Gold Nanoparticles on OMS-2-Catalyzed Aerobic Oxidative α,β-Dehydrogenation of β-Heteroatom-Substituted Saturated Ketones

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Abstract: In the presence of Au nanoparticles supported on manganese oxide OMS-2 (Au/OMS-2), α,β-dehydrogenation of β-heteroatom-substituted saturated ketones (heteroatom = N, O, S) to the corresponding α,β-unsaturated ketones using O_2 (in air) as the sole oxidant effectively proceeded. The catalysis of Au/OMS-2 was truly heterogeneous, and the catalyst could be reused at least four times.

Keywords: Gold nanoparticles, Heterogeneous catalysts, Oxidative dehydrogenation.

1. Introduction

β-Heteroatom-substituted α,β-unsaturated ketones (heteroatom = N, O, S) are versatile intermediates in the synthesis of pharmaceuticals chemicals. Oxidative dehydrogenation of β-heteroatom-substituted saturated ketones is one of the most promising procedures for the synthesis of β-heteroatom-substituted α,β-unsaturated ketones. Traditionally, the dehydrogenation has been carried out by using various stoichiometric oxidants, such as IBX and DDQ, or homogeneous Pd-based catalysts.[1] In this study, the gold nanoparticles supported on OMS-2 (manganese oxide-based octahedral molecular sieves)-catalyzed oxidative α,β-dehydrogenation of β-heteroatom-substituted saturated ketones has successfully been developed using molecular oxygen as the terminal oxidant, for the first time.[2]

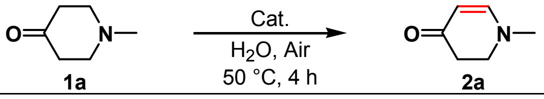
2. Experimental

Au/OMS-2 was prepared by the simple deposition-precipitation method. OMS-2 (2.0 g) was added to an aqueous solution of $HAuCl_4 \cdot 4H_2O$ (8.3 mM, 60 mL). After the mixture was vigorously stirred at room temperature for 15 min, the pH of the solution was quickly adjusted to 10 by addition of an aqueous solution of NaOH (1.0 M). The resulting mixture was further stirred for 24 h. The solid was filtered off, washed with deionized water (4 L), and dried in vacuo. Then, the hydroxide precursor was calcined at 300 °C for 2 h, giving Au/OMS-2 as a dark brown powder (Au content: 4.1 wt%, average Au size: 3.9 nm). The catalytic reaction was typically carried out according to the following procedure. Au/OMS-2 (3.6 mol%, 85 mg), substrate (0.5 mmol), solvent (2 mL), and a Teflon-coated magnetic stir bar were successively placed in a Pyrex glass reactor (volume *ca.* 20 mL). The reaction mixture was vigorously stirred at 50–90 °C, in 1 atm of air or O_2. After the reaction was completed, an internal standard (biphenyl) and a large amount of acetone were added to the reaction mixture, and conversions and yields were determined by GC analysis.

3. Results and discussion

Initially, various supported metal catalysts, such as Au/OMS-2, Pd/OMS-2, Ag/OMS-2, and Cu/OMS-2, were applied to the oxidative dehydrogenation of 1-methyl-4-piperidone (**1a**) to 2,3-dihydro-1-methyl-4(1*H*)-pyridinone (**2a**) using O_2 in air as the terminal oxidant. Au/OMS-2 showed the highest catalytic activity (Table 1, entries 1–4). OMS-2 was the best support among Al_2O_3, CeO_2, TiO_2, and OMS-2 (Table 1, entries 5–7). Additionally, a physical mixture of Au/Al_2O_3 and OMS-2 gave almost the same **2a** yield as Au/Al_2O_3 alone (Table 1, entry 8), which indicates that the OMS-2 support plays an important promoting role in the present reaction. It is likely that Au–H species formed during the present oxidative dehydrogenation and that the oxidation of the Au–H species to regenerate active Au species is included in the catalytic cycle. OMS-2 support can effectively oxidize the Au–H species and act as an electron-transfer mediator between Au nanoparticles and O_2.

Table 1. Oxidative dehydrogenation of **1a**.[a]



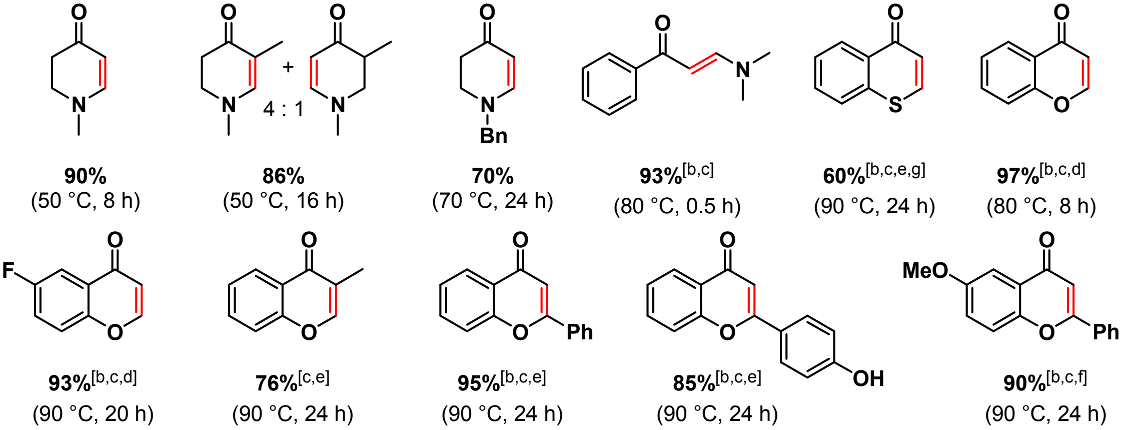
Entry	Cat.	Conv. [%]	Yield [%]
1	Au/OMS-2	82	78
2	Pd/OMS-2	30	24
3	Ag/OMS-2	1	<1
4	Cu/OMS-2	7	<1
5	Au/Al_2O_3	71	66
6	Au/CeO_2	59	55
7	Au/TiO_2	54	54
8	Au/Al_2O_3 + OMS-2[b]	70	64
9	OMS-2[b]	14	<1

[a] Reaction conditions: **1a** (0.5 mmol), cat. (3.6 mol%), H_2O (2 mL), 50 °C, air (1 atm), 4 h. Yields were determined by GC analysis. [b] OMS-2 (80 mg).

The production of **2a** was completely stopped by removal of Au/OMS-2. Furthermore, it was confirmed by ICP-AES analysis that Au and Mn species were hardly present in the filtrate (Au: 0.02%, Mn: 0.02%). These results revealed that the observed catalysis was truly heterogeneous. Moreover, Au/OMS-2 could be easily retrieved from the reaction mixture by simple filtration, and the catalyst could be reused at least four times without significant loss of its catalytic performance.

Various kinds of structurally diverse β-heteroatom-substituted saturated ketones (heteroatom = N, O, S) could be effectively converted into the corresponding α,β-unsaturated ketones in moderate to high yields (Table 2). Various cyclic enaminones, chromones, and flavones could effectively be produced by the present Au/OMS-2-catalyzed oxidative dehydrogenation.

Table 2. Substrate scope.[a]



[a] Reaction conditions: substrate (0.5 mmol), Au/OMS-2 (Au: 3.6 mol%), H_2O (2 mL), air (1 atm). Yields were determined by GC analysis. [b] O_2 (1 atm). [c] LiBr (1 mol%). [d] H_2O/1,4-dioxane (1.9 mL/0.1 mL). [e] H_2O/1,4-dioxane (1 mL/1 mL). [f] H_2O/DMA (1 mL/1 mL). [g] Au/OMS-2 (Au: 7.2 mol%).

4. Conclusions

Heterogeneously Au/OMS-2-catalyzed aerobic oxidative α,β-dehydrogenation of β-heteroatom-substituted saturated ketones has been developed. It is likely that OMS-2 support acts as an electron transfer mediator between Au nanoparticles and O_2. Various kinds of structurally diverse β-heteroatom-substituted α,β-unsaturated ketones were successfully obtained starting from the corresponding saturated ketones.

References

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