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Leached phase-separated porous glasses as support material in liquid phase heterogeneous catalysis – a short review

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Leached phase-separated porous glasses are interesting support materials for heterogeneous catalysts utilized for cross-coupling reactions and hydrogenation reactions in the liquid phase. The option to construct tailor-made porous structures and shapes of the particles results in materials with interesting properties for catalysis, such as narrow pore size distribution or specific surface area. Loading of porous glasses with various metals by the wet-impregnation technique leads to active catalysts for widespread applications in organic synthesis. This article reviews the application of porous glass-based catalysts for the construction of new C–C bonds as well as for chemoselective hydrogenation under microwave-assisted or classical heating conditions.

Keywords: chemoselectivity, citral, cross-coupling, hydrogenation, microwave heating.

1. Introduction

Porous glasses belong to the silica containing porous materials (silica content >95%) that can be produced by acidic as well as alkaline leaching of phase-separated alkali borosilicate glasses or sol–gel process [1]. Due to the conditions applied during the production process (starting material, sintering temperature, sintering duration, *etc*.), well-defined properties like pore size, pore volume, or specific surface area can be adjusted [2]. Another feature is the possibility of tailor-made shaping of the glasses. According to the application membranes, fibers or spherical particles can be formed, resulting in customized materials for the use as adsorbent [3], ion exchanger [4], stationary phase in chromatographic columns [5] or support material in catalysis [6], just to mention a few examples. Especially in the latter case a high specific surface up to 1000 m^2g^{-1} and tunable pore diameters are beneficial [7]. But also chemical, thermal and mechanical stability as well as slight surface acidity arising from silanol and remaining boranol groups are favored properties.

In the present article, heterogeneous catalysts based on porous glasses as support material and their application in Pd-catalyzed C–C coupling reactions like Suzuki–Miyaura or Mizoroki–Heck as well as liquid-phase hydrogenation under conventional heating or microwave-assisted conditions are reviewed.

2. Application in C–C cross-coupling reactions

Natural products, pharmaceuticals, or fine chemicals often consist of complex molecular structures, which are challenging to chemical synthesis. Therefore C–C cross-coupling reactions are outstanding tools due to the benefit of connecting small and cheap reactants to large molecules. Furthermore, a broad range of substrates like alkyl, (hetero)aryl, or functionalized compounds are tolerated. Since these cost and ecological efficient reactions only need catalytic amounts of expensive transition metals, technical importance has grown, honored with the Nobel Prize in Chemistry 2010 for the developers of Pd-catalyzed cross-coupling reactions [8, 9].

2.1. Suzuki–Miyaura cross-coupling

Discovered in 1979 by MIYAURA *et al.*, this type of Pd-catalyzed C–C coupling reaction uses aryl halides and organoboron reagents (*e.g.* phenylboronic acid) to form biaryls (Fig. 1) [10]. Due to thermal stability and low toxicity of organic boron compounds as well as a high tolerance towards functional groups, the Suzuki–Miyaura reaction has gained high technical importance [11]. In contrast to originally used $Pd(PPh_3)_4$ [10], the deposition of active metal species onto porous supports enables several benefits: *i*) easy separation of the catalyst and product combined with less metal contamination and *ii*) the reaction does not have to be carried out under inert conditions. Consequently, simple recycling and use in continuous processes are possible.

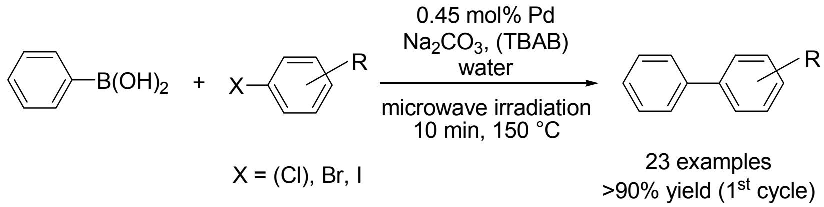

Fig. 1. Reaction scheme of the Suzuki–Miyaura cross-coupling reaction with Pd/porous glass catalysts [11].

The reaction cycle for homogeneous catalysis is initiated by an oxidative addition of an organic halide (R–X) to active Pd(0) species, generating reactive Pd(II). After a transmetallation step between R–Pd–X (X – leaving group like halides) and the boron compound (R'–$B(OR'')_2$), reductive elimination leads to the formation of a new σ–C–C bond (R–R′). Interestingly, in literature several studies can be found, applying also Pd(II) as active species in heterogeneous catalysis [12–14].

First investigations in this field of catalysis applying porous glasses as a support for heterogeneous Pd-catalysts were disclosed in 2005, cross-coupling of *p*-bromophenol and phenylboronic acid in water yielded 4-hydroxybiphenyl [15]. Utilizing glass with a pore size of 50 nm, particle size ranging from 100–200 µm, and a Pd-loading of 2 wt%, yields of >90% were achieved within 10 min irradiation with microwaves at 150 °C. As a basic promoter Na_2CO_3 was applied. Based on these results, further parameters like calcination temperature, influence of bases as well as glass properties and catalyst loading were examined [11]. Figure 2 shows a typical SEM-image of a Pd-catalyst on a porous glass support [16]. On the left-hand side the macroporous structure of the glass carrier is shown as well as the widely scattered Pd particles (white dots). With a higher resolution it became clear that the Pd particle size ranges from several nanometers to agglomerates of nearly 100 nm in diameter.

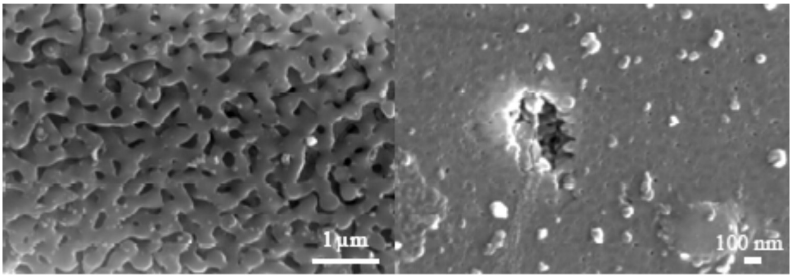

Fig. 2. SEM-micrographs of Pd on porous glass [16].

Regarding the Suzuki–Miyaura cross-coupling [11], it was demon-strated that the calcination step (used for catalyst preparation) had an influence on the catalytic activity. Low calcination temperatures (200 °C) and times (1 h) independently decreased the activity due to incomplete decomposition of the $Pd(OAc)_2$-precursor. On the other hand, high temperatures and long calcination times also lowered the yield of the reaction product. Sintering processes of the porous network result in a reduced surface area and, thus lower activity. Ideal conditions were identified: 300 °C and 2 h as calcination temperature and time, respectively. Regarding the influence of bases, inorganic ones (Na_2CO_3, KF, K_3PO_4) and organic (NaOAc, NEt_3, $HNEt_2$), full conversion could be achieved under the applied conditions (microwave heating, $T = 150$ °C, $t = 10$ min), but in recycling experiments organic bases showed disadvantages due to catalyst poisoning. Except for reactions with ammonia, the catalysts could be reactivated by cleaning with iodine/ethanol or thermal treatment (300 °C, 2 h). Employing Na_2CO_3, the catalyst showed such a high activity that the Pd-loading could be reduced to 0.25 wt% maintaining quantitative yields. Thus, catalysts were designed allowing up to 3450 turnovers during four reaction cycles with no decrease in conversion or product selectivity. Additionally to the described catalysts (Pd on porous glass support A), two glasses with different pore sizes and specific surface areas were applied as supports (see Table 1). It was shown that larger pore sizes inhibit

Table 1. Properties of porous glasses used as support material in heterogeneously-catalyzed Suzuki–Miyaura reaction [11].

Support	Particle size [µm]	Pore size [nm]	Specific surface area [m^2g^{-1}]
A	1250	45	85
B	800–2500	173	20
C	800–2500	300	14

deactivation processes caused by *N*-poisoning (NEt_3 as base), and furthermore reactivation was more effective, since larger pores could be cleaned more easily [11].

Finally a variety of substrates was tested in the Suzuki–Miyaura reaction (Fig. 1) containing aromatic compounds with OH-, Me-, MeO-, or NO_2-functions at either *ortho*-, *meta*-, or *para*-position. Additionally to the reaction conditions applied in case of *para*-bromophenol (deprotonation to water-soluble phenolate) and phenylboronic acid, phase transfer catalyst tetrabutylammonium bromide (TBAB) was necessary for substrates which are not able to be deprotonated by the base. In each case the catalyst was recycled and reused for another three trials. The majority of substrates yielded quantitatively the cross-coupling products and almost no deactivation was noticed. Aryl bromide and iodide proved to be very suitable substrates, whereas chlorides poorly reacted with boronic acid compounds. Also amine or aldehyde containing substrates were not suitable independent of which coupling agent they were attached to (aryl halide or boronic acid). Beside phenylboronic acid (Fig. 1) other organoboron reagents, *i.e.*, boronic acid esters or potassium phenyltrifluoroborate, have also been tested successfully [11].

2.2. Mizoroki–Heck cross-coupling

Another important C–C cross-coupling reaction carried out with Pd on porous glass catalysts is the Mizoroki–Heck reaction [11, 17]. In this example activated alkenes react with aryl halides to the corresponding arylalkenes (Fig. 3) [18].

The use of heterogeneous catalysts allows a ligand-free, air- and water-tolerant reaction as well as an ease of separation. Li *et al.* investigated this reaction under microwave-assisted and conventional heating conditions employing porous glass tubing (specific surface area: 250 m^2g^{-1}, 28% porosity) loaded with just 0.18 wt% Pd [17].

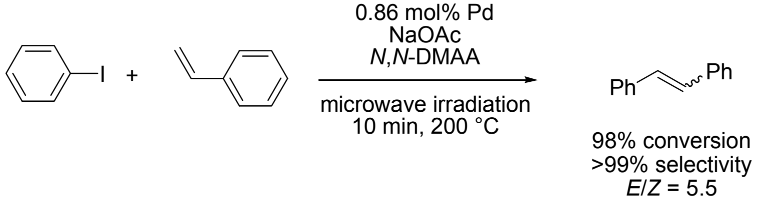

Fig. 3. Mizoroki–Heck cross-coupling reaction using Pd/porous glass particles as heterogeneous catalyst [11].

Experiments were carried out at elevated temperature (100–180 °C) in *N*,*N*-dimethylacetamide (DMAA). Best results were obtained with iodobenzene and styrene (Fig. 3) or allyl alcohol, respectively, under microwave-assisted conditions (full conversion in 1.5 or 3 h, respectively; conventional heating >100 h). The microwave-assisted coupling reaction between iodobenzene and styrene was investigated intensively, varying reaction time, temperature, basic additives, and solvents [11]. Experiments in the range of 150–200 °C showed higher conversion with increasing temperature, but lowered the selectivity towards *E*/*Z*-stilbene with increasing reaction time from 10 to 30 min. A reason is the formation of byproducts like 1,1-diphenylethene. Best results were found at 200 °C for 10 min (98% conversion, >99% selectivity). Regarding the *E*/*Z* ratio, values in the range of 4.9–6.8 were observed, clearly displaying a favored formation of the *E*-isomer. In the case of solvents and bases, DMAA as well as *N*,*N*-dimethylformamide were well suited in combination with organic bases like NaOAc or NEt_3. In these cases almost quantitative yields were obtained. Inorganic alkali bases (Na_2CO_3, LiF, NaF, KF, CsF) showed poor yields in the range of 10–49% due to low basicity. Solely K_3PO_4 was able to produce the desired product quantitatively. In solvents like acetonitrile, $NHMe_2$, H_2O or EtOH no reaction took place or unsatisfying results were achieved (yield <20%). Contrarily to the application of the catalyst in the Suzuki–Miyaura cross-coupling (Fig. 1), recycling experiments in the Mizoroki–Heck reaction (Fig. 3) were unsuccessful; probably due to the necessity for utilization of N-containing bases and solvents [11].

3. Application in hydrogenation reactions

One of the most important reaction-steps in industrial chemistry is the hydrogenation of unsaturated compounds. Typical applications are hardening of triglycerides and production of pharmaceuticals, nutritions, flavors or fragrances. Since molecular hydrogen is a cheap reducing agent and minimizes waste, its use is beneficial especially in large scale applications. On the other hand, due to the high dissociation enthalpy of the H_2 molecule ($\Delta_{\mathrm{diss}}H^0 = 434\ \mathrm{kJ\ mol^{-1}}$) thermal cleavage of the H–H bond requires temperatures >1000 °C, a value that is not affordable from energetic point of view. Furthermore, at these temperatures dehydrogenation processes already are initiated, resulting in a switched equilibrium and thus low yields. To avoid this significant disadvantage, catalytic active metal surfaces are needed. Recent research focuses on low-priced catalysts that can be prepared by simple procedures. Porous glass support catalysts with transition metals as active species, prepared by wet-impregnation technique provide thermal and chemical stability, large specific surface area, and narrow pore size distribution. High dispersion of the active metal centers leads to reactive catalysts, consequently only little amounts of expensive transition metal are necessary.

First investigations in the field of hydrogenation using porous glasses as support material for heterogeneous catalysts were carried out in the late 1970s [19]. Pt-, Pd-, or Ni-coated porous glasses were used to hydrogenate hydrocarbons, *e.g.*, benzene,

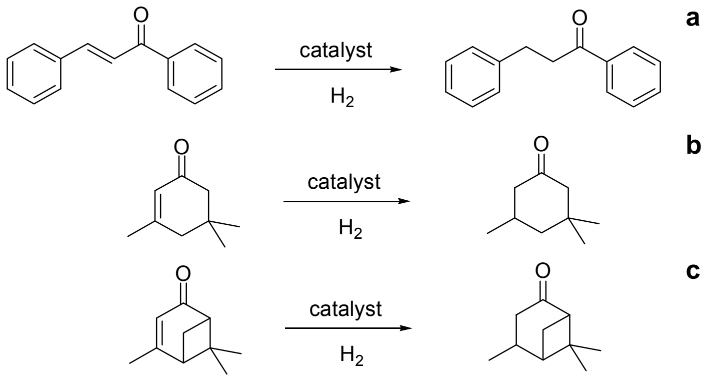

Fig. 4. Main product of the hydrogenation of benzalacetophenone (**a**), isophorone (**b**), and verbenone (**c**).

styrene, and cyclohexene in the gas phase. In case of styrene hydrogenation, microporous glasses (pore size = 0.4–1.1 nm, specific surface area = 265–300 m^2g^{-1}) showed structure-selective catalytic effects, which resulted in a preference for side-chain hydrogenation affording ethylbenzene. The importance of critical pore diameter amenable solely to similar sized molecules and molecular fragments was also shown in other studies [20]. It is reported that the dispersion of active metal species as well as the reaction rate are proportional to the specific surface area of the glass carrier [21]. However, in contrast to zeolites [22], a decrease in micropore size (< 1 nm) resulted in a shape selective hydrogenation of rather branched than linear olefins over porous glass supported Ni-catalysts [23].

Using commercially available macroporous glasses (pore size = 50 nm) as a support for Pd-catalysts, Freitag *et al.* investigated the chemoselective hydrogenation of α, β-unsaturated ketones (benzalacetophenone and isophorone; *cf.* Fig. 4) under mild reaction conditions (room temperature, atmospheric pressure) [15]. In both cases the carbonyl function was not or just slightly hydrogenated, respectively. Based on these results, further investigations of similar Pd/porous glass support catalysts in hydrogenation reactions were carried out [24]. Using X-ray photoelectron spectroscopy (XPS), *in-situ* reduction of the Pd-nanoparticles at the beginning of the hydrogenation experiments could be demonstrated by a shift in binding energy of the Pd 3*d*-electrons to lower values during the reaction. Thus, the reduction step prior to reaction was unnecessary. A multitude of industrially important building blocks (*e.g.*, aniline, 4-(4-hydroxyphenyl)butan-2-one ("raspberry ketone"), terpenes) could be obtained in high yields by hydrogenation of C–C, C–N or N–N double bonds [24–27]. No reduction of carbonyl or aromatic double bonds could be detected under the mild conditions applied. In a study by Stolle *et al.* the influence of catalytic active metal, support material (type of porous glass), solvent, and reaction conditions (T, $p(H_2)$) on the liquid-phase hydrogenation of benzalacetophenone was investigated (Fig. 4) [16]. Therefore, three different setups covering a wide range of reaction conditions, *i.e.*, for reactions: *i*) at room temperature and atmospheric pressure a shaking apparatus, *ii*) at slightly increased conditions ($T \leq 50$ °C, $p(H_2) \leq 0.8$ MPa) a microwave apparatus, and *iii*) at pressures up to 5.0 MPa and room temperature stainless steel autoclaves were applied. Furthermore, the active metal was varied to examine the influence on the chemically different double bonds (carbonyl, conjugated C–C double bond, aromatic C–C double bond). Several porous glasses as well as alumina or silica were used as support materials. Pd-coated support materials with similar physical properties, *i.e.*, pore size, particle diameter, specific surface area and pore volume, provided similar catalytic activity. Moreover, it was assumed that increased particle size in conjunction to lowered specific surface area leads to decreased mass transport and metal dispersion, which was in good agreement with the observed results. The polarity of the solvent had a direct influence on the reaction rate, since more polar solvents own a higher hydrogen absorption capacity. Consequently, in ethyl acetate, acetone, or alcohols (ethanol, methanol, 2-propanol) full conversion within 210 min was obtained [16]. Variation of the active metal species led to interesting results. Under mild conditions only catalysts based on Pd, Pd–Ce, and Pt showed activity, whereas at elevated T and $p(H_2)$ also Rh could be used as active metal. At 50 °C and 0.8 MPa full conversion as obtained with all catalysts except of Pd on porous glass, which was prepared using $PdCl_2$ as precursor. Here, halide traces block the active centers. With respect to the selectivity, only Pt and Rh catalysts were able to reduce the carbonyl function beside the conjugated double bond, while Pd and the bimetallic Pd–Ce solely hydrogenated the latter functionality [16].

Porous glass-based supported catalysts were also employed in microwave-assisted hydrogenations. Using this alternative heating method, liquid-phase hydrogenation of benzalacetophenone (Fig. 4**a**) [16], verbenone (Fig. 4**c**) [6], diphenylacetylene [6] and citral (Fig. 5) [6, 28] was studied. Each of these substrates is an important starting material in the synthesis of fine chemicals, but parallel and consecutive reaction paths require high selectivity towards the desired products. Regarding verbenone, a terpenoid with a C–C double bond in conjugation to a carbonyl function, the choice of the catalyst metal as well as the precursor had a major influence on product distribution [6]. The catalytic activity increased in the following order: Pd < Rh < Pt. It was also demonstrated that chloride containing precursors ($PdCl_2$, $RhCl_3 \times H_2O$) had a negative influence on the activity [6], shown in hydrogenation of benzalacetophenone as well [16]. While Pt and Rh (precursor $Rh(acac)_3$) on porous glass enabled the hydrogenation of the carbonyl group, Pd and Rh (precursor: $RhCl_3 \times H_2O$) were less active resulting in a chemoselective hydrogenation to the saturated ketone verbanone.

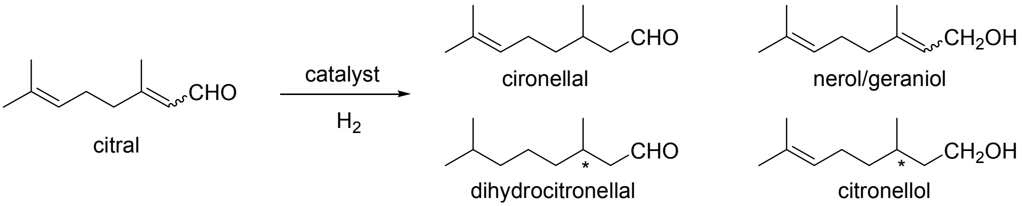

Fig. 5. Possible target products originating from hydrogenation of citral.

Interestingly, almost no difference in product distribution could be obtained by increasing the tem-perature from 25 to 50 °C at 0.8 MPa [6].

The hydrogenation of citral (Fig. 5) is more challenging, since this α, β-unsaturated aldehyde has an additional isolated C–C double bond beside the conjugated C=C–C=O system. Thus, catalysts have to selectively reduce either the conjugated C–C double bond or the carbonyl function yielding citronellal or unsaturated alcohols nerol and geraniol, respectively. On the other hand, the catalytic system has to prevent further hydrogenation to the less valuable compounds dihydrocitronellal or citronellol [29, 30]. Using metal-loaded porous glasses as catalysts in combination with microwave--assisted heating, Pd was identified as the most active metal and not even Pt was able to form the alcohol at 50 °C and 0.8 MPa [6]. Beside citronellal considerable amounts of the consecutive reaction product dihydrocitronellal were found (Fig. 5). Since citronellal is a very important compound, selectivity enhancement by the addition of ionic liquids was tested [28–31]. By *in-situ* formation of SCILL (solid catalyst with ionic liquid layer) catalysts, an additional phase was attached to the catalyst, which is able to influence the selectivity by a changed solubility of substrates and products [31]. Unfortunately, a loss in activity was connected with the addition of ionic liquid. Especially 1-ethyl-3-methylimidazolium acetate [C2mim][OAc], 1-ethyl-3-methylimidazolium trifluoroacetate [C2mim][TfOAc], and 1-butyl-3-methylimidazolium acetate [C4mim][OAc] proved to increase the selectivity towards citronellal [28]. Further experiments with separately prepared SCILL catalysts coated with either [C2mim][OAc] or the corresponding dicyanamide [C2mim][DCA] led to a very high citronellal selectivity (95%).

4. Conclusions

Porous glasses are interesting materials with a broad field of application, reaching from dental application over adsorption membranes to catalyst support material. Looking for tunable, well-defined materials that offer high specific surface area, narrow pore size distribution as well as chemically and thermal stability, porous glasses can be advantageous alternatives to conventional support materials like silica or alumina. Due to the production process, tailor-made properties can be generated. This feature as well as the possibility of shaping the glass allows customized usage in catalytic systems. The choice of pore size for instance may lead to structure-selective reactions or, considering macropores, to employment in continuous processes. Furthermore, the applicability in microwave-assisted organic syntheses and recent catalyst concepts, *e.g.*, SCILL catalysts, was investigated.

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