







## 28th International Conference on Organometallic Chemistry

FLORENCE, ITALY
Congress & Exhibition Centre
15 - 20 JULY 2018

www.icomc2018.com



## Nitrogen-Enriched Graphene Iron Oxide Nanoparticles as Innovative Catalysts: First Application to Cyclopropanation Reactions

Abhijnan Sarkar,<sup>a</sup> Dario Formenti,<sup>a,b</sup> Francesco Ferretti,<sup>a,b</sup> Kathrin Junge,<sup>b</sup> Fabio Ragaini,<sup>a,\*</sup> Matthias Beller.<sup>b,\*</sup>

abhijnan.sarkar@unimi.it

A new class of catalysts having a metal/metal oxide core surrounded by a few nitrogen-enriched graphene layers (NGR) has recently brought immense attention in research. Until now, NGR catalysts have mostly been employed for hydrogenation reactions. In this work, we expand the field of applicability of NGR catalysts to cyclopropanation reactions.

The activity of Fe<sub>2</sub>O<sub>3</sub>/NGr@C has been studied by using ethyl diazoacetate and  $\alpha$ -methylstyrene as substrates. Various parameters such as solvents, temperature and time were changed. Fe<sub>2</sub>O<sub>3</sub>/NGr@C-catalysts showed best activity in dimethoxyethane at 60 °C, affording high yields of the desired cyclopropanes (mixture of *cis* and *trans* isomers) and only 1-2 % of ethyl maleate and fumarate (Figure 1).

Figure 1. Fe<sub>2</sub>O<sub>3</sub>/NGr@C catalyzed olefin cyclopropanation.

The catalyst gradually deactivates after each recycle, but we were able to reactivate the recovered catalyst by treating it with dilute  $H_2O_2$  (1:10 with distilled water).

Like  $\alpha$ -methylstyrene, several olefins such as 4-chloro- $\alpha$ -methyl styrene, 4-methylstyrene, 2-methylstyrene, 3-methylstyrene, 4-chlorostyrene, 4-t-butylstyrene, 1-octene etc. have been tested in order to explore the substrate scope. The corresponding cyclopropanes were obtained in high to excellent isolated yields (84-98%). In all cases *trans* diastereoselectivity was found, but even the minor *cis* isomer could be isolated in a pure form.

## References

- 1. Li, M.; Xu, F.; Li, H.; Wang, Y. Catal. Sci. Technol. 2016, 6, 3670.
- 2. Pisiewicz, S.; Stemmler, T.; Surkus, A.-E.; Junge, K.; Beller, M. ChemCatChem 2015, 7, 62.
- 3. Jagadeesh, R. V.; Stemmler, T.; Surkus, A.-E.; Junge, H.; Junge, K.; Beller, M. Nat. Protoc. 2015, 10, 548.
- 4. Formenti, D.; Ferretti, F.; Topf, C.; Surkus, A.-E.; Pohl, M.-M.; Radnik, J.; Schneider, M.; Junge, K.; Beller, M.; Ragaini, F. *J. Catal.* **2017**, *351*, 79.
- 5. Formenti, D.; Topf, C.; Junge, K.; Ragaini, F.; Beller, M. Catal. Sci. Technol. 2016, 6, 4473.

<sup>&</sup>lt;sup>a</sup> Università degli Studi di Milano, Dipartimento di Chimica, via C. Golgi 19, 20133 Milano, Italy.

<sup>&</sup>lt;sup>b</sup> Leibniz-Institut für Katalyse e.V. an der Universität Rostock, Albert-Einstein-Strasse 29a, 18059 Rostock, Germany.