Conversion of glucaric acid to adipic acid by Pd−ReOx catalyst supported on carbon-based materials

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Significance and Relevance

Green Synthesis of adipic acid from renewable biomass is a topic of industrial interest and a very challenging goal of sustainable chemistry, therefore the development of highly efficient catalysts able to catalyze the reaction are highly desired. In fact, adipic acid represents a key monomer for the synthesis of one of the most important polymers intermediates in the chemical industry, nylon-66.

- *Preferred and 2nd choice for the topic: Green chemistry and biomass transformation, renewable resources conversion /*

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Introduction and Motivations

Adipic acid production from renewable biomass is a very challenging goal of green chemistry. Here we report on the performance of a bifunctional Pd−ReOx catalyst used for the sustainable synthesis of adipic acid via glucaric acid. Glucaric acid represents the oxidation product in the transformation of cellulose-derived glucose and, at the same time, the reagent of a second challenging step-reaction of deoxydehydration (DODH) for obtaining adipic acid. An activated carbon-supported bifunctional catalyst composed of palladium and rhenium oxide is reported to be powerful for the removal of four hydroxyl groups in glucaric acid, affording adipic acid with high yield.[1] This work presents the performance of the Pd−ReOx bifunctional-catalyst supported on different carbonaceous materials highlighting the role of the support for an efficient deoxygenation in the adipic acid synthesis.

Materials and Methods

The bifunctional catalyst composed of Pd metal and rhenium oxide, co-loaded on activated carbon (0.5% Pd−10% ReOx/AC) was prepared by a co-impregnation method. Four different commercially available activated carbons (AC) were tested as support: XC-72, Charcoal activated (Supelco), Chemviron F300, Norit-Hydro Darco GCW granular carbons crushed and reduced to powder.

AC (1.0 g) was first mixed with an aqueous solution of NH_4ReO_4 and $Pd(NO_3)_2$ at room temperature under continuous stirring. After stirring for 12 h, the solvent was evaporated at 353 K to get a solid product. The solid product was subsequently dried at 383 K for 12 h. Then, the Pd–ReOx/AC catalyst was obtained by heating the solid product at a rate of 2 K min^{-1} to 673 K and keeping at 673 K for 3 h under N_2 flow (40 mL min^{-1}). The loading amount of metal oxides ReOx, and Pd nanoparticles were fixed at 10.0 wt% and 0.5 wt%, respectively for the best case, but also other loads were investigated.

The glucaric acid conversion has been carried out in a 300mL autoclave using the following experimental setup: 700 mg of catalyst, 875 mg of D-glucaric acid potassium salt, 1400 mg of Amberlyst-15, and 175 mL of methanol were first added into the reactor. After purging with H_2 five times, the reactor was charged with 2 MPa of H_2 at room temperature. Then, the reaction started by heating the reactor to 383 K in an oil bath. After 24 h, the reaction was stopped by cooling the reactor to room temperature in cold water. The liquid products were analyzed with a GC (GC-7890B, Agilent)

by using dimethyl succinate as an internal standard, the yields were reported as percentage of dimethyl adipate (% DMA).

Results and Discussion

The prepared catalysts have been characterized by XRD, SEM, XPS, and physisorption measurements.

In the mixed Pd−ReO$_x$ catalysts, the deoxygenation operated by the rhenium oxide functions was synergically facilitated by the copresence of Pd which catalyzes the hydrogenation of the olefin intermediates and promotes the removal of four hydroxyl group (deoxygenation).

In the carbon-based samples investigated, micro and mesopores have been observed. A linear correlation was observed between the mesoporous volume (V$_{meso}$) typical of the catalysts shown in **Table 1** and the yield of dimethyl adipate (%) obtained from the catalytic conversion of potassium glucarate.

Table 1. *Physisorption characteristics of the investigated catalysts and conversion yields to DMA.*

SAMPLE	Composition	BET [m^2/g]	V$_{micro}$	V$_{tot}$ [cm^3/g]	V$_{meso}$	DMA yield (%)
Cat-2	Pd−ReO$_x$_AC_Charcoal	643	0.18566	0.39998	0.21432	41.3
Cat-3	Pd−ReO$_x$_AC_Hydro_Darco	909	0.29069	0.44870	0.15801	31.8
Cat-4	Pd−ReO$_x$_AC_VironF300	710	0.22968	0.31873	0.08905	24.1

The sample with the highest mesoporosity (Cat-2) is also the one with the highest DMA yield. In fact, from the comparison with the yield of Cat-3, which has a greater surface area, and a greater volume of micropores, compared to that of mesopores, it is evident that the best performances correlate with the presence of higher volumes of mesopores.

References

1. W. Deng, L. Yan, B. Wang, Q. Zhang, H. Song, S. Wang, Q. Zhang, Y. Wang. *Angew. Chem. Int. Ed.,* **2021**, 4712-4719.

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