Chinese Journal of Catalysis 42 (2021) 824–834

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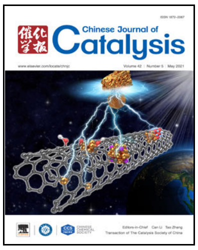

Article

# MIL-53 (Al) derived single-atom Rh catalyst for the selective hydrogenation of *m*-chloronitrobenzene into *m*-chloroaniline

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## ARTICLE INFO

*Article history:*
Received 8 May 2020
Accepted 7 July 2020
Available online 22 September 2020

*Keywords:*
Single-atom catalyst
Rhodium
Metal-organic framework
Hydrogenation
Chemoselectivity

## ABSTRACT

The catalytic hydrogenation of halonitroarenes to haloanilines is a green and sustainable process for the production of key nitrogen-containing intermediates in fine chemical industry. Chemoselective hydrogenation poses a significant challenge, which requires the rational design of the catalysts with proper hydrogenation ability for nitro group and simultaneously preventing dehalogenation of halogen group. Herein, a highly effective Rh@$Al_2O_3$@C single-atom catalyst (SAC) was developed for the hydrogenation of *m*-chloronitrobenzene (*m*-CNB) to *m*-chloroaniline (*m*-CAN), through an in-situ grafting of metal during the assembly of MIL-53 (Al), followed by confined pyrolysis. Extensive characterizations reveal an exquisite structure of the Rh@$Al_2O_3$@C, containing atomically dispersed Rh sites onto $Al_2O_3$ confined by the amorphous carbon. The five-coordinated aluminum ($Al^{V}$) species are essential for achieving the atomic dispersion of Rh atoms, providing the unsaturated coordinative sites for metal. Compared to the benchmark Rh/γ-$Al_2O_3$ and Rh/C nanocatalysts, the Rh@$Al_2O_3$@C SAC affords an excellent turnover frequency of 2317 $\text{mol}_{m\text{-CNB}}\cdot\text{mol}_{\text{Rh}}^{-1}\cdot\text{h}^{-1}$, the highest value to date in heterogeneous catalyst systems for the hydrogenation of *m*-CNB at 313 K and 20 bar $H_2$, together with a sustained selectivity to *m*-CAN (~98%) during five consecutive runs. The superior catalytic performance of the Rh@$Al_2O_3$@C is attributed to a proper modulation of electronic structure of hydrogenation metal by forming SAC, together with an enhanced accessibility of acid function sites.

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This work was supported by the Strategic Priority Research Program of the Chinese Academy of Sciences (XDB17020100), the National Natural Science Foundation of China (21703238, 21690084, 21802134), Educational Commission of Hunan Province (19B463), Collaborative Innovation Center of Manganese-Zinc-Vanadium Industrial Technology (MXF202001), and Research Startup Foundation of Jishou University (No.21).
DOI: 10.1016/S1872-2067(20)63697-X | http://www.sciencedirect.com/science/journal/18722067 | Chin. J. Catal., Vol. 42, No. 5, May 2021