

# Transfer hydrogenation with catalyst recycling in a rotating bed reactor

Transfer hydrogenation is an attractive alternative to conventional hydrogenation due to easy handling and high safety. When performed with costly heterogeneous transition metal catalysts, tedious filtration is typically required to isolate the product. This application note demonstrates transfer hydrogenation catalysed by palladium-containing beads. The catalyst beads were held in SpinChem® cartridges placed into a SpinChem® rotating bed reactor (RBR). This set-up resulted in high product conversions throughout more than 10 consecutive reactions without any need for filtration. Catalyst handling, washing and recycling was very quick and convenient giving a high productivity.

**Keywords:** Synthesis, Palladium on carbon, Easy handling, Quick recycling

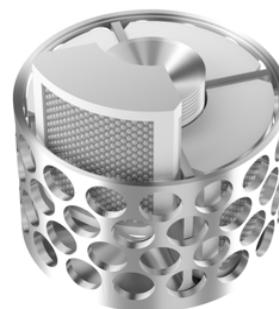
Hydrogenation is capable of reducing a great number of functional groups, broadly grouped into unsaturated carbon-carbon bonds (e.g. alkene, alkyne), carbon-heteroatom bonds (e.g. benzyl, nitrile, imine, carbonyls), and heteroatom-heteroatom bonds (e.g. nitro, azo, azide).

The hydrogenation is typically catalysed by transition metals, which can be either heterogeneous or homogeneous. Heterogeneous hydrogenation catalysts such as palladium on charcoal are suitable and cost-effective for many straight-forward reactions. Heterogeneous catalysts also have the obvious advantage of being removed from the product by filtration and optionally be easily recycled.

Hydrogenation reactions using hydrogen gas are usually efficient and clean. Drawbacks are the safety issues of handling hydrogen gas, need for reactors made for pressurized reactions, and the necessity of vigorous stirring to make these solid-liquid-gaseous reactions work well. Transfer hydrogenation offers an attractive alternative that addresses these three drawbacks. In transfer hydrogenation reactions, the hydrogen for the reduction is commonly derived from easily handled sources such as formic acid/ formates or cyclohexene and similar hydrocarbons.

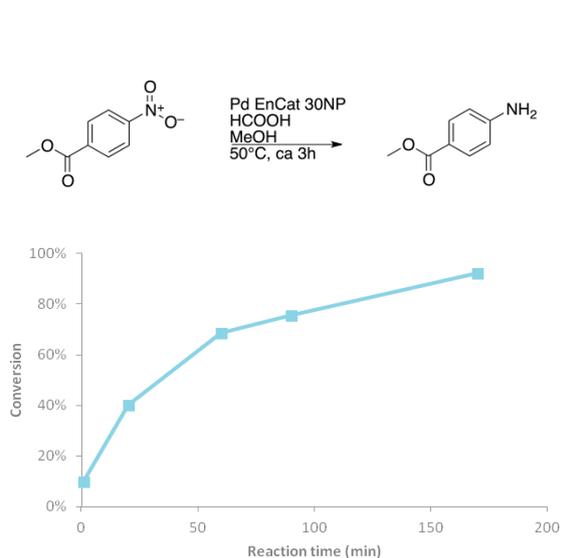
This application note demonstrates convenient transfer hydrogenation catalysed by palladium-containing beads (Reaxa's Pd(O) EnCat 30NP). The catalyst beads were held in SpinChem® cartridges placed into a SpinChem® rotating bed reactor (RBR) (Fig. 1)

The RBR approach allows the heterogeneous catalyst to be stationary in the reactor while the reaction solution is efficiently passed through the catalyst bed. Consequently, the reaction vessel and product is kept clean from catalyst. A RBR can also be used in pressurized reaction vessels for the applications where hydrogen gas is a better hydrogen source.



**Fig 1.** Image of SpinChem® cartridges placed into a SpinChem® rotating bed reactor.

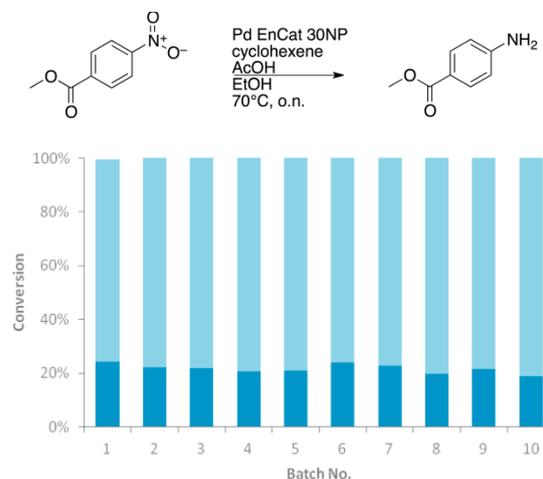
We first investigated conversion for the hydrogenation of methyl 4-nitrobenzoate in methanol using formic acid as hydrogen donor (Fig 3) catalysed by Reaxa EnCat® beads with encapsulated palladium. The reaction was performed with a SpinChem® RBR and reached 69% and 92% conversion after 60 and 170 minutes, respectively. No attrition was observed and no filtration was required to remove the catalyst and recover the product.



**Fig 3. Transfer hydrogenation with SpinChem® RBR S2 containing Reaxa Pd(0) EnCat® 30NP catalyst (7.0 g wet beads) distributed equally into four SpinChem® cartridges. The catalyst was washed with methanol to remove water before use. The RBR was inserted into a SpinChem® flower-baffled reaction vessel V2 held at 50 °C. A solution of methyl 4-nitrobenzoate (2.6, 14.4 mmol) in methanol (150 mL) was added to the vessel and the RBR was rotated at 500 rpm. Conversion was determined by GC-FID analysis of product after 20, 60, 90, and 170 min.**

Next we studied repeated reuse of the palladium catalyst by performing ten consecutive reaction cycles with a SpinChem® RBR set-up (Fig 4) using another hydrogen source. Between each reaction cycle, the vessel was emptied and the RBR with catalyst was washed with solvent and spun dry before new reaction solution was added.

The catalyst recycling was very successful, consistently reaching 100% conversion after 18 hours throughout the ten reaction cycles. Conversion after one hour remained stable at ca 22% with a hardly significant trend of decrease. From this we estimated that around 100 cycles can be performed without catalyst renewal.



**Fig 4. Catalyst recycling study for ten consecutive transfer hydrogenations with a SpinChem® RBR S2 in a flower-baffled reaction vessel V2 held at 70 °C. Reaxa Pd(0) EnCat® 30NP catalyst (5.0 g, wet beads) was distributed equally into four SpinChem® cartridges and washed with ethanol (abs.) to remove water before use. A solution/suspension of methyl 4-nitrobenzoate (2.6 g, 14.4 mmol), cyclohexene (15 mL, 148 mmol) and acetic acid (1.14 mL, 4.0 mmol) in ethanol (abs., 135 mL) was added to the reaction vessel and the RBR was rotated at 500 rpm for 18 h. The catalyst was washed by spinning the RBR at 500 rpm in ethanol (abs., 150 mL) at 70 °C between each cycle. The RBR was spun dry before and after wash. Conversion was determined by GC-FID analysis of product after 1 h (dark blue) and 18 h (light blue).**

#### Conclusions:

- Convenient transfer hydrogenation can be performed using heterogeneous catalysis in a SpinChem® RBR without any need for filtration.
- Catalyst recycling can be performed for more than 10 consecutive reactions without any significant decrease in conversion.



The SpinChem® rotating bed reactor (RBR) is revolutionizing mass transfer in heterogeneous reactions where solid phases are used for catalysis, enzymatic reactions, adsorption, scavenging and other processes. The convenience of a protected bed within an RBR significantly reduce the need for post-reaction work-up. The SpinChem® RBR concept is fully scalable from laboratory to production, thus providing both more efficient reaction development and improved production economy.

Products: SpinChem® RBR S2 (1221-001)