Development of Vanadium-decorated Platinum Nanoparticle Catalyst for Green Sustainable Hydrogenation of Amides to Amines

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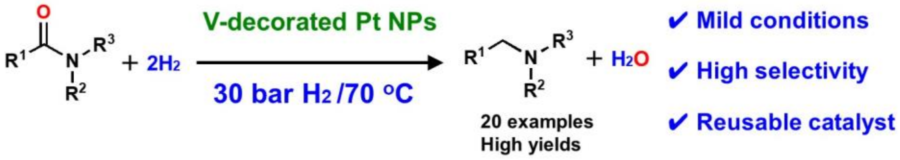
Abstract: Hydrogenation of amides to amines is an important reaction. However, the need for H_2 pressures and high temperatures is a crucial problem. No catalysts that are effective under ideally mild conditions, i.e., lower than 30 bar H_2 and 70 °C, have yet been reported. Here, the mild hydrogenation of amides was achieved for the first time, using a Pt/V bimetallic catalyst. Especially, the bimetallic catalyst could promote the hydrogenation under just 1 bar H_2 at 70 °C or 5 bar H_2 at room temperature. The mild reaction conditions enabled selective hydrogenation of various amides to amines, while inhibiting arene-hydrogenation.

Keywords: amide, hydrogenation, heterogeneous catalyst.

1. Introduction

Amine synthesis via amide hydrogenation is of crucial importance in organic synthesis. However, amide groups have low reactivity and are difficult to reduce. In 2005, a Roundtable of the ACS Green Chemistry Institute and leading global pharmaceutical companies decided “the catalytic hydrogenation of amides to amines with H_2 under mild conditions, ideally lower than 30 bar H_2 and 70 °C” is one of 12 key innovative research areas for the future sustainable production of pharmaceuticals. However, until now, no catalysts that are effective under the mild conditions, i.e., lower than 30 bar H_2/70 °C have been developed. The development of catalysts for amide reduction under mild and environmentally friendly conditions is therefore a great challenge.

Herein, we present the development of a hydroxyapatite-supported V-decorated Pt nanoparticle catalyst (Pt/V/HAP) that enables hydrogenation of amides to amines under mild conditions, i.e., lower than 30 bar H_2/70 °C (Scheme 1).[1] Furthermore, the bimetallic catalyst could promote the hydrogenation under just 1 bar of H_2 at 70 °C or 5 bar of H_2 at room temperature. This is the first time that hydrogenation of amides to amines under mild conditions has been achieved. The catalyst is easily recovered from the reaction mixture and retains its activity during recycling. Thus, the developed catalyst has a broad substrate scope, including aromatic amides, whereas conventional catalysts unavoidably cause arene-hydrogenation.



Scheme 1. Green hydrogenation of amides using V-decorated Pt nanoparticle catalyst

2. Experimental

Pt/V/HAP could be synthesized by the impregnation method using HAP, platinum acetylacetonate and vanadium acetylacetonate. The obtained solid was calcined at 300 °C to afford Pt/V/HAP. The hydrogenation of amides were conducted in the Teflon autoclave vessel. After the hydrogenation, Pt/V/HAP was removed by filtration, and the filtrate was analyzed by gas chromatography with naphthalene as an internal standard to determine the conversion and yields.

3. Results and discussion

A representative secondary-electron image of Pt/V/HAP shows the formation of Pt nanoparticles of mean diameter 2.2 nm on the HAP surface (Fig. 1a). The elemental distributions of Pt and V on HAP were determined using annular dark-field scanning transmission electron microscopy (ADF-STEM) coupled with energy-dispersive X-ray spectroscopy (EDX) (Fig. 1b–f). Elemental mapping of Pt/V/HAP reveals that V (shown in green in Fig. 1d) and Pt (shown in red in Fig. 1e) are highly dispersed on HAP and, importantly, that V surrounds Pt. EDX line analysis also shows the coexistence of Pt and V, confirming that the Pt nanoparticles are decorated with V species.

The Pt/V/HAP catalyst was active in the hydrogenation of N-acetylmorpholine under 30 bar H_2 at 70 °C, giving the desired amine in high yield without the formation of any by-products (Table 1, entry 1). Pt/V/HAP even catalyzed hydrogenation at room temperature under a lower H_2 pressure, i.e., 5 bar. Furthermore, the hydrogenation proceeded efficiently under atmospheric pressure of H_2 at 70 °C. To the best of our knowledge, this Pt/V bimetal is the first example of a catalyst that works at ambient temperature or just 1 bar of H_2. Pt/V/HAP showed high activity for various amides. A wide range of secondary and tertiary aliphatic amides were successfully hydrogenated, giving the desired amines as the sole product in excellent yields (entries 2-10). Pt/V/HAP enabled the highly selective hydrogenation of aromatic amides without arene-hydrogenation to afford the corresponding amines in excellent yields (entries 9 and 10). This is the first example of a heterogeneous catalyst for hydrogenation of amides to amines, while inhibiting arene-hydrogenation. The used Pt/V/HAP catalyst after the reaction was readily separated from the reaction mixture by filtration and reusable without any loss of its high activity even after the 10th recycling run. Pt/V/HAP is highly reusable unlike reported heterogeneous catalysts which suffer from a decrease in activity during recycling. Detailed characterization of the Pt/V catalyst by XAFS analysis showed that a cooperative catalysis between Lewis acidic property of V for activation of the C=O amide bond, and the C=O hydrogenation ability of adjacent Pt.

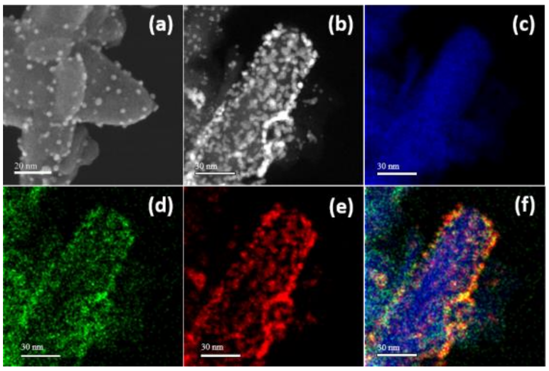
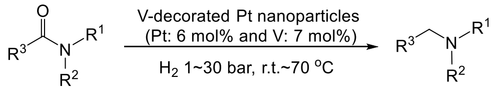
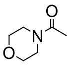
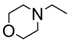
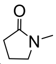
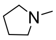
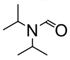
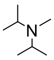
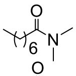
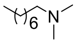
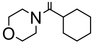
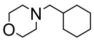
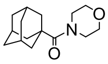
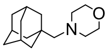
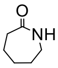
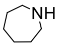
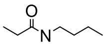
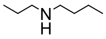
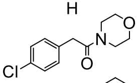
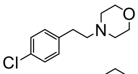
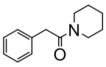
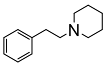


Figure 1. (a) Secondary-electron image of Pt/V/HAP treated with H_2. (b) ADF-STEM image of Pt/V/HAP treated with H_2. Elemental mapping images of (c) Ca, (d) V, and (e) Pt. (f) Composite overlay image formed from (c), (d), and (e).

Table 1. Hydrogenation of amides to amines using Pt/V/HAP



Entry	Substrate	Product	Time, h	Yield, %
1			8	99
2			48	92
3			18	99
4			18	94
5			48	97
6			48	99
7			24	92
8			24	90
9			8	96
10			24	90

4. Conclusions

A hydrogenation of amides to amines under mild conditions was achieved using a V-decorated Pt bimetallic catalyst. The Pt/V catalyst promoted amide hydrogenation to amines at ambient temperature or just 1 bar of H_2 for the first time. Various amides, including aromatic ones, were converted to the corresponding amines in high yields without arene-hydrogenation. This catalytic system has the significant advantages of mild operating conditions, simple work-up procedures, high catalyst reusability, and a broad substrate scope, enabling green sustainable hydrogenation of amides to amines.

References

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