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Introduction

Sulfoxides are now widely utilized as chirons in numerous asymmetric transformations wherein the sulfoxide groups, after stereoselective introduction, are removed by deoxygenation to their corresponding sulfides followed by hydrodesulfurization.^{1*a,b*} In other transformations such as homologation of aromatic aldehydes, deoxygenation of the sulfoxide moieties plays a crucial role.¹ To date, a variety of catalytic procedures have been developed for the deoxygenation of sulfoxides; these typically utilize reducing agents such as zinc metal, silanes, boranes, phosphines, and alcohols.² The use of molecular hydrogen (H₂) as a reducing agent in combination with heterogeneous catalysts is more desirable from the viewpoint of green chemistry. However, to the best of our knowledge, there are only a few reports on heterogeneously catalyzed deoxygenation of sulfoxides with H₂.³ In 2014,

Platinum-supporting hollandite-type vanadiumchromium mixed oxides as efficient heterogeneous catalysts for deoxygenation of sulfoxides under atmospheric H₂ pressure†

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Deoxygenation of sulfoxides to their corresponding sulfides is an important reaction, and the development of efficient heterogeneous catalysts that can utilize molecular hydrogen (H₂) as a reducing agent is highly desired. In this study, we successfully developed a new concept in heterogeneous catalysts, platinumsupporting hollandite-type vanadium-chromium mixed oxide catalysts ($Pt/V_{(1-x)}Cr_x$ -Hol, x: Cr/(V + Cr) molar ratio of the precursor solution), for sulfoxide deoxygenation with H₂. Hollandite-type vanadium-chromium mixed oxides (V_(1-x)Cr_x-Hol) that did not support platinum could stoichiometrically deoxygenate methyl phenyl sulfoxide to methyl phenyl sulfide, and the V^{3+} species in $V_{(1-x)}Cr_x$ -Hol were oxidized to V^{4+} after deoxygenation. However, the V⁴⁺ species could not be re-reduced with H_2 . By supporting platinum nanoparticles on $V_{(1-x)}Cr_x$ -Hol, the re-reduction of the oxidized vanadium species with H₂ became possible. Thus, in the presence of $Pt/V_{(1-x)}Cr_x$ -Hol, catalytic sulfoxide deoxygenation with H₂ as the reducing agent can be realized; the deoxygenation occurs on $V_{(1-x)}Cr_x$ -Hol, and the role of platinum is to re-reduce the oxidized vanadium species with H_2 . In the presence of $Pt/V_{0.7}Cr_{0.3}$ -Hol, various types of structurally diverse sulfoxides could be selectively converted into their corresponding sulfides under atmospheric H₂ pressure (1 atm). In addition, the present system was applicable to the deoxygenation of pyridine N-oxides to their corresponding pyridines. The observed catalysis was truly heterogeneous, and the $Pt/V_{0.7}Cr_{0.3}$ -Hol catalyst could be reused for sulfoxide deoxygenation, although the performance was reduced

> Mitsudome *et al.* demonstrated sulfoxide deoxygenation under atmospheric H₂ pressure (1 atm) with a heterogeneous Ru/TiO₂ catalyst for the first time.^{3*a*} Shimizu *et al.* subsequently developed an efficient catalytic deoxygenation system under high pressure H₂ conditions (H₂ 7 atm) by utilizing a Pt–MoO_x/TiO₂ catalyst.^{3*b*}

> In this study, we developed a new concept in heterogeneous catalysts for the deoxygenation of sulfoxides to their corresponding sulfides based on the properties of hollanditetype vanadium-chromium mixed oxides (Fig. 1). Hollanditetype oxides are composed of double-chains of edge-sharing MO_6 octahedra (M = transition metal), forming 2 × 2 and 1 × 1 tunnel structures, and various types of cations or anions can be situated in the 2×2 tunnel.⁴ Owing to the presence of the tunnel ions, the lattice transition metals tend to possess mixed valence states, which lead to specific properties of hollandite-type oxides such as specific electron and ion conductivities.⁵ Not only these properties but also the sizes, morphologies, and stabilities of hollandite-type oxides can be finely tuned by substitutional doping into the lattice and/or changing the tunnel ions.⁶ Thus, we envisaged that suitably designed hollandite-type oxides could probably act as efficient

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Fig. 1 Design concept of heterogeneous catalysts for sulfoxide deoxygenation with H_2 based on hollandite-type vanadium-chromium mixed oxides.

heterogeneous catalysts for various types of functional group transformations. Hollandite-type manganese oxides are reported to be quite effective for numerous oxidation reactions.⁷ Also, we recently reported that hollandite-type manganese oxides show higher catalytic performances and stability for several oxidation reactions such as aerobic oxygenation of sulfides and alkylarenes than manganese oxides with other structures and that the performance can be much improved by substitutional doping of several transition metals into the hollandite framework.⁸

The noticeable new findings in this study are as follows (Fig. 1): (i) the stoichiometric deoxygenation of methyl phenyl sulfoxide to methyl phenyl sulfide proceeded efficiently in the presence of a hollandite-type vanadium oxide composed of V³⁺ and V⁴⁺ (V-Hol), while the reaction hardly proceeded when V₂O₃ and VO₂ were used; (ii) by substitutional doping of Cr³⁺ into the framework to form hollandite-type vanadium-chromium mixed oxides ($V_{(1-x)}Cr_x$ -Hol, x: Cr/(V + Cr) molar ratio of the precursor solution), the specific surface areas significantly increased in comparison with that of V-Hol, and $V_{(1-x)}Cr_x$ -Hol oxides were more stable than V-Hol; (iii) after deoxygenation, the V^{3+} species in $V_{(1-x)}Cr_x$ -Hol were oxidized to V^{4+} with retention of the hollandite structures, but the V^{4+} species could not be re-reduced with H₂; (iv) by supporting platinum nanoparticles on $V_{(1-x)}Cr_x$ -Hol (Pt/ $V_{(1-x)}Cr_x$ -Hol), the re-reduction of the oxidized vanadium species with H₂ was made possible; (v) in the presence of Pt/ V_{0.7}Cr_{0.3}-Hol, various types of structurally diverse sulfoxides could be converted into their corresponding sulfides under atmospheric H₂ pressure, and the deoxygenation of pyridine N-oxides to their corresponding pyridines was also possible; and (vi) the observed catalysis was truly heterogeneous, and Pt/V_{0.7}Cr_{0.3}-Hol could be reused for sulfoxide deoxygenation.

Results and discussion

Synthesis of hollandite-type oxides and their use in sulfoxide deoxygenation

To begin with, we prepared a hollandite-type vanadium oxide (V-Hol) according to a previous report with minor modifications involving the liquid-phase reaction of VOCl₃ with benzyl alcohol (see the Experimental section).⁹ The X-ray diffraction (XRD) pattern of V-Hol matched well with that reported in the ICDD PDF database (JCPDS 50-1797), corresponding to $V_{8,18}O_{16}$ ·1.46H₂O with a hollandite-type structure (Fig. 2). According to the previous report, V-Hol contains oxide ions in the 2 \times 2 tunnel.⁹ The specific surface area of the V-Hol sample prepared in this study was 18 m² g⁻¹, which was not significantly high with respect to its surface area when used as a catalyst. Substitutional doping of additional metal cations into the metal oxide framework is one of the most commonly utilized strategies to control the catalytic properties, sizes, and morphologies. In our previous study, we found that substitutional doping of Mo⁶⁺ into hollandite-type manganese oxides can significantly increase their specific surface areas.8 It is expected that six coordinated cations having crystal radii similar to those of vanadium cations (V³⁺, V⁴⁺, and V⁵⁺) can be readily introduced into the octahedral hollandite framework. Thus, to increase the specific surface area, we attempted to introduce several transition metal cations such as Ti⁴⁺, Cr³⁺, Mn³⁺, Fe³⁺, Co²⁺, Ni²⁺, and Cu²⁺. The preparation of pure hollandite-type mixed oxides was successful only when Cr³⁺ was used.

In this study, five types of hollandite-type vanadium-chromium mixed oxides with various vanadium and chromium



Fig. 2 XRD patterns of V-Hol and $V_{(1-x)}Cr_x$ -Hol.

contents (V_(1-x)Cr_x-Hol, x: Cr/(V + Cr) molar ratio of the precursor solution, x = 0.1, 0.2, 0.3, 0.4, and 0.5) were successfully prepared using essentially the same procedure as that for V-Hol with $Cr(acac)_3$ (acac = acetylacetonate) as the chromium source (see the Experimental section). The specific surface areas and the elemental analysis data for $V_{(1-x)}Cr_x$ -Hol are summarized in Table 1. The specific surface areas increased with the chromium content; the specific surface areas of V_{0.9}Cr_{0.1}-Hol, V_{0.8}Cr_{0.2}-Hol, V_{0.7}Cr_{0.3}-Hol, V_{0.6}Cr_{0.4}-Hol, and $V_{0.5}Cr_{0.5}$ -Hol were 37, 61, 81, 115, and 180 m² g⁻¹, respectively, which were significantly larger than that of the parent undoped V-Hol (18 m² g⁻¹) (Table 1). The XRD patterns of $V_{(1-x)}Cr_x$ -Hol are shown in Fig. 2. From these XRD patterns, we concluded that all $V_{(1-x)}Cr_x$ -Hol samples possessed a hollandite-type structure. No additional diffraction peaks attributed to segregated Cr2O3 were observed, and small changes in the lattice parameters of $V_{(1-x)}Cr_x$ -Hol with respect to chromium were observed as a result of changing the doping level. These results indicated that Cr³⁺ species were efficiently doped into the hollandite framework. The XRD peak intensities became weaker as the chromium content was increased, suggesting the low crystallinity and/or formation of smaller crystals of $V_{(1-x)}Cr_x$ -Hol. Transmission electron microscopy (TEM) images revealed that V-Hol possessed a rod-like morphology, and the average length and width of the rods were 200 \pm 50 and 50 \pm 5 nm, respectively (Fig. 3a). As shown in Fig. 3, the lengths and widths decreased as the chromium content was increased, resulting in the formation of grain-like aggregates of ultrafine nanocrystals; for example, the average length and width of $V_{0.5}Cr_{0.5}$ -Hol were 30 ± 10 and 5 ± 2.5 nm, respectively (Fig. 3f). Therefore, the larger specific surface areas of $V_{(1-x)}Cr_x$ -Hol possibly resulted from the formation of nanocrystals. The normalized vanadium K-edge X-ray absorption near edge structure (XANES) spectra of V-Hol and $V_{(1-x)}Cr_x$ -Hol are shown in Fig. 4a. The absorption edges of V-Hol and V(1-x)Crx-Hol were located between those of V_2O_3 (V^{3+} reference) and VO_2 (V^{4+} reference) (Fig. 4a). Therefore, the vanadium species in V-Hol and $V_{(1-x)}Cr_x$ -Hol possibly possess mixed valence states of V^{3+} and V⁴⁺. The normalized chromium K-edge XANES spectra of $V_{(1-x)}Cr_x$ -Hol reveal that the oxidation state of the chromium species in $V_{(1-x)}Cr_x$ -Hol was +3 (Fig. 4b).

The deoxygenation of methyl phenyl sulfoxide (1a) to methyl phenyl sulfide (2a) was performed with hollanditetype oxides under an Ar atmosphere. In the presence of an ex-

Table 1 Properties of V-Hol and $V_{(1-x)}Cr_x$ -Hol						
	BET surface area $(m^2 g^{-1})$	Content (wt%)		Cr/(V + Cr)		
Sample		V	Cr	(mol%)		
V-Hol	18	53.7	_	_		
V _{0.9} Cr _{0.1} -Hol	37	48.4	5.5	10.1		
V _{0.8} Cr _{0.2} -Hol	61	42.1	8.5	16.5		
V _{0.7} Cr _{0.3} -Hol	81	38.2	12.8	24.8		
V _{0.6} Cr _{0.4} -Hol	115	29.6	18.9	38.5		
V _{0.5} Cr _{0.5} -Hol	180	25.8	20.8	44.1		



Fig. 3 TEM images of (a) V-Hol, (b) $V_{0.9}Cr_{0.1}$ -Hol, (c) $V_{0.8}Cr_{0.2}$ -Hol, (d) $V_{0.7}Cr_{0.3}$ -Hol, (e) $V_{0.6}Cr_{0.4}$ -Hol, and (f) $V_{0.5}Cr_{0.5}$ -Hol.

cess amount of V-Hol (300 mg, ca. 6.3 equiv. vanadium species with respect to 1a), the deoxygenation proceeded efficiently at 100 °C in n-decane, affording 2a in 74% yield (Table 2, entry 1). After the deoxygenation of 1a, V-Hol was retrieved by filtration, and the XRD pattern was obtained. As can be seen in Fig. 5, the hollandite structure was intrinsically preserved after deoxygenation, while peak shifts toward higher angles were observed. Therefore, we consider that the V³⁺ species in V-Hol may have been partially oxidized during deoxygenation.^{10,11} The oxidized vanadium species could not be re-reduced, even when the reaction was carried out under a H₂ atmosphere. Although the hollandite structure of V-Hol was intrinsically stable during the reaction in non-polar solvents, such as n-decane, the use of polar solvents was problematic. When the reaction was performed in N,Ndimethylformamide (DMF), V-Hol was partially converted into vanadium oxide(s) with different structure(s) (Fig. S1, ESI⁺). To realize catalytic deoxygenation with H₂, we attempted to prepare a platinum-supporting V-Hol catalyst by a precipitation method in an aqueous medium (see the Experimental section). However, the catalyst preparation failed because V-Hol was completely converted into V₆O₁₃ during the preparation (Fig. S2, ESI[†]). Owing to the aforementioned



Fig. 4 Normalized (a) vanadium and (b) chromium K-edge XANES spectra of V-Hol, $V_{(1-x)}Cr_x$ -Hol, and reference materials (V₂O₃, VO₂, and Cr₂O₃).

instability, we did not utilize V-Hol for further examinations of sulfoxide deoxygenation. In contrast, the doping of Cr^{3+} species could stabilize the hollandite structure; $V_{(1-x)}Cr_x$ -Hol oxides were highly stable even in polar solvents and strong aqueous basic media (Fig. S1 and S2, ESI†).





Fig. 5 XRD patterns of the as-prepared V-Hol and V_(1-x)Cr_x-Hol (black lines), and the patterns of the retrieved V-Hol and V_(1-x)Cr_x-Hol after the deoxygenation of **1a** under the conditions described in Table 2 (red lines).

When $V_{(1-x)}Cr_x$ -Hol (300 mg, ca. 3.0–5.7 equiv. of vanadium species with respect to 1a) were used, the deoxygenation of 1a also proceeded significantly, giving 2a in 20-83% yields (Table 2, entries 2–6). The XRD analysis of $V_{(1-x)}Cr_x$ -Hol retrieved after the deoxygenation revealed that the hollandite structure was intrinsically preserved after the reaction (Fig. 5). In these cases, the XRD peaks were shifted toward higher angles, indicating the oxidation of $V_{(1-x)}Cr_x$ -Hol after the reaction. As mentioned above, in the vanadium K-edge XANES spectrum of the freshly prepared V_{0.7}Cr_{0.3}-Hol, the absorption edge was located between those of V_2O_3 (V^{3+} reference) and VO_2 (V⁴⁺ reference), indicating that V_{0.7}Cr_{0.3}-Hol possesses mixed valence states of V^{3+} and V^{4+} (Fig. 6a). After this had been used for the deoxygenation, the absorption edge was shifted toward higher energy, and the spectrum approached that of VO_2 (Fig. 6a), indicating that the V^{3+} species in V_{0.7}Cr_{0.3}-Hol were oxidized to V⁴⁺ during deoxygenation. In contrast, the chromium K-edge XANES spectrum of V_{0.7}Cr_{0.3}-Hol was almost unchanged after deoxygenation

Vanadium oxide Vanadium oxide Image: Non-decane Vanadium oxide Image: Non-decane Non-decane Non-decane Image: Non-decane Non-decane Non-decane Non-decane Image: Non-decane Non-deca					
1	V-Hol	3.16	74		
2	V _{0.9} Cr _{0.1} -Hol	2.85	66		
3	V _{0.8} Cr _{0.2} -Hol	2.48	83		
4	V _{0.7} Cr _{0.3} -Hol	2.25	71		
5	V _{0.6} Cr _{0.4} -Hol	1.74	50		
6	V _{0.5} Cr _{0.5} -Hol	1.52	20		
7	VO_2	3.62	<1		
8	V_2O_3	4.00	3		

Reaction conditions: vanadium oxides (300 mg), 1a (0.5 mmol), *n*-decane (1 mL), Ar (1 atm), 100 °C, 24 h. Yields were determined *via* GC analysis using naphthalene as an internal standard.

(Fig. 6b). Consequently, the V^{3^+} species in $V_{0.7}Cr_{0.3}$ -Hol acted as the reducing agent for deoxygenation,¹¹ whereas the Cr^{3^+} species did not. Also, in the case of $V_{0.7}Cr_{0.3}$ -Hol, the oxidized vanadium species could not be re-reduced, even when the reaction was performed under a H₂ atmosphere.

No production of 2a was observed when VO₂ was used for the deoxygenation of 1a (Table 2, entry 7). Although the V^{3+} species in the hollandite-type oxides used in this study could effectively deoxygenate 1a (Table 2, entries 1-6), the reaction using V_2O_3 , which contains V^{3+} , gave 2a in only 3% yield (Table 2, entry 8). Although the specific surface area of V_2O_3 was 5 m² g⁻¹, which was slightly smaller than that of V-Hol (18 $m^2 g^{-1}$), the performance of V-Hol was much better than that of V_2O_3 (Table 2, entry 1 vs. entry 8). Therefore, the higher performance of the hollandite-type oxides as compared with V₂O₃ is probably not caused by the difference in their specific surface areas. Although we cannot conclusively explain the reason for the higher performance of the hollandite-type oxides, we consider that the specific properties of hollandite-type oxides, such as specific electron and ion conductivities, play an important role.⁵ It has been reported that V-Hol contains oxide ions for charge compensation in the 2×2 tunnel.⁹ Thus, after the two-electron transfer from the vanadium species to a sulfoxide, it is possible that



Fig. 6 Normalized (a) vanadium and (b) chromium K-edge XANES spectra of the as-prepared $V_{0.7}Cr_{0.3}$ -Hol, the retrieved $V_{0.7}Cr_{0.3}$ -Hol after the deoxygenation of **1a** under the conditions described in Table 2, and the reference materials (V_2O_3 , VO_2 , and Cr_2O_3).

the oxide ion is smoothly transferred from the sulfoxide to the tunnel of the hollandite-type oxides.

Catalytic sulfoxide deoxygenation with H₂ using platinumsupporting hollandite-type oxides

As described in the previous section, the oxidized vanadium species in $V_{(1-x)}Cr_x$ -Hol could not be re-reduced with H₂. Herein, we prepared platinum-supporting $V_{(1-x)}Cr_x$ -Hol catalysts ($Pt/V_{(1-x)}Cr_x$ -Hol). Catalytic sulfoxide deoxygenation with H₂ is expected to be realized through the following catalytic mechanism: (i) two-electron transfer from $V_{(1-x)}Cr_x$ -Hol to a sulfoxide and successive oxide ion transfer from the sulfoxide to $V_{(1-x)}Cr_x$ -Hol, producing the desired sulfide; (ii) H₂ dissociation on platinum; (iii) two-electron transfer from two hydrogen atoms to the oxidized V(1-x)Crx-Hol via platinum (re-reduction of $V_{(1-x)}Cr_x$ -Hol); and (iv) reaction of two protons and the oxide ion, producing water as the co-product. Four types of effective $Pt/V_{(1-x)}Cr_x$ -Hol catalysts (x = 0.2, 0.3, 0.4, and 0.5; Pt contents: 1.0-1.4 wt%)¹² were successfully prepared by a simple precipitation method in an aqueous medium (see the Experimental section). As we expected, catalytic sulfoxide deoxygenation with H₂ as the reducing agent was realized in the presence of Pt/V_(1-x)Cr_x-Hol, and Pt/V_{0.7}Cr_{0.3}-Hol was the best catalyst (Fig. S3, ESI⁺);¹³ for example, when Pt/V_{0.7}Cr_{0.3}-Hol (30 mg, Pt: 0.43 mol%, V: 45 mol%) was used, the deoxygenation of 1a proceeded efficiently under mild conditions (H₂ 1 atm, 100 °C, in *n*-decane), affording the desired sulfide 2a in 98% yield after 2 h (Fig. 7). Under the same reaction conditions, commonly utilized supported platinum catalysts such as Pt/Al₂O₃ (30 mg, Pt: 0.43 mol%) and Pt/C (9.0 mg, Pt: 0.46 mol%) were not effective for the deoxygenation of 1a and afforded 2a in only 5% and 6% yields, respectively, thus indicating that the vanadium species (not platinum) play an important role in the present Pt/V(1-x)Crx-Hol-catalyzed sulfoxide deoxygenation.14

The XRD pattern of Pt/V_{0.7}Cr_{0.3}-Hol just before its use in the deoxygenation (just after the H₂ pretreatment, see the Experimental section) is shown as black lines in Fig. 8. In the XRD pattern of Pt/V_{0.7}Cr_{0.3}-Hol retrieved after the deoxygenation of 1a under an Ar atmosphere, the diffraction peaks were shifted toward higher angles (Fig. 8, red lines), which was virtually the same as the effect observed in Fig. 5, indicating the oxidation of the V3+ species in Pt/V0.7Cr0.3-Hol. When the oxidized catalyst was treated under the conditions described in Fig. 7 without sulfoxides (H2 1 atm, 100 °C, in *n*-decane), the diffraction peaks were shifted to their original positions (Fig. 8, blue lines), thus showing that the oxidized vanadium species were re-reduced by H₂ through platinum catalysis. All the aforementioned experimental results support the proposed mechanism. This mechanism is completely different from the reported one using Pt-MoOx/TiO2 under rather harsh conditions (typically, H₂ 7 atm, 120 °C, solventfree).3b

To verify whether the observed catalysis was truly caused by solid $Pt/V_{0.7}Cr_{0.3}$ -Hol or leached metal species, the



Fig. 7 Scope of the $Pt/V_{0.7}Cr_{0.3}$ -Hol-catalyzed-deoxygenation of (a) sulfoxides and (b) pyridine *N*-oxides. Reaction conditions: $Pt/V_{0.7}Cr_{0.3}$ -Hol (30 mg, Pt: 0.43 mol%, V: 45 mol%), sulfoxides or pyridine *N*-oxides (0.5 mmol), *n*-decane (1 mL), H₂ (1 atm), 100 °C. $Pt/V_{0.7}Cr_{0.3}$ -Hol was utilized after pretreatment in 1 atm of H₂ at 150 °C for 30 min. Yields were determined *via* GC analysis using naphthalene as an internal standard. ^aReuse experiment.

following control experiments were conducted. The deoxygenation of 1a was performed under the conditions described in Fig. 7, and the Pt/V_{0.7}Cr_{0.3}-Hol catalyst was removed from the reaction mixture by hot filtration at ca. 40% yield of 2a. Then, the filtrate was again heated at 100 °C under atmospheric H₂ pressure (1 atm). In this case, no further production of 2a was observed (Fig. S4, ESI⁺). In addition, we confirmed via inductively coupled plasma atomic emission spectroscopy (ICP-AES) that no vanadium, chromium, or platinum species were present in the filtrate (below 0.1%). These results clearly indicate that the observed catalysis for the present Pt/V_{0.7}Cr_{0.3}-Holcatalyzed sulfoxide deoxygenation is truly heterogeneous.¹⁵ After the reaction was completed, Pt/V_{0.7}Cr_{0.3}-Hol could be easily retrieved from the reaction mixture by simple filtration. We performed a reuse experiment using the retrieved catalyst. Unfortunately, the catalytic performance of Pt/V_{0.7}Cr_{0.3}-Hol somewhat decreased; a 98% yield of 2a was obtained with the freshly prepared catalyst, while a 75% yield was obtained with the reused catalyst for the deoxygenation of 1a under the conditions described in Fig. 7. We confirmed by TEM analysis that the average particle size of platinum increased after its use; the average particle size of the freshly prepared Pt/V_{0.7}Cr_{0.3}-Hol was 0.6 nm, and this increased to 1.8 nm after use (Fig. S5, ESI⁺). Therefore, the deactivation is probably caused by the increase in the platinum particle sizes.

Finally, we turn our attention to the examination of the substrate scope for the current Pt/V_{0.7}Cr_{0.3}-Hol-catalyzed deoxygenation. In the presence of Pt/V_{0.7}Cr_{0.3}-Hol, various types of structurally diverse sulfoxides could be converted into their corresponding sulfides under atmospheric H₂ pressure (1 atm) (Fig. 7). Aryl sulfoxides could be almost quantitatively converted into the corresponding sulfides. Notably, the present Pt/V_{0.7}Cr_{0.3}-Hol-catalyzed system was effective for sulfoxide substrates with other reducible substituents such as C=C double bonds, Cl, and Br; the deoxygenation of sulfoxides proceeded selectively to produce the corresponding sulfides without the reduction of these functionalities. An alkyl sulfoxide was also converted into its corresponding alkyl sulfide, although a longer reaction time was required to attain a high yield in comparison with the reaction with aryl sulfoxides. Interestingly, the present Pt/V_{0.7}Cr_{0.3}-Hol-catalyzed system was also applicable to the deoxygenation of pyridine N-oxides. Deoxygenation of pyridine N-oxides is an important reaction for the synthesis of substituted pyridines, and the development of an efficient catalytic system is highly desirable.¹⁶ In the presence of Pt/V_{0.7}Cr_{0.3}-Hol, pyridine N-oxide and its derivatives, which possess electron-donating as well as electron-withdrawing substituents on the pyridine rings, were converted into their corresponding pyridines under atmospheric H_2 pressure (1 atm) (Fig. 7).



Fig. 8 XRD patterns ((a) overall views and (b) magnified views) of Pt/ V_{0.7}Cr_{0.3}-Hol just after the H₂ pretreatment (black lines), the retrieved Pt/V_{0.7}Cr_{0.3}-Hol after the deoxygenation of **1a** under an Ar atmosphere (red lines), and Pt/V_{0.7}Cr_{0.3}-Hol after treatment under the conditions described in Fig. 7 without sulfoxides (H₂ 1 atm, 100 °C, in *n*-decane) (blue lines).

Conclusions

We have successfully developed a new concept in heterogeneous sulfoxide deoxygenation catalysts, Pt/V(1-x)Crx-Hol, based on hollandite-type vanadium-chromium mixed oxides. In the presence of Pt/V_{0.7}Cr_{0.3}-Hol, various types of structurally diverse aryl and alkyl sulfoxides could be converted into their corresponding sulfides under atmospheric H₂ pressure (1 atm). Other reducible functional groups were completely tolerant to reduction, and the deoxygenation of sulfoxides proceeded selectively. Moreover, the deoxygenation of pyridine N-oxides to their corresponding pyridines proceeded efficiently in the presence of Pt/V_{0.7}Cr_{0.3}-Hol. The observed catalysis was truly heterogeneous, and the Pt/V_{0.7}Cr_{0.3}-Hol catalyst could be reused for sulfoxide deoxygenation, though the performance was somewhat decreased. Our proposed sulfoxide deoxygenation proceeds through the following catalytic mechanism: (i) two-electron transfer from $V_{(1-x)}Cr_x$ -Hol to a sulfoxide, and successive oxide ion transfer from the sulfoxide to $V_{(1-x)}Cr_x$ -Hol, producing the desired sulfide; (ii) H₂ dissociation on platinum; (iii) two-electron transfer from two hydrogen atoms to the oxidized $V_{(1-x)}Cr_x$ -Hol via platinum; and (iv) reaction of two protons and the oxide ion, with water as the co-product. This mechanism is significantly different from previously reported ones.

Experimental section

Materials

VOCl₃, VO₂, V₂O₃, V(acac)₃, VO(acac)₂, and H₂Pt(OH)₆ were purchased from Aldrich. Cr(acac)₃ was purchased from Kanto Chemical. Pt/C (Pt content: 5.0 wt%) was purchased from N. E. Chemcat Corporation. An aqueous solution of poly(*N*-vinyl-2-pyrrolidone)-stabilized Pt colloidal nanoparticles (Pt-PVP, Pt: 4 wt%) was purchased from Tanaka Kikinzoku Kogyo. Substrates, solvents, and naphthalene (internal standard for GC analysis) were purchased from Tokyo Chemical Industry, Kanto Chemical, Wako Pure Chemical Industry, or Apollo Scientific. All reagents were used as received without further purification.

Preparation of catalysts

V-Hol was prepared according to the following procedure.9 VOCl₃ (2.0 mL; 3.68 g, 21.24 mmol) was slowly added to benzyl alcohol (80 mL) under Ar. The mixture was stirred at room temperature for several minutes. The solution gradually turned from red to green-blue. The reaction solution was transferred to a Teflon-lined vessel for solvothermal reaction and heated at 150 °C for 24 h. The resulting black suspension was filtered, and the precipitate was washed with ethanol (500 mL) and dried at 60 °C in open air, affording 0.8 g of V-Hol. For the preparation of $V_{(1-x)}Cr_x$ -Hol, $Cr(acac)_3$ was initially added to benzyl alcohol (10-50 mol% with respect to the total metal content), followed by the above procedure, affording 1.0-3.0 g of V_(1-x)Cr_x-Hol. Pt/V_(1-x)Cr_x-Hol catalysts were prepared as follows. H₂Pt(OH)₆ (1.5 wt% with respect to the supports) was dispersed in water (30 mL). The pH of the suspension was adjusted to 12.9 with aqueous NaOH (0.1 M). At this pH, H₂Pt(OH)₆ was dissolved completely. Then, $V_{(1-x)}Cr_x$ -Hol (0.5 g) was added to the platinum-containing solution, and the mixture was stirred at room temperature. After 15 min, the pH of the suspension was kept at 7.5 for 15 min using aqueous HNO₃ (0.1 M), and then the solution was stirred for a further 6 h. The precipitate was recovered by filtration, washed with a large amount of water (300 mL), and dried in vacuo at room temperature overnight, affording Pt/ $V_{(1-x)}Cr_x$ -Hol. The Pt contents in Pt/V_{0.8}Cr_{0.2}-Hol, Pt/V_{0.7}Cr_{0.3}-Hol, Pt/V_{0.6}Cr_{0.4}-Hol, and Pt/V_{0.5}Cr_{0.5}-Hol were 1.1, 1.4, 1.1, and 1.0 wt%, respectively. Pt/Al₂O₃ (Pt content: 1.4 wt%) was prepared using the same procedure. Pt/V2O5 (Pt content: 0.66 wt%), Pt/VO₂ (Pt content: 0.60 wt%), and Pt/V₂O₃ (Pt content: 0.69 wt%) were prepared via an impregnation method using an aqueous solution of Pt-PVP.

Characterization of V-Hol and V_(1-x)Cr_x-Hol

The XRD patterns were recorded using a Rigaku SmartLab instrument with Cu K α radiation (λ = 1.5418 Å, 45 kV, 200 mA). The BET surface areas were measured by N₂ adsorption at -196 °C using a Micromeritics ASAP 2010 instrument. The contents of vanadium, chromium, and platinum in the catalyst samples were determined *via* ICP-AES using a Shimadzu

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ICPS-8100 apparatus. The TEM images were obtained using a JEM-2000EX II apparatus at an accelerating voltage of 200 kV. The TEM specimens were prepared by dispersing the samples in ethanol, sonicating them for 10 min, and leaving them to stand for 30 min before depositing on a carbon-coated copper grid. The XANES spectra were measured at the beam line BL11S2 of the Aichi Synchrotron Radiation Center. Each sample was formed into a pellet, doubly wrapped in an Al laminate pack, and heat-sealed. The samples were attached to a sample holder. Vanadium and chromium foils were used for energy calibration.

Deoxygenation reactions

GC quantitative analyses were performed on a Shimadzu GC-2014 apparatus with an FID detector equipped with a TC-1 or Stabilwax capillary column. GC-MS analyses for product identification were performed on a GCMS-QP2010 apparatus equipped with an InertCap 5 capillary column at an ionization voltage of 70 eV. Sulfoxide deoxygenation was performed as follows. Pt/V(1-x)Crx-Hol (30 mg) or vanadium-based oxide (300 mg), sulfoxide (0.5 mmol), n-decane (1 mL), and naphthalene (internal standard, 0.2 mmol) were placed in a Schlenk-type reactor. Then, H₂ or Ar (1 atm) was sealed into the reactor, and the reaction was performed at 100 °C for 2-24 h with stirring. For the catalytic deoxygenation using Pt/ V_(1-x)Cr_x-Hol, the catalyst was pretreated at 150 °C under 1 atm of H₂ for 30 min just before use. It is well known and we confirmed in a separate experiment that Pt(0) nanoparticles are formed after such H₂ treatment. After the reaction, the reaction mixture was diluted with toluene or acetone (3 mL), and the spent catalyst was separated by filtration and washed with acetone. Then, the filtrate was analyzed by GC and GC-MS. The products were confirmed by comparing their GC retention times and GC-MS spectra with authentic data. The spent catalyst was washed with acetone and water and then dried in vacuo at room temperature before being reused.

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- 11 In the presence of $V(acac)_3$ (equimolar amount with respect to 1a), the deoxygenation of 1a proceeded to some extent under the conditions described in Table 2, giving 2a in 10% yield for 3 h. Conversely, $VO(acac)_2$ was not effective for the deoxygenation. Therefore, the V^{3+} species likely played an important role in sulfoxide deoxygenation.
- 12 The preparation of platinum-supporting catalysts using V-Hol and $V_{0.9}Cr_{0.1}$ -Hol was unsuccessful because of the low stabilities of V-Hol and $V_{0.9}Cr_{0.1}$ -Hol in the catalyst preparation aqueous medium (see the Experimental section).
- 13 The specific surface areas increased with the chromium content (Table 1). Differential thermal analysis (DTA) revealed that the stabilities of $V_{(1-x)}Cr_{x}$ -Hol against oxidation increased with the chromium content (Fig. S6†). The increases in their specific surface areas and stabilities should positively affect their catalytic activities. However, the vanadium contents in $V_{(1-x)}Cr_{x}$ -Hol decreased (Table 1) and the average oxidation states of vanadium species in $V_{(1-x)}Cr_{x}$ -Hol gradually increased (Fig. 4a) as the chromium content was increased. Therefore, the amounts of V^{3+} species (active species) in the Pt/ $V_{(1-x)}Cr_{x}$ -Hol catalysts decreased as the chromium content was increased. For the above-mentioned

reasons, a volcano-shaped relationship was likely observed between the chromium contents and the reaction rates for the deoxygenation of 1a (Fig. S3b†).

- 14 Platinum-supporting vanadium oxide catalysts such as Pt/ V₂O₅ (30 mg, Pt: 0.20 mol%), Pt/VO₂ (30 mg, Pt: 0.18 mol%), and Pt/V₂O₃ (30 mg, Pt: 0.21 mol%) were less effective than Pt/V_{0.7}Cr_{0.3}-Hol and gave 2a in 37%, 12%, and 10% yields even after 4 h, respectively, under the conditions described in Fig. 7.
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