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Chemoselective hydrogenation of α,β -unsaturated aldehydes on hydrogenated MoO_x nanorods supported iridium nanoparticles



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ABSTRACT

As reducible supports, metal oxides present the varied charge effect after hydrogen doping and partial reduction, accomplishing the tunable metal-support interactions and the promoted catalytic turnover in heterogeneous catalysis. Herein, the one-pot fabrication of hydrogenated MoO_x (H-MoO_x) nanorods supported Ir (Ir/H-MoO_x) was developed, which simultaneously combined the generation of active centers (Ir) and the hydrogen doping on supports (H-MoO_x). Because of the accumulated electrons around MoO_6 octahedras after hydrogen doping, the electronic perturbations arising from H-MoO_x supports led to the negatively charge $\text{Ir}^{\delta-}$ species being beneficial for the selective hydrogenation of $\text{C}=\text{O}$ moiety in α,β -unsaturated aldehydes. In the hydrogenation of cinnamaldehyde to cinnamyl alcohol, Ir/H-MoO_x delivered selectivity as high as $\sim 93\%$, performing among the best of current metal-based catalysts. Additionally, the efficacy for various substrates with multiple groups further verified our Ir/H-MoO_x system to be competitive for chemoselective hydrogenation.

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1. Introduction

Reducible metal oxides, referring to the metal oxides with variable valence states and relatively easy to be reduced, are promising catalyst supports [1–3]. The partial reduction or hydrogen doping of such oxides results in the emerging “hydrogenated metal oxides” (H-MO_x), which consequently possesses the abundant oxygen vacancies, M-OH and M-H on surface, and more importantly the tuneable band states with metallic features [4–6]. Such variations would further affect the size, morphology, and valence state of loading metals via metal-support interactions, facilitating the achievement of high catalytic conversion with satisfied selectivity [1,3]. Particularly, hydrogenated molybdenum oxides (H-MoO_x) have been highlighted due to the enhanced acidity with H doping and the tailored electronic configuration associated with various valence states (Mo^{6+} , Mo^{5+} , Mo^{4+} , Mo^{3+} and Mo^{2+}) [7,8]. Besides as functional segments in organic optoelectronic devices, photodetectors and energy storage materials [7,9–11], they also

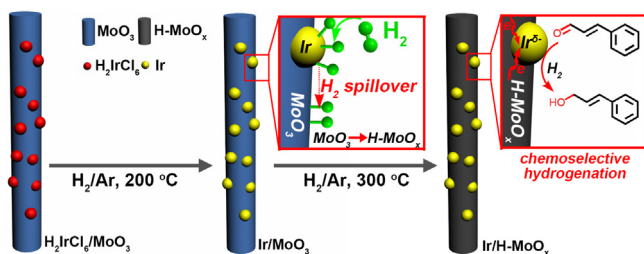
serve as important supports or additives for catalytic hydrogenation [12–16]. On one hand, acidic H-MoO_x is active for the acid-catalyzed ring-opening and cyclization processes, which can provide important synergy towards the selective hydrogenation of biomass-derived oxygenates [15–17]. On the other hand, the abundant oxygen vacancies on H-MoO_x can facilitate the adsorption of oxygen-containing groups (e.g., $\text{C}=\text{O}$) in substrates, improving both activity and selectivity in comparison with only metal catalysts [12]. However, the electronic metal-support interactions of H-MoO_x are rarely discussed in this subject, which are reasonably expected in the regard of its metallic band states.

Chemoselective hydrogenation of α,β -unsaturated aldehydes into their corresponding unsaturated alcohols is an important step towards value-added chemicals used in flavorings, perfumes, and pharmaceuticals [18,19]. Due to the higher free reaction enthalpy of $\text{C}=\text{O}$ (40 kJ mol^{-1}) than that of $\text{C}=\text{C}$ (35 kJ mol^{-1}), saturated aldehydes instead of desired unsaturated alcohols are the thermodynamically favoured products [19]. It is fundamental and challenging to develop selective catalysts to hydrogenate carbonyl from the conjugated ethylenic ($\text{C}=\text{C}$) and carbonyl ($\text{C}=\text{O}$) groups. Iridium (Ir) with large d-bands shows high activity for α,β -unsaturated aldehydes hydrogenation, however the selectivity is usually unsatisfied because of the adsorption/activation of both $\text{C}=\text{C}$ and $\text{C}=\text{O}$ on the large unoccupied d-orbitals [20,21]. An

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Scheme 1. Schematic illustration for the one-pot fabrication of Ir/H-MoO_x nanorods for chemoselective hydrogenation.

increasing electronic density around Ir is desired to optimize the hydrogenation routes, in which excessive electrons will enhance the repulsive force with C=C, and also promote the electron feedback to π^* in polar C=O [18,22]. Such regulation can be achieved via electronic metal-support interactions on designed supports [4,23]. In the regard of the large-density states around increasing Fermi level (E_F) and the appreciable delocalized electrons [10,24,25], H-MoO_x is expected to present feasible electronic interactions for chemoselective hydrogenation. As evidenced in very recent work, the introduction of H-MoO_x into Ir/SiO₂ catalysts benefited the selective hydrogenation of crotonaldehyde to crotyl alcohol [12], which was ascribed to the promotion of C=O adsorption on H-MoO_x surface, and the electronic metal-support interactions were unfortunately ignored. By contrast, in cinnamaldehyde hydrogenation, the undesired C=C hydrogenation on Pd, rather than C=O, was promoted by using H-MoO_x as the supports [14]. These interesting, but controversial findings indicate the importance of the varied interactions associated with H-MoO_x supports, which needs uncovering and further optimization.

Regarding the feasible hydrogen doping into oxides by H₂ spillover from noble metals [25], we herein develop a one-pot fabrication of H-MoO_x nanorods supported Ir (Ir/H-MoO_x) catalysts for chemoselective hydrogenation. As shown in Scheme 1, Ir nanoparticles (NPs) generate from the reduction of H₂IrCl₆ by H₂/Ar at mild temperature, which serve as active-sites for disassociating H₂ molecules to H atoms upon further heating [26]. The highly active H atoms migrate to the surface of MoO₃, and further diffuse into the bulk, thereby leading to the in-situ hydrogenation of MoO₃. Such fabrication, simultaneously combining the generation of active metal centres and the hydrogen doping on supports, ensures the interactions between ultrafine Ir and fresh H-MoO_x surface. The accumulated electrons around the MoO₆ octahedral of H-MoO_x promote the strong electronic interactions with Ir, resulting in negatively charge Ir^{δ-} species favouring the activation and turnover of C=O. As expected, Ir/H-MoO_x catalysts show high selectivity for the hydrogenation of α,β -unsaturated aldehydes into unsaturated alcohols. In cinnamaldehyde (CAL) hydrogenation, the Ir/H-MoO_x present the cinnamylalcohol (COL) selectivity as high as 93%, outperforming the Ir on other supports (e.g., MoO₃, SiO₂, ZrO₂, and active carbon (AC)) and even conventional metal catalysts. Moreover, the efficacy for various substrates that possess multiple groups (e.g., crotonaldehyde, citral, furfural and nitroarenes) further verifies our Ir/H-MoO_x to be competitive for chemoselective hydrogenation.

2. Experimental

2.1. Catalyst preparation

2.1.1. MoO₃ nanorods

The precursor of Mo₃O₁₀(C₆H₈N)₂·2H₂O nanowires were fabricated according to our previous report [27]. And the MoO₃ nanorods

used as catalyst supports in this work were obtained via calcining Mo₃O₁₀(C₆H₈N)₂·2H₂O at 400 °C for 2 h under air flow.

2.1.2. Ir/H-MoO_x, Ir/MoO₃, Ir/MoO₃(c) (MoO₃(c): commercial MoO₃), Ir/TiO₂, Ir/ZrO₂, Ir/AC, and Ir/SiO₂

Corresponding support was impregnated with H₂IrCl₆ aqueous solution and then stirred at 80 °C for 4 h. The samples were dried at 50 °C overnight, followed by a reduction with a stream of 5 vol% H₂/Ar at 300 °C for 2 h. For Ir/MoO₃, a lower temperature of 200 °C was adopted for the reduction, employing MoO₃ nanorods as the support.

2.1.3. Pt/CNT (CNT: carbon nanotubes) and Ag/SiO₂

CNT or SiO₂ was impregnated with metal-source aqueous solution and then stirred for 4 h at 80 °C. The samples were then dried at 50 °C overnight, followed by a reduction with a stream of 5 vol% H₂/Ar at 300 °C for 2 h.

2.1.4. Au/SiO₂

A typical deposition-precipitation procedure was employed to prepare Au/SiO₂ catalyst. Briefly, SiO₂ was dispersed with the aqueous solution of HAuCl₄, and pH was adjusted to 9.0 by dropwise addition of 0.25 M NH₃·H₂O (aq.). After stirring for 6 h and aging for another 2 h, the catalysts were washed with deionized water for five times and then dried at 50 °C overnight, followed by a reduction with a stream of 5 vol% H₂/Ar at 300 °C for 2 h.

2.2. Physical characterization

X-ray diffraction (XRD) analysis was performed on Bruker D8 diffractometer using Cu K α radiation ($\lambda = 1.54056 \text{ \AA}$). Scanning electronic microscopy (SEM) and transmission electron microscopy (TEM) investigations were taken on a ZEISS ULTRA55 and a JEOL JEM 2100F, respectively. Energy dispersive spectrum (EDS) attached on TEM was carried out on a JEOL JEM 2100F. The UV-vis diffuse reflection spectra (UV-vis DRS) were carried out on Varian Cary 5000 at room temperature. X-ray photoelectron spectroscopy (XPS) was processed on a Perkin-Elmer PHI X-tool, using C 1s (B. E.=284.6 eV) as a reference. The metal loading was determined by an inductively coupled plasma-atomic emission spectroscopy (ICP-AES). The Brunauer-Emmett-Teller (BET) specific surface areas were determined by adsorption-desorption of nitrogen at liquid nitrogen temperature, using an automatic gas adsorption analyzer (Quantachrome Autosorb-iQ-MP). The hydrogen temperature-programmed reduction (H₂-TPR) and CO chemisorption measurement were both conducted on a XianQuan instrument TP 5076, and the NH₃ temperature-programmed desorption (NH₃-TPD) analysis was carried out on a Micromeritics instrument ChemSorb 2920.

2.3. Catalytic performance measurement

CAL hydrogenation was carried out in a 100 mL stainless steel autoclave (Parr 4848 reactor controller), in which 25 mg of catalyst, 2 mmol of CAL, 20 mL of EtOH and 30 mL of H₂O were loaded. The reactor was sealed and purged with H₂ to remove the air for 3 times, and then the reactor was heated to the desired temperature. Hydrogen (2 MPa) was purged into the reactor after desired temperature was reached and the stirrer was started. The products were analyzed by Shimadzu GC-2014C with a FID detector. The conversion (conv.; %), selectivity to COL and hydrocinnamaldehyde (HCAL) were calculated with the formulas.

$$C_{\text{CAL}} = \frac{N_{\text{CAL},0} - N_{\text{CAL}}}{N_{\text{CAL},0}} \times 100 \quad (1)$$

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