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Hydrodeoxygenation of sulfoxides to sulfides by Pt and MoOx co-loaded TiO$_2$ catalyst

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Abstract

Supported metal nanoparticle catalysts were studied for the hydrogeoxygenation of sulfoxides to sulfides under solvent-free and mild conditions (50-155 °C, 1 or 7 atm H$_2$). 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 MoOx co-loaded TiO$_2$ (Pt-MoOx/TiO$_2$) showed the highest activity. Pt-MoOx/TiO$_2$ was reusable after the reaction and was effective for the reduction of various sulfoxides and showed higher turnover number (TON) than previously reported catalysts. Using Pt-MoOx/TiO$_2$, benzylphenylsulfone was reduced by H$_2$ to give phenylbenzyl sulfide via benzylphenyl sulfoxides, which represented the first example of catalytic conversion of a sulfone to a sulfide by H$_2$. Characterization studies of Pt-MoOx/TiO$_2$ show that the surface of TiO$_2$ 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 oxides-covered TiO$_2$.

Introduction

Deoxygenation of sulfoxides to the corresponding sulfides is an important transformation in organic synthesis.[1] Several catalytic methods have been developed to reduce sulfoxides using stoichiometric amount of reducing agents, including silanes,[2] borane,[10,11] phosphine,[12-15] which suffer from use of hazardous reagents and production of by-products that are sometimes difficult to remove from the reaction media. Recently, greener catalytic methods with alcohols[16-20] as reducing agents were developed, but they also suffered from low atom-efficiency. The catalytic deoxygenation of sulfoxides by H$_2$, as the most atom-efficient method, is a more challenging reaction, but the previous catalytic methods[21-23] 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 H_2 using 5 mol% of Ru/TiO_2, which exhibited a high TON (500) for hydrogeoxygenation of diphenyl sulfoxide. Further improvement in this heterogeneous hydrogeoxygenation method will lead to a greener route to sulfides from sulfoxides. Additionally, hydrogeoxygenation of sulfones to sulfides, which is unprecedented in the literature, is a challenging target in catalysis.

Recently, we found that Pt and MoOx co-loaded TiO_2 (Pt-MoOx/TiO_2) showed high activity for three types of hydrogenation reactions: (1) catalytic methylation of secondary amines by CO_2 and H_2,[25] (2) reductive amination of levulinic acid by H_2 to N-alkyl-5-methyl-2-pyrrolidones,[26] (3) selective synthesis of primary amines by the reductive amination of ketones.[27] The results motivated us to study a possible application of Pt-MoOx/TiO_2 to the reduction of S=O bonds. Considering that we have not characterized the structure of Pt-MoOx/TiO_2 in detail, estimation of the structure of Pt-MoOx/TiO_2 is an additional issue to be addressed.

We report herein a new catalytic system for the hydrodeoxygenation of various sulfoxides and a sulfone to sulfides under mild conditions (50-155 °C, 1 or 7 atm H_2) using Pt-MoOx/TiO_2 as a reusable heterogeneous catalyst. Substrate scope, catalyst reuse and catalyst characterization studies are also carried out to show the structure and catalytic performance of Pt-MoOx/TiO_2.

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 GCMS (Shimadzu GCMS-QP2010) analyses were carried out with Ultra ALLOY capillary column UA$^+$-1 (Frontier Laboratories Ltd.) using N_2 and He as the carrier gas.

Catalyst Preparation

TiO_2 (JRC-TIO-4, 50 m^2 g^{-1}), MgO (JRC-MGO-3), CeO_2 (JRC-CEO-3) and HBEA zeolite (JRC-Z-HB25, SiO_2/Al_2O_3= 25±5) were supplied from Catalysis Society of Japan. SiO_2 (Q-10, 300 m^2 g^{-1}) was supplied from Fuji Silysia Chemical Ltd. Active carbon (C) was purchased from Kanto Chemical. γ-Al_2O_3 was prepared by calcination of γ-AlOOH (Catapal B Alumina, Sasol) for 3 h at 900 °C. Nb_2O_5 was prepared by calcination of $Nb_2O_5 \cdot nH_2O$ (supplied by CBMM) at 500 °C for 3 h. ZrO_2 was prepared by hydrolysis of zirconium oxynitrate 2-hydrate by an aqueous NH_4OH 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$_X$/TiO$_2$ (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 sequential impregnation method using M^1 source [aqueous HNO$_3$ solutions of Pt(NH$_3$)$_2$(NO$_3$)$_2$, Rh(NO$_3$)$_3$ or Pd(NH$_3$)$_2$(NO$_3$)$_2$, NH$_4$ReO$_4$, RuCl$_3$ or aqueous solution of nitrates (Ni, Cu)], M^2 source [(NH$_4$)$_6$Mo$_7$O$_{24}$·4H$_2$O, NH$_4$VO$_3$, niobium oxalate, (NH$_4$)$_{10}$W$_{12}$O$_{41}$·5H$_2$O or NH$_4$ReO$_4$] and TiO$_2$. For the preparation of Pt-MoOx/TiO$_2$ (5 wt% Pt, 7 wt% Mo) as an example, 5 g of TiO$_2$ and 0.88 mmol of (NH$_4$)$_6$Mo$_7$O$_{24}$•4H$_2$O 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 MoO$_3$-loaded TiO$_2$ (MoO$_3$/TiO$_2$). MoO$_3$/TiO$_2$ was added to aqueous HNO$_3$ solution of Pt(NH$_3$)$_2$(NO$_3$)$_2$, 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 aqueous HNO$_3$ solution of Pt(NH$_3$)$_2$(NO$_3$)$_2$. Before each catalytic experiment, catalysts were prepared by pre-reduction of the precursor in a pyrex tube under a flow of H$_2$ (20 cm^3 min^{-1}) at 300 °C for 0.5 h.

Catalyst characterization

X-ray absorption near-edge structures (XANES) at 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-MoO$_X$/TiO$_2$ pre-reduced in 100% H$_2$ (20 cm^3 min^{-1}) for 0.5 h at 300 °C was cooled to room temperature in H$_2$ and was sealed in cells made of polyethylene under N$_2$, and then the XANES spectrum was taken at room temperature. XANES analysis was performed using the REX version 2.5 program (RIGAKU).

Oxidation state of Mo species in the pre-reduced Pt-MoO$_X$/TiO$_2$ was estimated by X-ray photoelectron spectroscopy (XPS) using a JEOL JPS-9010MC (Mg$K\alpha$ 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 self-supporting wafer (ϕ = 2 cm) and mounted into the quartz IR cell with CaF$_2$ windows. Spectra were measured 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, IR spectra of adsorbed pyridine were obtained. For the IR study of CO adsorption (Fig. 4), the disk of

Pt-loaded catalysts in situ pre-reduced under H_2 (20 cm^3 min^{-1}, 300 °C, 0.5 h), was cooled to 40 °C under He, followed by flowing CO(5%)/He (20 cm^3 min^{-1}) for 180 s. After purging with He (40 cm^3 min^{-1}) for 600 s, the IR spectrum of adsorbed CO was obtained.

Catalytic Tests

Pt-MoO_X/TiO_2 was used as the standard catalyst. After the pre-reduction at 300 °C, the catalyst in the closed glass tube with a septum inlet was cooled to room temperature under H_2. *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 cm^3. 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, 7, 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, isolated yields of products were determined as follows. After the reaction, 2-propanol (4 mL) was added to the mixture, and the catalyst was separated by centrifugation. Then, the reaction mixture was concentrated under vacuum evaporator to remove the volatile compounds. Then, sulfides were isolated by column chromatography using silica gel 60 (spherical, 63-210 μm, Kanto Chemical Co. Ltd.) with hexane/ethylacetate (2/1 to 5/1) as the eluting solvent, followed by analyses by ^1H NMR, ^{13}C NMR and GCMS. 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-MoOx/TiO₂

First, we characterized the structure of the MoO_3/TiO_2 support. The N_2 adsorption result showed that the surface area of MoO_3/TiO_2 was 54 m^2 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(IV) oxide species on TiO_2 are monolayer or small clusters (polymeric molybdates) of Mo(IV) oxide. TEM images of MoO_3/TiO_2 were also essentially identical to that of TiO_2.

Fig. 1 compares IR spectra (the ring-stretching region) of pyridine adsorbed on MoO_3/TiO_2 and TiO_2. For both of the support materials, strong bands due to the coordinatively bound pyridine on Lewis acid (1445 and *ca* 1607 cm^{-1})[29,30] are observed. The bands for MoO_3/TiO_2 are higher in intensity than those for TiO_2, which indicates that the relative amount of Lewis acid

sites of TiO_2 is increased by the loading of MoO_3. It is known that the position of the band around 1607 cm^{-1} increases with increase in the Lewis acid strength of metal oxides.[29] The higher wavenumber of the band for MoO_3/TiO_2 (1607 cm^{-1}) than TiO_2 (1604 cm^{-1}) indicates that Lewis acid strength of TiO_2 is increased by the loading of MoO_3. Considering that the surface density of Mo on MoO_3/TiO_2 (7.4 Mo atoms nm_{-TiO2}^{-2}) is larger than the monolayer coverage of Mo on the TiO_2 support (6 Mo atoms nm_{-TiO2}^{-2}),[28] these results suggest that the surface of TiO_2 is covered by small (or thin layer) polymeric molybdates whose surface contains coordinatively unsaturated Mo cations as Lewis acid sites. This structural model of MoO_3/TiO_2 is consistent with that in the literature for MoO_3/TiO_2 with a monolayer coverage of Mo.[28] Additionally, the spectrum for MoO_3/TiO_2 shows a broad and weak band at1538 cm^{-1} due to pyridinium ion (PyH^+) produced by the reaction of pyridine with Brønsted acid site.

Next, the structure of the representative catalyst, $Pt-MoOx/TiO_2$ 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 MoO_3/TiO_2 and $Pt-MoOx/TiO_2$. As expected, the Mo $3d_{5/2}$ binding energy (BE) of MoO_3/TiO_2 (232.6 eV) corresponds to the oxidation state of Mo^{6+}.[31,32] The Mo $3d_{5/2}$ peak of $Pt-MoOx/TiO_2$ appeared at lower BE of 230.5 eV assignable to Mo^{4+} species,[31,32] but peaks due to metallic Mo^0 (227.9 eV) [31] and PtMo alloys (227.8 eV)[32] were not observed. Combined with the structural model of MoO_3/TiO_2 discussed above, the Mo species on the $Pt-MoOx/TiO_2$ catalyst can be small (or thin layer) MoO_2 species.

The bulk oxidation state of Pt species in $Pt-MoOx/TiO_2$ was studied by Pt L_3-edge XANES (Fig. 3). The XANES feature of $Pt-MoOx/TiO_2$ is quite close to that of Pt foil, indicating metallic state of the Pt species in $Pt-MoOx/TiO_2$. The surface oxidation state of Pt species in $Pt-MoOx/TiO_2$ was studied by IR spectra of CO adsorbed on the sample (Fig. 4). The IR spectrum of CO adsorbed on $Pt-MoOx/TiO_2$ showed a strong band at 2073 cm^{-1} due to linearly coordinated CO on a metallic Pt^0 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 representative TEM images of $Pt-MoO_X/TiO_2$. 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 particle was 4.7 ± 1.1 nm. This value is close to the average diameter of Pt particles (4.1 nm)[25] estimated by CO adsorption experiment assuming that CO is adsorbed on the surface of spherical Pt particles at a stoichiometry of CO/(surface Pt atom) = 1/1. Summarizing the structural results, the dominant Pt species in $Pt-MoOx/TiO_2$ are around 4-5 nm sized Pt metal nanoparticles. Mo oxides are not observed in the high resolution TEM image, which support that MoO_2 species on $Pt-MoOx/TiO_2$ are small clusters or thin layer species.

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 in 7 atm H_2 at 50 ˚C for 4 h using 0.1 mol% of the catalyst. Among various Pt catalysts, including bimetal loaded TiO_2 (Pt-MO_X/TiO_2; M = 7 wt% Mo, V, Nb, W, Re; entries 2-6), Pt-MoOx co-loaded Al_2O_3 (entry 7) and Pt-loaded metal oxides (entries 8-16), Pt-MoO_X/TiO_2 (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 MoO_3/TiO_2 (8%) and Pt/TiO_2 (28%), which indicates synergistic effect between Pt and MoO_3. Pt-MoO_X/TiO_2 showed higher yield than the various metal (Rh, Pd, Re, Ru, Ni, Cu)-loaded MoO_X/TiO_2 catalysts (entries 17-22). Summarizing the screening result, it is found that Pt-MoO_X/TiO_2 is the best catalyst in the 22 types of the heterogeneous catalysts tested in Table 1. Under the same conditions, Pt-MoO_X/TiO_2 catalysts with Pt loading 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 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 interaction between surface Mo cation and carbonyl oxygen, while the Pt is proposed to act as 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.

Catalytic performance of Pt-MoO_X/TiO_2

As shown in Fig. 6, the Pt-MoO_X/TiO_2 catalyst showed good reusability for the hydrogenation of diphenyl sulfoxide under the conditions 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 ºC for 1 h and reduced in H_2 at 300 ºC for 0.5 h. The recovered catalyst showed high yields (> 89%) of diphenyl sulfide for the next 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 H_2 at 50 or 120 °C. The reactions of aromatic (entries 1-7), benzylic (entry 8) and aliphatic (entries 9, 10) sulfoxides resulted in the formation of the corresponding sulfides with high isolated yields (85-97%). The method showed chemoselective

hydrogenation of sulfoxides without 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 high TON under ambient pressure (1 atm) of H_2 in a glass reactor under solvent-free conditions at 155 ˚C. As shown in eqn. (1), 1 mmol of diphenyl sulfoxide was hydrogenated by $Pt-MoO_X/TiO_2$ containing 0.001 mmol (0.01 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 in 1 atm H_2 for 120 h by smaller amount of the catalyst (0.02 mol%) gave diphenyl sulfide in 88% yield, corresponding to TON of 4400 with respect to 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).
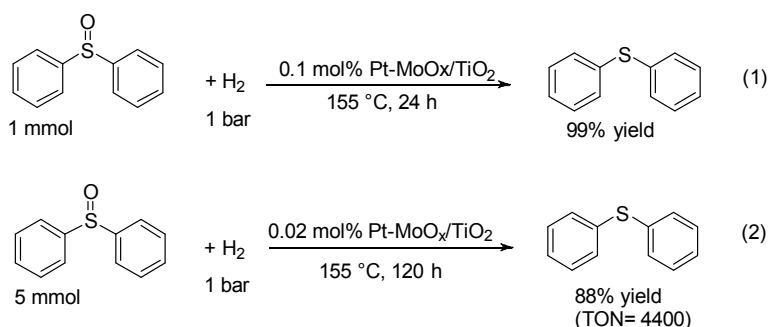
In general, transition metal surfaces interact strongly with sulfur atoms in sulfides, resulting in deactivation of the catalysts. To test sulfur-tolerance of the $Pt-MoO_X/TiO_2$ catalyst during the catalytic reaction, we studied the effect of the concentration of a model sulfide, 4-(methylthio)aniline, on the initial formation rate of diphenyl sulfide for hydrogenation of diphenyl sulfoxide by $Pt-MoOx/TiO_2$ (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 $Pt-MoO_X/TiO_2$ catalyst shows a moderate sulfur-tolerance during the reaction. This sulfur-tolerance may be a possible reason of the high TON of this catalytic system.

Interestingly, the present catalytic system was found to be effective for hydrogenation of a sulfone. Fig. 8 shows a time-yields profile for the reduction of benzyl phenyl sulfone under 7 atm H_2 in the presence of 0.1 mol% of the $Pt-MoOx/TiO_2$ catalyst (containing 0.001 mmol of Pt). The result shows a profile characteristic to consecutive reaction pathway. The yield of un-reacted 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-MoOx/TiO$_2$ showed that the surface of TiO$_2$ was covered by small (or thin layer) MoO$_2$ species with exposed Mo cations as Lewis acid sites and 4-5 nm sized Pt metal nanoparticles were loaded on the support. Pt-MoOx/TiO$_2$ 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 H_2), which showed higher TON than previously reported catalysts. Pt-MoOx/TiO$_2$ catalyzed the reduction of benzyl phenyl sulfone by H_2 to benzyl phenyl sulfide, which represented the first example of catalytic conversion of a sulfone to a sulfide by H_2.
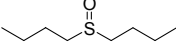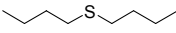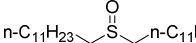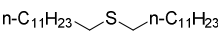
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References
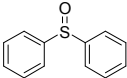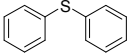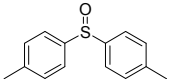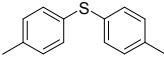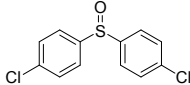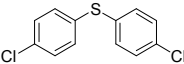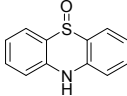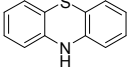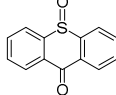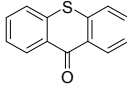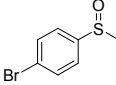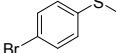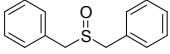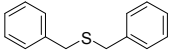
1. a) M. Madesclaire, *Tetrahedron*, 1988, **44**, 6537– 6580; b) R. Hille, *Chem. Rev.*, 1996, **96**, 2757–2816.

2. a) J. H. Enemark, J. J. A. Cooney, J.-J. Wang, R. H. Holm, *Chem. Rev.*, 2004, **104**, 1175–1200; b) J. H. Espenson, *Coord. Chem. Rev.*, 2005, **249**, 329–341.

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.

10. 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*, 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. Commu*n., 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, *ChemCatChem*, 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.

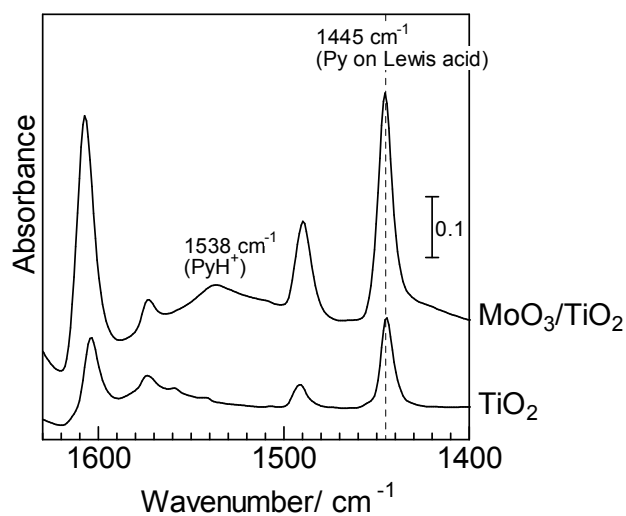33. D. A. G. Aranda and M. Schmal, *J. Catal*., 1997, **171**, 398–405.

Table 1. Catalyst screening for hydrogenation of diphenyl sulfoxide to diphenyl sulfide.
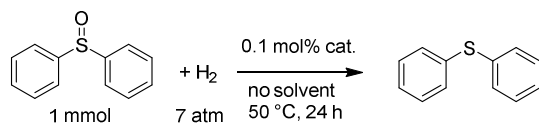
Entry	Catalysts	Conv. (%)	GC yield (%)
1	MoO_3/TiO_2	9	8
2	$Pt-MoOx/TiO_2$	100	97
3	$Pt-ReOx/TiO_2$	69	67
4	$Pt-WOx/TiO_2$	56	54
5	$Pt-NbOx/TiO_2$	41	40
6	$Pt-VOx/TiO_2$	37	36
7	$Pt-MoOx/Al_2O_3$	73	71
8	Pt/Al_2O_3	58	56
9	Pt/Nb_2O_5	56	54
10	$Pt/HBEA$	48	47
11	Pt/MgO	42	39
12	Pt/CeO_2	41	38
13	Pt/ZrO_2	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

Table 2. Pt-MoOx/TiO$_2$-catalyzed sulfides synthesis from various sulfoxides.

$$R^1\overset{\overset{O}{\parallel}}{S}R^2 + H_2 \xrightarrow[\substack{\text{no solvent}\\ 120\ ^\circ\text{C, 24 h}}]{0.1\ \text{mol\% Pt-MoO}_x/\text{TiO}_2} R^1\text{S}R^2$$

1 mmol, 7 atm

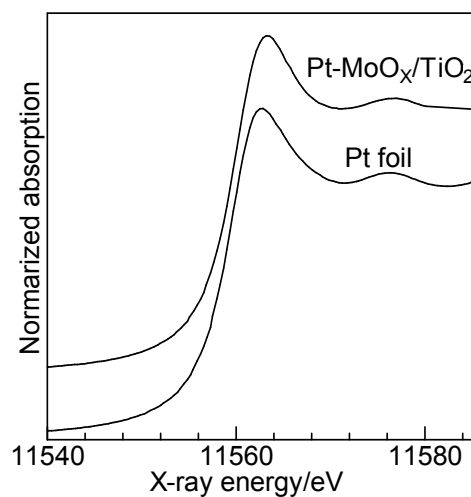| Entry	Sulfoxide	Sulfide	Isolated yield (%)
1[a]			97
2			92
3			88
4			87
5			85
6			94
7			91
8[b]			96
9			98[c]
10	n-C$_{11}$H$_{23}$—S(=O)—n-C$_{11}$H$_{23}$	n-C$_{11}$H$_{23}$—S—n-C$_{11}$H$_{23}$	91

[a] T = 50 °C, [b] t = 36 h, [c] GC yield

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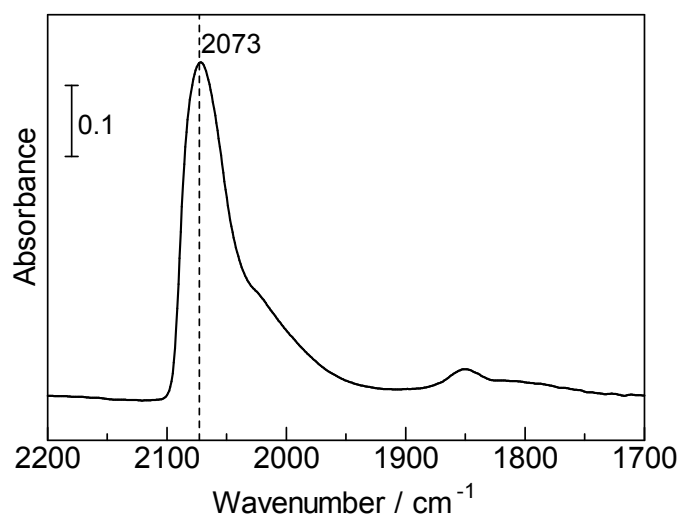**Fig. 1** IR spectra of pyridine adsorbed on support materials (40 mg) at 200 ˚C
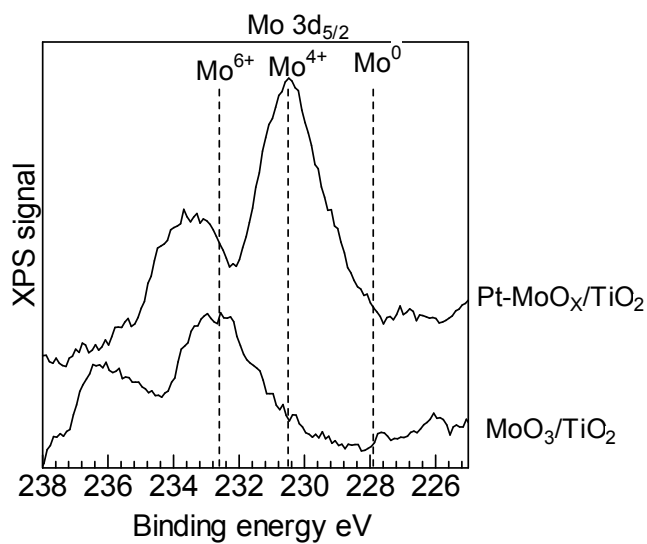
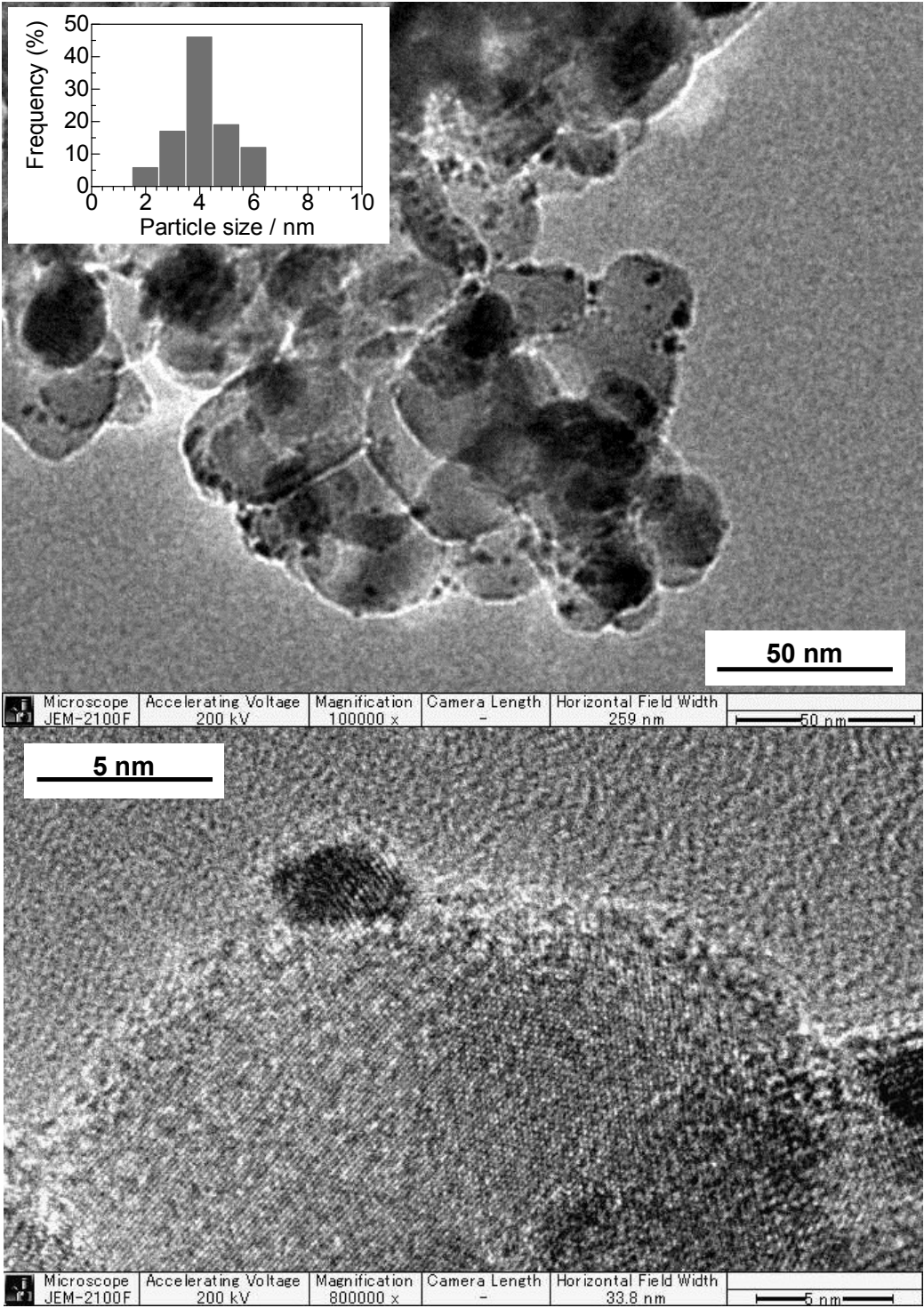**Fig. 2** XPS spectra of Mo 3d region of MoO_3/TiO_2 and Pt-MoOx/TiO_2.

Fig. 3. Pt L$_3$-edge XANES spectra of Pt-MoOx/TiO$_2$ and Pt foil.
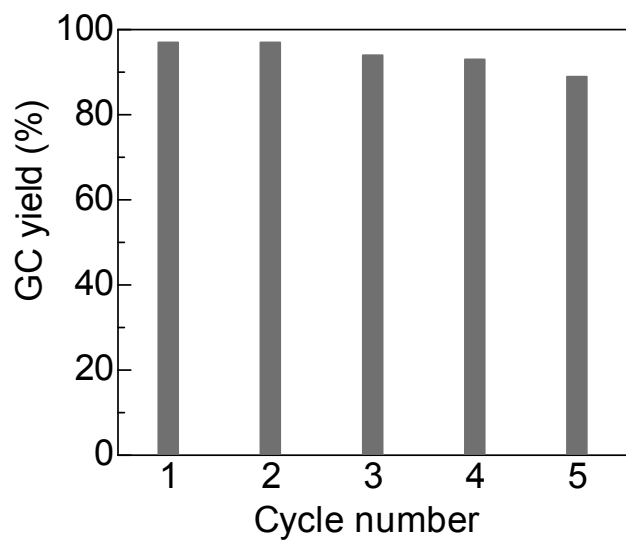

Fig. 4. IR spectra of CO adsorbed on Pt-MoO$_X$/TiO$_2$ at 40 ˚C.
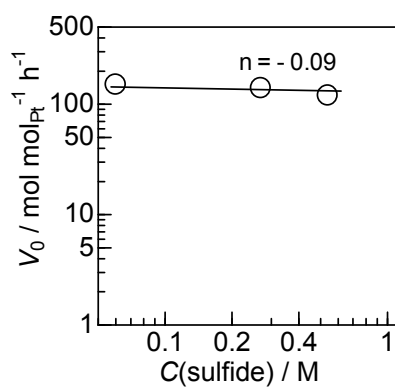
Fig. 5 Representative TEM images and Pt particle size distribution of Pt-MoO$_X$/TiO$_2$. The volume-area mean diameter of Pt particle was 4.7 ± 1.1 nm.

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

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-MoOx/TiO$_2$.

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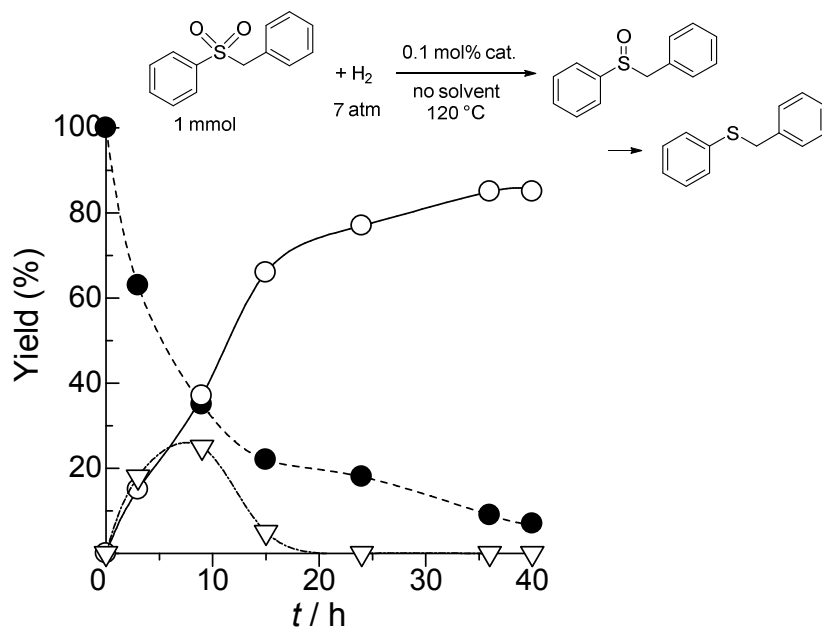
Fig. 8 Time dependence of GC yields for the reduction of benzyl phenyl sulfone at 120 ˚C under 7 atm H_2 by 0.1 mol% Pt-MoOx/TiO$_2$ catalyst: (●) unreacted benzyl phenyl sulfone, (▽) benzyl phenyl sulfoxide, (○) benzyl phenyl sulfide.

Table of Contents

We report the first reusable catalyst for hydrodeoxygenation of various sulfoxides to sulfide as well as the first example of hydrodeoxygenation of a sulfone to a sulfide.

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