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## Platinum-supporting hollandite-type vanadium–chromium mixed oxides as efficient heterogeneous catalysts for deoxygenation of sulfoxides under atmospheric $H_2$ pressure

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**Fig. S1** XRD patterns of as-prepared V-Hol and  $V_{0.7}Cr_{0.3}$ -Hol (black lines), and the patterns of the retrieved V-Hol and  $V_{0.7}Cr_{0.3}$ -Hol after the deoxygenation of **1a** using DMF solvent (red lines). Reaction conditions: V-Hol or  $V_{0.7}Cr_{0.3}$ -Hol (30 mg), **1a** (0.5 mmol), DMF (1 mL), Ar (1 atm), 100°C, 24 h.



Fig. S2 XRD patterns of (a) V-HoI, (b) Pt/V-HoI, (c)  $V_{0.7}Cr_{0.3}$ -HoI, and (d) Pt/ $V_{0.7}Cr_{0.3}$ -HoI.



**Fig. S3** (a) Reaction profiles and reaction rate of the deoxygenation of **1a** using  $Pt/V_{(1-x)}Cr_x$ -Hol and (b) relationship between the chromium contents and the reaction rates. Reaction conditions:  $Pt/V_{(1-x)}Cr_x$ -Hol, (30 mg), **1a** (0.5 mmol), *n*-decane (1 mL), H<sub>2</sub> (1 atm), 100°C. Catalysts were pretreated under 1 atm H<sub>2</sub> at 150°C. Yields were determined by GC analysis using naphthalene as an internal standard.



**Fig. S4** Effect of removal of  $Pt/V_{0.7}Cr_{0.3}$ -Hol on the deoxygenation of **1a**; without (•) or with removal of  $Pt/V_{0.7}Cr_{0.3}$ -Hol (0). The arrow indicates the removal of  $Pt/V_{0.7}Cr_{0.3}$ -Hol. Reaction conditions:  $Pt/V_{0.7}Cr_{0.3}$ -Hol (30 mg), **1a** (0.5 mmol), *n*-decane (1 mL), 100°C, H<sub>2</sub> (1 atm). Catalysts were pretreated under 1 atm H<sub>2</sub> at 150°C for 30 min. Yields were determined by GC analysis using naphthalene as an internal standard.



**Fig. S5** TEM images and Pt particle size distributions of (a) as-prepared Pt/V<sub>0.7</sub>Cr<sub>0.3</sub>-Hol (mean diameter: 0.6 nm,  $\sigma$  = 0.1 nm) and (b) Pt/V<sub>0.7</sub>Cr<sub>0.3</sub>-Hol retrieved after the deoxygenation of **1a** under the conditions described in Fig. 7 (mean diameter: 1.8 nm,  $\sigma$  = 0.4 nm). The size distributions were determined using 200 particles.



**Fig. S6** DTA profiles of V-Hol and  $V_{(1-x)}Cr_x$ -Hol samples. DTA profiles were measured under air atmosphere. The arrows indicate the decomposition temperatures of their hollandite structures.