ (20 cm³ min⁻¹) for 0.5 h at 300 °C was cooled to room temperature in H₂ and was sealed in cells made of polyethylene under N₂, and then the XANES spectrum was recorded at room temperature. XANES analysis was performed using the REX version 2.5 program (RIGAKU).

The oxidation state of Mo species in the pre-reduced Pt-MoO_x/TiO₂ was estimated by X-ray photoelectron spectroscopy (XPS) using a JEOL JPS-9010MC (Mg K α irradiation). Binding energies were calibrated with respect to C_{1s} at 285.0 eV.

TEM measurement of the pre-reduced $Pt-MoO_x/TiO_2$ was carried out by using a JEOL JEM-2100F TEM operated at 200 kV.

In situ infrared (IR) spectra were recorded at 40 °C using a JASCO FT/IR-4200 equipped with a quartz IR cell connected to a conventional flow reaction system. The sample was pressed into a 40 mg of a self-supporting wafer ($\phi = 2$ cm) and mounted into the quartz IR cell with CaF2 windows. Spectra were recorded accumulating 30 scans at a resolution of 4 cm^{-1} . A reference spectrum of the catalyst wafer taken under He at measurement temperature was subtracted from each spectrum. For the IR study of pyridine adsorption on support materials (Fig. 1), the sample disc, pre-heated in He flow at 500 °C for 0.5 h, was exposed to pyridine (1 µL as liquid) vaporized at 200 °C under He flow at 200 °C. After purging with He for 600 s, the IR spectra of the adsorbed pyridine were obtained. For the IR study of CO adsorption (Fig. 4), the disk of Pt-loaded catalysts *in situ* pre-reduced under H₂ (20 cm³ min⁻¹, 300 °C, 0.5 h), was cooled to 40 °C under He, followed by flowing CO(5%)/He $(20 \text{ cm}^3 \text{ min}^{-1})$ for 180 s. After purging with He $(40 \text{ cm}^3 \text{ min}^{-1})$ for 600 s, the IR spectrum of the adsorbed CO was obtained.

Catalytic tests

Pt-MoOx/TiO2 was used as the standard catalyst. After the prereduction at 300 °C, the catalyst in a closed glass tube with a septum inlet was cooled to room temperature under H₂. *n*-Dodecane (0.05 g) was injected to the pre-reduced catalyst inside the glass tube through the septum inlet, then the septum was removed under air, and sulfoxides (1.0 mmol) and a stirrer bar were charged to the tube, followed by inserting the tube inside a stainless autoclave with a dead space of 28 cm³. Soon after being sealed, the reactor was flushed with H_2 and charged with 7 atm H_2 at room temperature. Then the reactor was heated at 50 or 120 °C under stirring (180 rpm) for 24 h. The reactions under ambient H_2 pressure, eqn (1) and (2), were carried out in a closed glass tube with balloon hydrogen at 155 °C. For the reactions in Table 1 and Fig. 1, 6-8 conversions and yields of sulfides were determined by GC using *n*-dodecane as an internal standard adopting the GC-sensitivity estimated using the commercial compounds. For the scope and limitation study in Table 2, the isolated yields of products were determined as follows. After the reaction, 2-propanol



Fig. 1 IR spectra of pyridine adsorbed on support materials (40 mg) at 200 °C.

(4 mL) was added to the mixture, and the catalyst was separated by centrifugation. Then, the reaction mixture was concentrated in a vacuum evaporator to remove the volatile compounds. Then, sulfides were isolated by column chromatography using silica gel 60 (spherical, $63-210 \mu$ m, Kanto Chemical Co. Ltd) with hexane/ethylacetate (2/1 to 5/1) as the eluting solvent, followed by analyses by ¹H NMR, ¹³C NMR and GCMS. The concentration of Pt in the solution after the standard reaction was checked by inductive coupling plasma (ICP-AES) using ICPE-9000 (Shimadzu).

Results and discussion

Characterization of Pt-MoO_x/TiO₂

First, we characterized the structure of the MoO_3/TiO_2 support. The N₂ adsorption result showed that the surface area of MoO_3/TiO_2 was 54 m² g⁻¹. The XRD pattern of MoO_3/TiO_2 showed no diffraction lines due to Mo oxides (result not shown), which indicate the absence of crystalline MoO_3 particles on MoO_3/TiO_2 . According to the literature,²⁸ the non-crystalline Mo(rv) oxide species on TiO_2 are monolayer or small clusters (polymeric molybdates) of Mo(rv) oxide. TEM images of MoO_3/TiO_2 were also essentially identical to that of TiO_2 .

Fig. 1 compares the IR spectra (the ring-stretching region) of pyridine adsorbed on MoO₃/TiO₂ and TiO₂. For both of the support materials, strong bands due to the coordinatively bound pyridine on a Lewis acid (1445 and *ca* 1607 cm^{-1})^{29,30} are observed. The bands for MoO₃/TiO₂ are higher in intensity than those for TiO₂, which indicates that the relative amount of Lewis acid sites of TiO₂ is increased by the loading of MoO₃. It is known that the position of the band around 1607 $\rm cm^{-1}$ increases with the increase in the Lewis acid strength of metal oxides.²⁹ The higher wavenumber of the band for MoO₃/TiO₂ (1607 cm^{-1}) than TiO_2 (1604 cm^{-1}) indicates that the Lewis acid strength of TiO₂ is increased by the loading of MoO₃. Considering that the surface density of Mo on MoO₃/TiO₂ (7.4 Mo atoms nm^{-2} -TiO₂) is larger than the monolayer coverage of Mo on the TiO_2 support (6 Mo atoms $nm^{-2}-TiO_2$),²⁸ these results suggest that the surface of TiO₂ is covered by small (or thin layer) polymeric molybdates whose surface contains coordinatively unsaturated Mo cations as Lewis acid sites. This structural model of MoO₃/TiO₂ is consistent with that in the literature for MoO₃/TiO₂ with a monolayer coverage of Mo.²⁸ Additionally, the spectrum for MoO₃/TiO₂ shows a broad and weak band at1538 cm⁻¹ due to the pyridinium ion (PyH⁺) produced by the reaction of pyridine with the Brønsted acid site.

Next, the structure of the representative catalyst, Pt–MoO_x/ TiO₂ pre-reduced at 300 °C, was characterized by various spectroscopic methods. The oxidation state of Mo species was studied by XPS. Fig. 2 compares the XPS spectra (Mo $3d_{5/2}$ region) of MoO₃/TiO₂ and Pt–MoO_x/TiO₂. As expected, the Mo $3d_{5/2}$ binding energy (BE) of MoO₃/TiO₂ (232.6 eV) corresponds to the oxidation state of Mo⁶⁺.^{31,32} The Mo $3d_{5/2}$ peak of Pt– MoO_x/TiO₂ appeared at a lower BE of 230.5 eV assignable to Mo⁴⁺ species,^{31,32} but peaks due to the metallic Mo⁰ (227.9



Fig. 2 XPS spectra of the Mo 3d region of MoO_3/TiO_2 and $Pt-MoO_{\rm x}/TiO_2.$



Fig. 3 Pt L₃-edge XANES spectra of Pt-MoO_x/TiO₂ and Pt foil.

eV)³¹ and PtMo alloys (227.8 eV)³² were not observed. Combined with the structural model of MoO₃/TiO₂ discussed above, the Mo species on the Pt-MoO_x/TiO₂ catalyst can be small (or thin layer) MoO₂ species.

The bulk oxidation state of Pt species in Pt–MoO_x/TiO₂ was studied by Pt L₃-edge XANES (Fig. 3). The XANES feature of Pt–MoO_x/TiO₂ is quite close to that of the Pt foil, indicating the metallic state of the Pt species in Pt–MoO_x/TiO₂. The surface oxidation state of Pt species in Pt–MoO_x/TiO₂ was studied by the IR spectra of CO adsorbed on the sample (Fig. 4). The IR spectrum of CO adsorbed on Pt–MoO_x/TiO₂ showed a strong band at 2073 cm⁻¹ due to linearly coordinated CO on a metallic Pt⁰ site^{32,33} together with a weak band due to bridged CO adspecies on a Pt metal plane (1850 cm⁻¹).^{32,33} This indicates that the surface of Pt is metallic.

Fig. 5 shows the representative TEM images of Pt-MoO_x/ TiO₂. From low resolution (upper side) and high resolution (lower side) TEM images, the Pt particle size distribution was obtained as shown in the figure. The volume-area mean diameter of Pt particles was 4.7 ± 1.1 nm. This value is close to the average diameter of Pt particles (4.1 nm)²⁵ estimated by the CO adsorption experiment assuming that CO is adsorbed on the surface of spherical Pt particles at a stoichiometry of CO/



Fig. 4 IR spectra of CO adsorbed on Pt-MoO_x/TiO₂ at 40 °C.



Fig. 5 Representative TEM images and Pt particle size distribution of Pt-MoO_x/TiO₂. The volume-area mean diameter of Pt particles was 4.7 \pm 1.1 nm.

(surface Pt atom) = 1/1. Summarizing the structural results, the dominant Pt species in Pt–MoO_x/TiO₂ are around 4–5 nm sized Pt metal nanoparticles. Mo oxides are not observed in the high resolution TEM image, which supports that MoO₂ species on Pt–MoO_x/TiO₂ are small clusters or thin layer species.

 Table 1
 Catalyst screening for hydrogenation of diphenyl sulfoxide to diphenyl sulfide

[$ \begin{array}{c} 0 \\ S \\ 1 mmol \end{array} $ + H ₂ + H	0.1 mol% cat. no solvent 50 °C, 24 h) ^S
Entry	Catalysts	Conv. (%)	GC yield (%)
L	MoO ₂ /TiO ₂	9	8
2	$Pt-MoO_{2}/TiO_{2}$	100	97
3	Pt-ReO _x /TiO ₂	69	67
1	Pt-WO, TiO2	56	54
5	Pt-NbO _r /TiO ₂	41	40
5	Pt-VO _x /TiO ₂	37	36
7	$Pt-MoO_x/Al_2O_3$	73	71
3	Pt/Al ₂ O ₃	58	56
)	Pt/Nb ₂ O ₅	56	54
10	Pt/HBEA	48	47
1	Pt/MgO	42	39
12	Pt/CeO ₂	41	38
13	Pt/ZrO_2	34	31
14	Pt/TiO_2	30	28
15	Pt/SiO_2	25	23
16	Pt/C	25	24
17	Rh-MoO ₃ /TiO ₂	75	72
18	Pd-MoO ₃ /TiO ₂	57	55
19	Re-MoO ₃ /TiO ₂	40	39
20	Ru-MoO ₃ /TiO ₂	34	33
21	Ni-MoO ₃ /TiO ₂	26	24
22	Cu-MoO ₃ /TiO ₂	15	14

Optimization of catalysts

Table 1 shows the influence of catalyst composition on the catalytic activity for hydrogenation of diphenyl sulfoxide to diphenyl sulfide under solvent-free conditions under 7 atm H2 at 50 °C for 24 h using 0.1 mol% of the catalyst. Among various Pt catalysts, including bimetal loaded TiO₂ (Pt-MO_r/ TiO₂; M = 7 wt% Mo, V, Nb, W, Re; entries 2–6), Pt–MoO_x coloaded Al₂O₃ (entry 7) and Pt-loaded metal oxides (entries 8-16), Pt-MoO_x/TiO₂ (entry 2) showed the highest yield of diphenyl sulfide (97%) as well as the highest conversion of diphenyl sulfoxide (100%). The yield for $Pt-MoO_x/TiO_2$ (97%) is much higher than those for MoO₃/TiO₂ (8%) and Pt/TiO₂ (28%), which indicates a synergistic effect between Pt and MoO₃. Pt- MoO_x/TiO_2 showed a higher yield than the various metal (Rh, Pd, Re, Ru, Ni, Cu)-loaded MoO_x/TiO₂ catalysts (entries 17–22). Summarizing the screening result, it is found that Pt-MoO_x/ TiO₂ is the best catalyst in the 22 types of the heterogeneous catalysts tested as shown in Table 1. Under the same conditions, Pt-MoO_x/TiO₂ catalysts with Pt loadings of 0.1 and 1 wt% showed 61% and 80% yields (results not shown), which were lower than the standard catalyst with 5 wt% Pt loading.

In our previous studies on the hydrodeoxygenation of carbonyl compounds by Pt-loaded catalysts, we showed that the catalytic activity was highly support-dependent; Lewis acidic supports (such as MoO_x/TiO_2) showed a higher activity than the other supports.^{26,27} The role of the Lewis acid sites is shown to be the activation of C=O bonds by Lewis acid-base interactions between the surface Mo cation and carbonyl oxygen, while the

Table 2 $Pt-MoO_x/TiO_2$ -catalyzed sulfide synthesis from various sulfoxides





Fig. 6 Catalyst reuse for hydrogenation of diphenyl sulfoxide to diphenyl sulfide.

4 cycles. ICP-AES analysis of the solution after the first reaction showed that the Pt content in the solution was below the detection limits. The results indicate that $Pt-MoO_x/TiO_2$ is a reusable heterogeneous catalyst for this reaction.

As summarized in Table 2, the present solvent-free hydrogenation method was applicable to various sulfoxides under 7 atm H₂ at 50 or 120 °C. The reactions of aromatic (entries 1–7), benzylic (entry 8) and aliphatic (entries 9 and 10) sulfoxides resulted in the formation of the corresponding sulfides with high isolated yields (85–97%). The method showed chemoselective hydrogenation of sulfoxides without the conversion of other reducible functional groups: Cl– (entry 3), Br– (entry 7), carbonyl (entry 5) groups.

It is important to note that the catalytic system shows a high TON under ambient pressure (1 atm) of H₂ in a glass reactor under solvent-free conditions at 155 °C. As shown in eqn (1), 1 mmol of diphenyl sulfoxide was hydrogenated by Pt-MoO_x/TiO₂ containing 0.001 mmol (0.1 mol%) of Pt, and diphenyl sulfide was obtained in 99% yield after 24 h. As shown in eqn (2), hydrogenation of 5 mmol of diphenyl sulfoxide under 1 atm H₂ for 120 h by a smaller amount of the catalyst (0.02 mol%) gave diphenyl sulfide in 88% yield, corresponding to a TON of 4400 with respect to the total number of Pt atoms in the catalyst. This value is higher than that of previously reported catalysts.^{21–24} However, the reaction of 30 mmol of diphenyl sulfoxide with 0.01 mol% of the catalyst for 120 h resulted in only 28% yield (not shown).



 $^{a}T = 50 \, ^{\circ}\text{C}. \, ^{b}t = 36 \, \text{h}. \, ^{c}\text{GC}$ yield.

Pt is proposed to act as a H_2 dissociation site.^{26,27} We speculate the same cooperative mechanism of Pt and Lewis acid sites in the present catalytic system, in which Mo cations as Lewis acid sites activate S=O bonds in the substrates.

n-C11H23

n-C₁₁H₂₃

.S

96

98⁶

91

_n-C₁₁H₂₃

Catalytic performance of Pt-MoO_x/TiO₂

As shown in Fig. 6, the Pt–MoO_x/TiO₂ catalyst showed good reusability for the hydrogenation of diphenyl sulfoxide under the conditions given in Table 1. After the reaction, 2-propanol (4 mL) was added to the mixture, and the catalyst was separated by centrifugation. The catalyst was dried at 100 °C for 1 h and reduced under H₂ at 300 °C for 0.5 h. The recovered catalyst showed high yields (>89%) of diphenyl sulfide for the next

 8^b

9

10



Fig. 7 Initial formation rate of diphenyl sulfide vs. concentration of a sulfide, 4-(methylthio)aniline, for hydrogenation of diphenyl sulfoxide to diphenyl sulfide at 50 °C under 7 atm H_2 by 0.1 mol% Pt-MoO_x/TiO₂.



Fig. 8 Time dependence of GC yields for the reduction of benzyl phenyl sulfone at 120 °C under 7 atm H₂ by 0.1 mol% Pt-MoO_x/TiO₂ catalyst: (•) unreacted benzyl phenyl sulfone, (∇) benzyl phenyl sulfoxide, (\bigcirc) benzyl phenyl sulfide.

In general, transition metal surfaces interact strongly with sulfur atoms in sulfides, resulting in the deactivation of the catalysts. To test the sulfur-tolerance of the Pt-MoO_x/TiO₂ catalyst during the catalytic reaction, we studied the effect of the concentration of a model sulfide, 4-(methylthio)aniline, on the initial formation rate of diphenyl sulfide for the hydrogenation of diphenyl sulfoxide by Pt-MoO_x/TiO₂ (Fig. 7). The reaction rate slightly decreased with the sulfide concentration, but the reaction order with respect to the sulfide (n = -0.09) was close to zero. The result indicates that the Pt-MoO_x/TiO₂ catalyst shows a moderate sulfur-tolerance during the reaction. This sulfur-tolerance may be a possible reason for the high TON of this catalytic system.

Interestingly, the present catalytic system was found to be effective for the hydrogenation of a sulfone. Fig. 8 shows a time-yield profile for the reduction of benzyl phenyl sulfone under 7 atm H_2 in the presence of 0.1 mol% of the Pt-MoO_x/TiO₂ catalyst (containing 0.001 mmol of Pt). The result shows

a profile characteristic of a consecutive reaction pathway. The yield of unreacted benzyl phenyl sulfone decreased with time. The yield of the partially hydrogenated product (benzyl phenyl sulfoxides) increased with time and then decreased. After 40 h, a completely deoxygenated product (benzyl phenyl sulfide) was selectively obtained in 85% yield. To our knowledge, the result represents the first example of catalytic hydrogenation of a sulfone to a sulfide by H_2 .

Conclusions

Characterization of Pt–MoO_x/TiO₂ showed that the surface of TiO₂ was covered by small (or thin layer) MoO₂ species with exposed Mo cations as Lewis acid sites and 4–5 nm sized Pt metal nanoparticles were loaded on the support. Pt–MoO_x/TiO₂ was found to be an effective and reusable catalyst for the reduction of sulfoxides to sulfides under solvent-free and mild conditions (50–155 °C, 1 or 7 atm H₂), which showed a higher TON than previously reported catalysts. Pt–MoO_x/TiO₂ catalyzed the reduction of benzyl phenyl sulfone by H₂ to benzyl phenyl sulfide, which represented the first example of catalytic conversion of a sulfone to a sulfide by H₂.

Acknowledgements

This work was supported by Grant-in-Aids for Scientific Research B (26289299) from MEXT (Japan), a MEXT program "Elements Strategy Initiative to Form Core Research Center" and a Grant-in-Aid for Scientific Research on Innovative Areas "Nano Informatics" (25106010) from JSPS.

References

- 1 M. Madesclaire, Tetrahedron, 1988, 44, 6537-6580.
- 2 R. Hille, Chem. Rev., 1996, 96, 2757-2816.
- 3 A. C. Fernandes and C. C. Romão, *Tetrahedron*, 2006, 62, 9650–9654.
- 4 I. Cabrita, S. C. A. Sousa and A. C. Fernandes, *Tetrahedron Lett.*, 2010, **51**, 6132–6135.
- 5 S. Enthaler, Catal. Sci. Technol., 2011, 1, 104-110.
- 6 S. Enthaler, ChemCatChem, 2011, 3, 666-670.
- 7 S. Krackl, A. Company, S. Enthaler and M. Driess, *ChemCatChem*, 2011, 3, 1186–1192.
- 8 Y. Mikami, A. Noujima, T. Mitsudome, T. Mizugaki, K. Jitsukawa and K. Kaneda, *Chem. – Eur. J.*, 2011, 17, 1768–1722.
- 9 J. M. S. Cardoso and B. Royo, *Chem. Commun.*, 2012, 48, 4944–4946.
- A. C. Fernandes and C. C. Romão, *Tetrahedron Lett.*, 2007, 48, 9176–9179.
- 11 S. Enthaler, S. Krackl, E. Irran and S. Inoue, *Catal. Lett.*, 2012, **142**, 1003–1010.
- 12 Z. Zhu and J. H. Espenson, *J. Mol. Catal. A: Chem.*, 1995, 103, 87–94.

- 13 J. B. Arterburn and M. C. Perry, *Tetrahedron Lett.*, 1996, 37, 7941–7944.
- 14 R. Sanz, J. Escribano, R. Aguado, M. R. Pedrosa and F. J. Arnáiz, *Synthesis*, 2004, 1629–1632.
- 15 M. Bagherzadeh, M. M. Haghdoost, M. Amini and P. G. Derakhshandeh, *Catal. Commun.*, 2012, **23**, 14–19.
- 16 N. García, P. García-García, M. A. Fernández-Rodríguez, R. Rubio, M. R. Pedrosa, F. J. Arnáiz and R. Sanz, *Adv. Synth. Catal.*, 2012, 354, 321–327.
- 17 S. C. A. Sousa, J. R. Bernardo and A. C. Fernandes, *Tetrahedron Lett.*, 2012, 53, 6205–6208.
- 18 S. C. A. Sousa, J. R. Bernardo, P. R. Florindo and A. C. Fernandes, *Catal. Commun.*, 2013, 40, 134–138.
- 19 N. García, P. García- García, M. A. Fernández-Rodríguez, D. García, M. R. Pedrosa, F. J. Arnáiz and R. Sanz, *Green Chem.*, 2013, **15**, 999–1005.
- 20 Y. Takahashi, T. Mitsudome, T. Mizugaki, K. Jitsukawa and K. Kaneda, *Chem. Lett.*, 2014, **43**, 420–422.
- 21 K. Ogura, M. Yamashita and G. Tsuchihashi, *Synthesis*, 1975, 385–387.
- 22 B. R. James, F. T. T. Ng and G. L. Rempel, *Can. J. Chem.*, 1969, 47, 4521–4526.
- 23 P. M. Reis, P. J. Costa, C. C. Romáo, J. A. Fernandes, M. J. Calhorda and B. Royo, *Dalton Trans.*, 2008, 1727–1733.

- 24 T. Mitsudome, Y. Takahashi, T. Mizugaki, K. Jitsukawa and K. Kaneda, *Angew. Chem., Int. Ed.*, 2014, 53, 8348– 8351.
- 25 K. Kon, S. M. A. H. Siddiki, W. Onodera and K. Shimizu, *Chem. Eur. J.*, 2014, **20**, 6264–6267.
- 26 A. S. Touchy, S. M. A. H. Siddiki, K. Kon and K. Shimizu, *ACS Catal.*, 2014, 4, 3045–3050.
- 27 Y. Nakamura, K. Kon, A. S. Touchy and K. Shimizu, *Chem-CatChem*, 2015, 7, 921–924.
- 28 G. Tsilomelekis and S. Boghosian, J. Phys. Chem. C, 2011, 115, 2146–2154.
- 29 D. T. Lundie, A. R. McInroy, R. Marshall, J. M. Winfield, P. Jones, C. C. Dudman, S. F. Parker, C. Mitchell and D. Lennon, *J. Phys. Chem. B*, 2005, **109**, 11592– 11601.
- 30 M. Tamura, K. Shimizu and A. Satsuma, *Appl. Catal., A*, 2012, **433–434**, 135–145.
- 31 A. Katrib, J. W. Sobczak, M. Krawczyk, L. Zommer, A. Benadda, A. Jablonski and G. Maire, *Surf. Interface Anal.*, 2002, 34, 225–229.
- 32 S. Zafeiratos, G. Papakonstantinou, M. M. Jacksic and S. G. Neophytides, *J. Catal.*, 2005, 232, 127–136.
- 33 D. A. G. Aranda and M. Schmal, J. Catal., 1997, 171, 398– 405.