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Review

Catalyst recycling—A survey of recent progress and current status

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ABSTRACT

This review gives a comprehensive treatment to show and illustrate current efforts in the field of recyclable catalysis. Results of recycling studies performed with a wide range of soluble homogeneous and immobilized complexes as well as heterogeneous catalysts developed in recent years have been collected and discussed. Among others, transformations including hydrogenation, reduction, oxidation, varied asymmetric syntheses and coupling reactions are covered. A thorough analysis of the available data and discussion of issues related to recyclability in general are also given. The review includes selected literature examples until the beginning of 2017.

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Abbreviations: AAS, atomic absorption spectroscopy; AB, ammonia–borane ($H_3N{:}BH_3$); acac, acetylacetonate; BAIB, [bis(acetoxy)iodo]benzene; bdmi, 1-butyl-2,3-dimethylimidazolium; BARF, tetrakis-[3,5-bis(trifluoromethyl)phenyl]borate; BINAM, 1,1′-binaphthyl-2,2′-diamine; BINAP, 2,2′-bis(diphenylphosphano)-1,1′-binaphthyl; bmim, 1-butyl-3-methylimidazolium; BOX, bisoxazoline; BWT, black wattle tannin; C_{10}mim, 1-decyl-3-methylimidazolium; C*nh*, carbon nanohorn; C*nt*, carbon nanotube; DABCO, 1,4-diazabicyclo[2.2.2]octane; dansyl, [5-(dimethylamino)naphthalene-1-sulfonyl]; dba, dibenzylideneacetone; DMAc, *N,N*-dimethylacetamide; DMF, *N,N*-dimethylformamide; dmpz, 3,5-dimethylpyrazole; DA, dopamine; DPEN, 1,2-diphenyl-1,2-diaminoethane; *ee*, enantiomeric excess; emim, 1-ethyl-3-methylimidazolium; FESEM, field emission scanning electronic microscopy; FSG, fluorous silica gel; F-SPE, fluorous solid-phase extraction; GO, graphene oxide; rGO, reduced graphene oxide; *graph*, graphite; HBPE, hyperbranched polyethylene; HMS, hexagonal mesoporous silica; HPEI, hyperbranched polyethylenimine; HRTEM, high-resolution transmission electron microscopy; ICP-AES, inductively coupled plasma atomic emission spectroscopy; ICP-OES, inductively coupled plasma optical emission spectroscopy; IL, ionic liquid; *l*/*br*, linear to branched ratio; LC, laponite clay; MCF, mesocellular foam; MAB, methylamine–borane ($MeH_2N{:}BH_3$); mim, methylimidazolium; MTBE, methyl *tert*-butyl ether; MW, microwave heating; NHC, *N*-heterocyclic carbene; NMP, *N*-methyl-2-pyrrolidone; Oct, octyl; *olac*, oleic acid; omim, 1-methyl-3-octylimidazolium; PAA, polyacrylic acid; PE, polyethylene; PEI, polyethyleneimine; PEG, poly(ethylene glycol); PET, polyethylene terephthalate; PIB, polyisobutylene; pmim, 1-propyl-3-methylimidazolium; PMO, periodic mesoporous organosilica; *poly*, polymer; ppy, 2-phenylpyridine; PS, polystyrene; PVP, poly(4-vinylpyridine); PVPy, poly(*N*-vinyl-2-pyrrolidone); RCM, ring-closing metathesis; rGO, reduced graphene oxide; $scCO_2$, supercritical $scCO_2$; SFM, scanning force microscopy; TBAAc, tetrabutylammonium acetate; TBAB, tetrabutylammonium bromide; TBHP, *tert*-butyl hydroperoxide; TEOS, tetraethyl orthosilicate; TEMPO, 2,2,6,6-tetramethylpiperidine 1-oxyl; TfO, triflato (CF_3SO_3, trifluoromethylsulfonato); TGA, thermogravimetric analysis; TOF, turnover frequency; TON, turnover number; TPPTS, $P(C_6H_4\text{-}m SO_3Na)_3$; TRPTC, thermoregulated phase-transfer catalysis; TsDPEN, *N*-(*p*-toluenesulfonyl)-1,2-diphenylethylenediamine; VSM, vibrating sample magnetometer.

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1. Introduction

"Green" has become a buzzword in recent decades for sustainability. Sustainable chemistry is of extremely high importance stimulating the development of clean processes and technologies. It includes waste reduction, minimization of materials and energy, renewability, introduction and use of environmentally benign reagents and efficient processes. In particular, recycling, that is the reuse of catalysts, the topic of this review, is an important issue when considering the limited availability and dwindling supply of expensive noble metals. A long catalyst lifetime and the ability to easily recycle the catalyst are highly desirable for industrial applications. That is, both environmental and economic considerations push for the development of processes that enable the separation and recovery as well as reuse of the catalyst. The general requirements of any catalyst are high activity, selectivity and stability for prolonged use. Furthermore, a catalytic process should have low environmental impact.

Homogeneous (soluble) metal complexes are well-known for their high, in certain instances, extremely high activities and selectivities to induce varied transformations. No wonder that they are widely used in both academia and industry in synthetic organic chemistry and commercial chemical technologies. The downside, however, is often low stability and the difficulty in reutilization because of the complexity of their separation being time consuming and requiring high energy. These problems may be solved using "non-conventional" solvents (ionic liquids, water, fluorinated and supercritical solvents) and multiphase homogeneous catalysis [1]. Heterogenization that is immobilization of catalytically active species on suitable carriers may provide another solution to these needs [2]. Solid heterogeneous catalysts are easy to handle and can easily be separated by simple techniques (filtration, centrifugation, magnetic separation, etc.) allowing catalyst recycling. Immobilization, however, introduces additional synthetic steps in catalyst preparation. Furthermore, the activity and selectivity of immobilized catalysts are frequently lower compared to the corresponding soluble homogeneous complexes. One of the main reasons is the much lower number of available active sites, compared to the single-site nature of homogeneous complexes. Additionally, deactivation resulting from poisoning, metal leaching and decomposition take place (see a detailed discussion in Section 7.3). A further major problem is environmental concerns arising from the use of costly and often poisonous materials applied in catalyst synthesis.

To compile a general review of the field of catalyst recycling is an immense task. A review by Cole-Hamilton [3], as well as two excellent books edited by Cole-Hamilton and Tooze [4] and de Vos, Vankelecom and Jacobs [5] have been published. However, all three have focused only on soluble and immobilized homogeneous complexes. Additional related reviews covering even narrower fields are also available for interested readers [1,6]. Gladysz has discussed general problems of catalyst recycling in two relevant papers [7].

A comprehensive review about catalyst recycling comprising varied possibilities of catalyst recovery and reuse and, at the same time, covering diverse transformations has not been compiled before. This review is intended to be illustrative by presenting and discussing a selection of varied examples of the last 6–7 years with a handful of results from 2017. Nevertheless, it is a comprehensive treatment to show and illustrate current efforts in the development of the field. In addition to recent achievements, a few noteworthy examples from earlier studies will also be treated here as appropriate. A thorough analysis of the available data and discussion of issues related to recyclability in general are also included.

The aim of this review is to show a wide spectrum of reactions and catalyst systems with the potential of catalyst recycling. Still, the strict selection rules applied in related previous reviews by the principal author are also applicable here [8]. Specifically, the general rule for data selection is that decrease in percentage activity (conversion or yield) cannot be higher than the number of cycles. Of studies with 5–9 runs only results without decreases in activity are treated. There are, however, a few notable exceptions (for example, novel catalysts and rarely studied reactions). A further precondition for selection, in all cases, is the availability of appropriate catalyst characterization information. Whereas consistently high yields in repeated runs cannot be taken as satisfactory evidence for high catalyst stability, they testify to the robust nature of a catalyst system, which is a necessary requirement for long-term uses (see also Section 2).