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Hydrophobicity in nanocatalysis

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Abstract. Nanocatalysts are usually used in the synthesis of petrochemical products, fine chemicals, biofuel production, and automotive exhaust catalysis. Due to high activity and stability, recyclability, and cost-effectiveness, nanocatalysts are a key area in green chemistry. On the other hand, water as a common by-product or undesired element in a range of nanocatalyzed processes may be promoting the deactivation of catalytic systems. The advancement in the field of hydrophobicity in nanocatalysis could relatively solves these problems and improves the efficiency and recyclability of nanocatalysts. Some recent developments in the synthesis of novel nanocatalysts with tunable hydrophilic-hydrophobic character have been reviewed in this article and followed by highlighting their use in catalyzing several processes such as glycerolysis, Fenton, oxidation, reduction, ketalization, and hydrodesulfurization. Zeolites, carbon materials, modified silicas, surfactant-ligands, and polymers are the basic components in the controlling hydrophobicity of new nanocatalysts. Various characterization methods such as N2 adsorption-desorption, scanning and transmission electron microscopy, and contact angle measurement are critical in the understanding of hydrophobicity of materials. Also, in this review, it has been shown that how the hydrophobicity of nanocatalyst is affected by its structure, textural properties, and surface acidity, and discuss the important factors in designing catalysts with high efficiency and recyclability. It is useful for chemists and chemical engineers who are concerned with designing novel types of nanocatalysts with high activity and recyclability for environmentally friendly applications.

Keywords: carbon material; hydrophobicity; nanocatalyst; silica; zeolite

1. Introduction

Catalysis is a central discipline in fine (Bonrath *et al.* 2021) and bulk chemicals industries (Benvenuto and Plaumann 2021) and also in the green chemical field (Sáenz-Galindo *et al.* 2020). Catalysis as the backbone of the petroleum industries, production of fertilizers, and emission control systems for automobiles, is the Achilles heel in the modern national economy (Hagen 2015). Because of the growing request for designing chemical processes with high yield and selectivity, waste reduction (or prevention), less energy consumption, and use of sustainable conditions, a lot of consideration has been absorbed to optimizing the functioning conditions (factors of process engineering) and developing catalysts with enhanced yield and selectivity (Beeckman 2020).

In the recent three decades, with the revolution in the synthesis and characterization of nanomaterials, especially nanoparticles and nanoporous materials, nanocatalysis has obviously appeared as a field at the border between homogeneous and heterogeneous catalytic systems, which propose inimitable answers to search optimized conditions for catalyst development (Calvino-Casilda *et al.* 2019). Major attention is paid to improve modern catalysts, which may contain both metal/metal oxide nanoparticles and a nanostructured surface as support. It is expected these nanocatalysts demonstrate the following benefits of both heterogeneous and homogenous systems, such as high yield and selectivity, chemical and thermal stability, and easy separation and reusing. Along this line, understanding the size effect constitutes a crucial challenge in the mainstream of nanocatalyst research context (Rodrigues *et al.* 2019).

Catalysts especially transition metal-based ones are generally hydrophilic, due to the hydrophilic character of supports (e.g., silica, titania, and alumina), the hydroxyl groups on their surfaces, and lewis acidity of the catalytic center (Liu *et al.* 2018). Water, either as solvent, impurity, or by-product can be adsorbed on hydrophilic catalytic center or supports resulted in the partial deactivation of the catalyst, ejection of hydrophobic reactants, or the hydrolysis of frameworks (Gholami *et al.* 2015, Gayubo *et al.* 2002, Wolf *et al.* 2020, and Prašnikar *et al.* 2019). Accordingly, lipophilization of metal oxides, functionalization of lipophilic polymer, remove of acidic hydroxyl groups and use of carbon material and perfluoro-based surfactant have appeared as exceedingly important tools for hydrophobization of catalysts (Cavuoto *et al.* 2020). Consequently, it is theorized that catalysts with appropriate hydrophobicity may have further improved the adsorption of lipophilic reagents and desorption of hydrophilic reagents and water, which considerably improve stability and recyclability, and catalytic efficiency in many processes containing organic reagents (Cavuoto *et al.* 2020). The challenge is to advance new methods for the plan and preparation of high-performance nanocatalysts with tunable surface wettability, via correlating their morphology with hydrophobicity so as to recognize the essential principles of

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hydrophobicity in nanocatalysts.

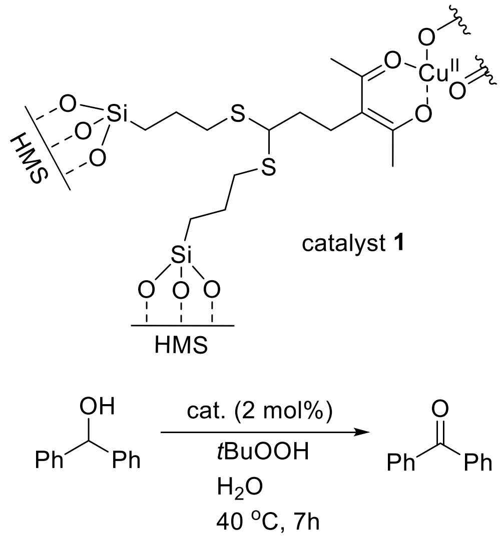
The primary basis of this review is based on the material backbones including zeolite, nanosilica, organic polymer, and carbon nanomaterials. Additionally, it is our goal to demonstrate nanocatalyst preparation methods and highlight publications in this field. Furthermore, due to the large number of reports in this area, we focused mainly on the latest publications from 2016 until 2021 especially on non-electrocatalytic systems applied in synthetic processes or environmental catalysis.

2. Tunning hydrophobicity in nanocatalysts

2.1 Silica

Silicas especially silica nanomaterials, due to high surface area, biocompatibility and stability, are broadly employed in solid catalysis mostly as support for metal species such as metal complexes and nanoparticles (Singh *et al*. 2020). The number of silanol groups (Si-OH) affects the silica surface hydrophilicity and water adsorption. However, a high silanol density on the silica surface can be resulted in high wettability and poor hydrothermal stability via hydrolysis of the siloxane (Si-O-Si) bonds (Blin *et al*. 2019). In order to improve the hydrothermal stability of silica, silanol density can be reduced by functionalization, mainly with alkoxysilanes, to increase the surface (Jadhav *et al*. 2015).

In 1995, Tanev and Pinnavaia synthesized a slightly disordered mesoporous silica material, the so-called Hexagonal Mesoporous Silica (HMS) by using neutral amine as a structure-directing agent (Tanev and Pinnavia 1995). Due to the advantages of HMS such as hydrothermal stability and relative affordability the use of this mesoporous silica as catalyst support has received increasing attention in recent years (Gholamian and Hajjami 2019, Macina *et al*. 2017). Also, the grafting or co-condensation techniques by suitable trialkoxysilane substances can also be applied to functionalize HMS for special goals such as immobilization of transition metals ions and nanoparticles. These immobilized metal complexes or nanoparticles have been then used in numerous metal-catalyzed reactions. In 2016, Lai and coworkers reported the synthesis of acetylacetone-modified HMS with mercaptopropyltrimethoxysilane and 2-butoxy-3,4-dihydropyran followed by complexation with copper acetylacetonate Cu(acac)$_2$ to give catalyst **1** (Lai *et al*. 2016). The final catalyst was prepared by the coating of catalyst **1** with ionic liquid 1-Octyl-3-Methylimidazolium Bis(trifluoromethanesulfonyl)imide ([OMIm]NTf$_2$) to give catalyst **2**. This material was a highly active catalyst in the oxidation of benzhydrol in comparison with the catalyst not containing ionic liquid (Scheme 1). Due to the hydrophobicity of [OMIm]NTf$_2$ with long alkyl tail and a hydrophobic anion (Avilés *et al*. 2020), this process, which was performed in water, can be accelerated by a hydrophobic layer made by loading [OMIm]NTf$_2$ onto the catalyst. The reusing study of catalyst **2** has also been effectively performed for three runs.

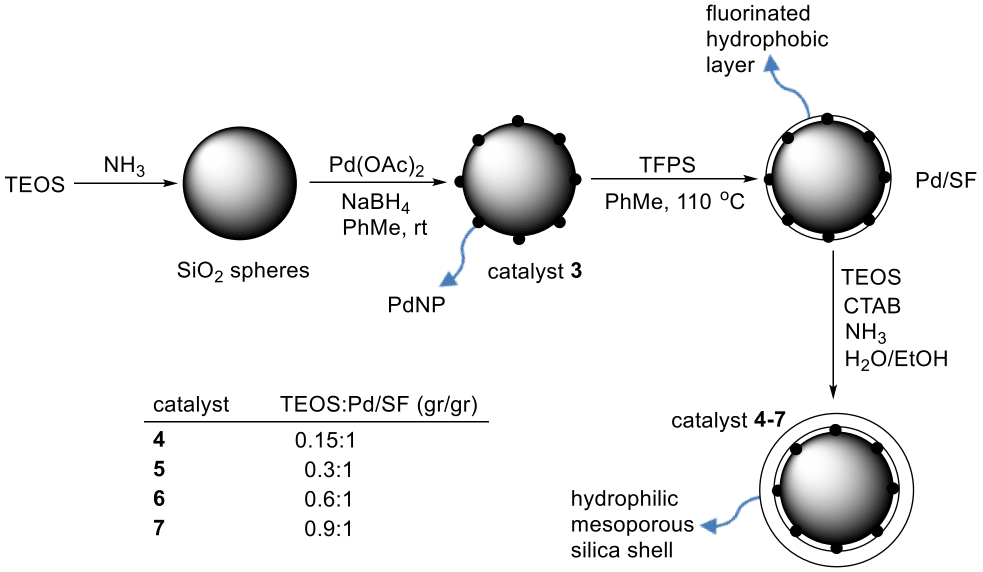


cat.	yield (%)
catalyst **1**	14
catalyst **2**	99

Scheme 1 HMS-supported copper-catalyzed oxidation of benzhydrol

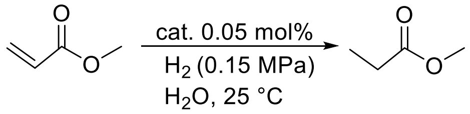
In 2017, in a study reported by Hao et al., the synthesis of onion-like nanomaterial has been described (Hao *et al*. 2017). This layered nanostructure has been fabricated through immobilization of 5-8 nm palladium nanoparticles PdNPs on the surface of the 140-170 nm SiO$_2$ spheres (catalyst **3** followed by hydrophobization with 3,3,3-Trifluoropropyltrimethoxysilane (Pd/SF) and growing a hydrophilic CTAB-templated nanoporous silica layer around its surface by sol-gel polymerization of tetraethoxysilane (TEOS) to give catalyst **4**-**7** with BET surface area up to 392 m^2/g (Scheme 2). In this work, the silica shell thickness and hydrophilic-hydrophobic character of the Pd/SF@NS were precisely controlled by changing the ratio of TEOS to Pd/SF. Catalytic efficiency (CE) of Pd/SF and Pd/SF@NS was studied in the hydrogenation of alkyl acrylates at ambient H$_2$ pressure in water (Scheme 3). It has also been proved that the presence of fluorinated hydrophobic layer and thickness of SiO$_2$ shell affords an optimum balance between hydrophilicity and hydrophobicity; as a result, hydrophobic layer on catalyst **4**-**7** is helpful to adsorb the organic reagents and dispersibility of catalyst in the aqueous phase can be tuned via varying the SiO$_2$ shell thickness. Finally, optimization of hydrophilicity/hydrophobicity in catalyst **5**, has been resulted in the best catalytic efficiency for the hydrogenation in water.

Zhang *et al*. (2017) prepared nanoporous perfluoroalkyl-sulfonylimide-functionalized acidic silica (Scheme 4) by copolymerization of 4-styrenesulfonyl(perfluoroalkyl-sulfonyl)imide with 3-(trimethoxysilyl)propyl methacrylate followed by sol-gel condensation with TEOS and MeSi (OMe)$_3$. Mesoporous perfluoromethyl-sulfonylimide-functionalized silica (catalyst **8**) and Microporous perfluorobutylsulfonylimide-functionalized silica (catalyst **9**) were considered as alternative candidates for SO$_3$H-



catalyst	TEOS:Pd/SF (gr/gr)
4	0.15:1
5	0.3:1
6	0.6:1
7	0.9:1

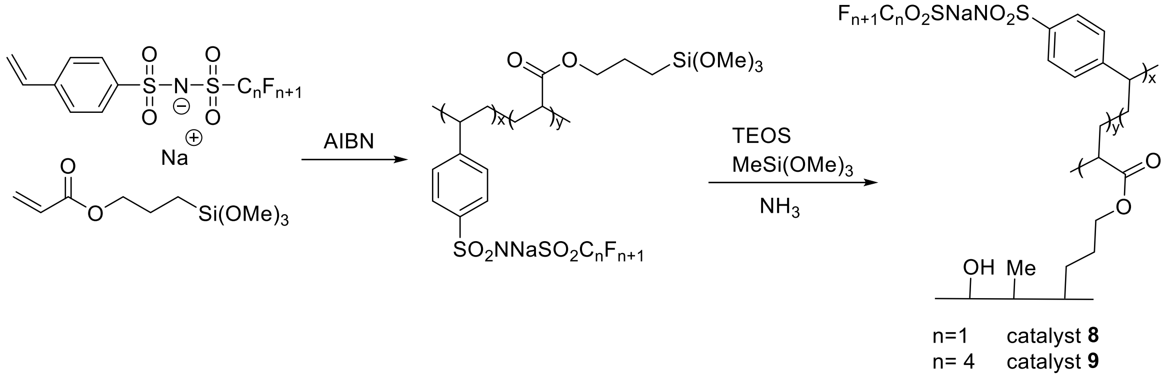
Scheme 2 Synthesis of onion-like catalyst 4-7



cat.	CE (mol/mol.h)
catalyst **3**	399.3
catalyst **4**	560.3
catalyst **5**	631.8
catalyst **6**	502.9
catalyst **7**	449.8

CE: Catalytic Efficiency (converted reactant mole per Pd mole per hour)

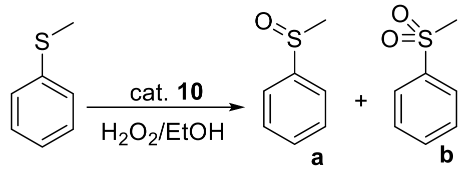
Scheme 3 efficiency of catalyst 3-7 in the hydrogenation of methyl acrylate



Scheme 4 Preparation of nanoporous perfluoroalkylsulfonylimide-functionalized acidic silica

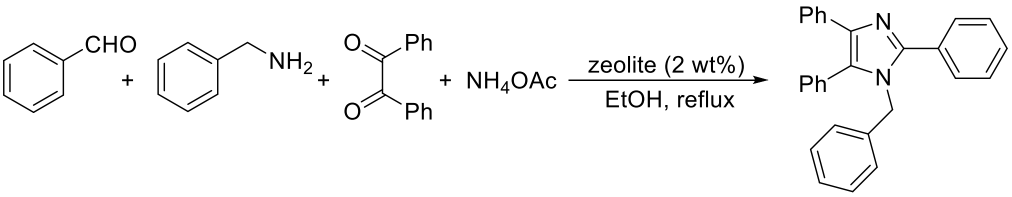
containing solid acid due to their strong acidity and water stability. Lipophilicity of methyl group from MeSi(OMe)$_3$, the water-repellent effect of perfluoroalkyl group, and isolate water molecules from acid sites in catalysts **8** and **9** were led to the application as an acid catalyst in catalytic fructose dehydration to 5-hydroxy- methylfurfural.

In 2018, Cruz *et al.* (2019) introduced recoverable Ti-based catalysts for the selective oxidation of thioanisole with hydrogen peroxide at room temperature. These hydrophobic catalysts (BET surface area, 738-807 m^2g^{-1}) was prepared through lipophilization of 90 nm-sized mesoporous silica nanoparticles (MSN) with 881 m^2g^{-1} BET surface area by hexamethyldisilazane (HMDS) followed by immobilization of titanium complexes such as



cat. (mol%)	time (min)	temp. (°C)	conversion (%)	a	b
0.75	5	r.t.	98	99	1
0.5	120	50	100	1	99

Scheme 5 Ti-catalyzed selective oxidation of thioanisole



zeolite	Si/Al	time (min)	surface area ($m^2.g^{-1}$)	yield (%)
H-BEA	12	60	680	86
H-BEA	15	60	710	95
H-BEA	25	60	732	83
H-BEA	34	60	750	75
H-Y	2.43	165	480	83
H-MOR	11	140	412	80
H-ZSM-5	15	165	320	70

Scheme 6 zeolite-catalyzed synthesis of 1-benzyl-2,4,5-triphenyl-1H-imidazole

$Ti(O^iPr)_4$, $TiCpCl_3$ or $TiO(acac)_2$. An increase in surface hydrophobicity by the protection of silanol groups with HMDS enhanced the diffusion of lipophilic reagents to the titanium centers supported on the MSN surface. The catalytic performance of lipophilic MSN-supported $TiCpCl_3$ (catalyst **10**) has been summarized in Scheme 5.

Hydrophobic core-shell based methyl modified $Fe_2O_3@SiO_2$ nanocatalysts were prepared through the solvent thermal method, Stöber process, followed by hydrophobization with chlorotrimethylsilane, where the silica coat was used as a bridge contacting Fe_2O_3 core and hydrophobic groups of methyl to achieve a highly hydrophobic surface of Fe_2O_3-based catalyst (Yu *et al.* 2018, Xu *et al.* 2021). These nanocatalysts showed high efficiency in Fischer-Tropsch synthesis for CO hydrogenation with very low CO_2 selectivity due to the prevention of readsorption of water.

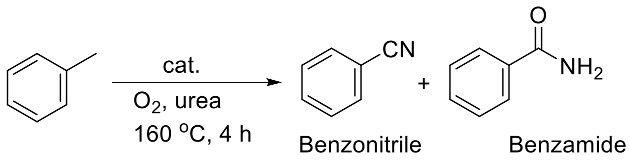
In a similar way, a super-hydrophobic titanosilicate nanosphere was prepared by coating a layered organo-titanosilicate onto a hydrophobic silica sphere. The resulted materials show high catalytic efficiency in cyclohexene epoxidation at near ambient temperature using hydrogen peroxide (Li *et al.* 2019).

2.2 Zeolite and metal-organic frameworks

Zeolites are one of the most known green nanomaterials in catalysis (Bukhtiyarova and Echevsky 2019, Tan *et al.* 2021), membranes, and separation processes (Rashed and Palanisamy 2018). In these aluminosilicate shape-selective and ion-exchangeable materials, physical and chemical properties were precisely controlled by tuning Si/Al ratio. Usually, both of Brønsted and Lewis acidity in zeolites increases with dealumination but dealumination of zeolites or increase of Al/Si ratios usually resulted in hydrothermal instability (Auepattana-aumrung *et al.* 2020). Surface hydrophobization of zeolite decrease absorption of water and prevents dealumination, resulted in increasing the catalyst stability (Hosseiniamoli *et al.* 2020, Fawaz *et al.* 2019) and the affinity with lipophilic reagents (Dinh *et al.* 2018).

Various zeolites H-ZSM-5, H-BEA, H-Y, and H-MOR have been used by Galba and coworkers in the one-pot, 4-component synthesis of 1-benzyl-2,4,5-triphenyl-1H-imidazoles by benzil, NH_4OAc, benzaldehydes, and benzylamine (Galba *et al.* 2017). An important feature of these zeolites is that the hydrophobic property of H-BEA because of the higher Si/Al ratio versus the other zeolites resulted in the better catalytic performance in ethanol (Scheme 6). In this study, it appears that low to moderate acidity (hydrophobicity), as well as higher surface area and Si/Al ratio of H-BEA, are key reasons for better catalytic performance.

Wang and co-workers synthesized manganese oxide fixed inside the S-1 zeolite crystals (catalyst **11**) by grinding a mixture of tetrapropylammonium hydroxide (TPAOH) and SiO_2-MnO_x composite, followed by thermal treatment at 180°C and calcination (Wang *et al.* 2017). Also, SiO_2-MnO_x composite was synthesized by impregnation of silica nanoparticles with $Mn(NO_3)_2$, NH_4NO_3, and NH_4OH



	yield %	
cat.	Benzonitrile	Benzamide
11	88.6	1
12	4.5	84.1

Scheme 7 Catalytic oxidative cyanation of toluene to benzonitrile

followed by reduction at 400°C by H_2-N_2 flow. Selective oxidative cyanation of toluene to benzonitrile was performed using this efficient catalyst by urea at 160°C. Due to the hydrophobic nature of micropores in S-1 zeolite, the diffusion of organic substrate and nitrile product is more favorable than the diffusion of water, which prevents the side reaction of nitrile hydration to benzamide, leading to high efficiency for producing benzonitrile (Scheme 7). Notably, the benzonitrile yield is extremely low (4.5%) over catalyst including MnO_x particles supported on the external surface of S-1 zeolite (catalyst **12**). Also according to the temperature-programmed desorption (TPD) analysis, catalyst **11** displayed relatively high toluene desorption temperature (200°C) and low water desorption temperature (117°C) that indicates the hydrophobicity of catalyst **11**.

Owing to the hydrophobicity of S-1, a core-shell-based catalyst containing ultrasmall palladium oxide nanoparticles anchored in silicalite-1 (Pd@S-1) was designed for methane combustion (Wang *et al.* 2020). Because of the hydrophobicity of S-1 compared to other zeolites, Pd@S-1 could efficiently prevent the diffusion of water vapor into the nanoparticle surface, aimed to the excellent water stability. In 2019, Javed and co-workers prepared a ZSM-5 anchored Fe-based microcapsule catalyst coated by S-1 shell. Growing S-1 shell thickness, increased hydrophobicity of heterogeneous catalyst's surface, leading to a promising performance in water-gas shift reaction, and favorable way to control unwanted carbon dioxide selectivity over Fischer-Tropsch catalysts.

Hydrophobicity/hydrophilicity degree are also significant in the catalytic performance of the Ti-zeolite-based catalysts. The destruction and recrystallization technique was investigated to synthesis Ti-Beta zeolite by Wang and co-workers (Wang *et al.* 2019a). Ti-Beta-Re zeolite included the deconstruction of the dealuminated Beta framework with the lower amount of silanol groups that provided higher catalytic activity for the epoxidation of cyclohexene with hydrogen peroxide in acetonitrile.

In 2018, Jin *et al.* (2018) synthesized Y zeolite by anchoring methyl groups into faujasite framework through the crystallization, attaining hydrophobic micropores for selective absorption of organic molecules but preventing H_2O diffusion. Further anchoring of titania particles in this zeolite led to core-shell catalysts that joint the functions of both wettability and selectivity for the zeolite and TiO_2 photocatalyst. Because of the synergistic effect of these functions, this hydrophobic catalyst exhibited superior efficiency in the photodegradation of wet formaldehyde with relative humidity.

Jin and co-workers (2020) have continued their studies on the solid catalyst system for improved methanol yield and selectivity in methane oxidation by in situ produced H_2O_2 at 70°C. The catalyst was prepared by anchoring 3-9 nm-sized AuPd nanoparticles within ZSM-5 zeolite, followed by tailoring hydrophobicity of the external surface of ZSM-5 by the post-silylation method. The organosilanes seem to permit diffusion of H_2, O_2, and CH_4 to the zeolite pores, while confining the in situ produced H_2O_2 there to increase its reaction efficiency.

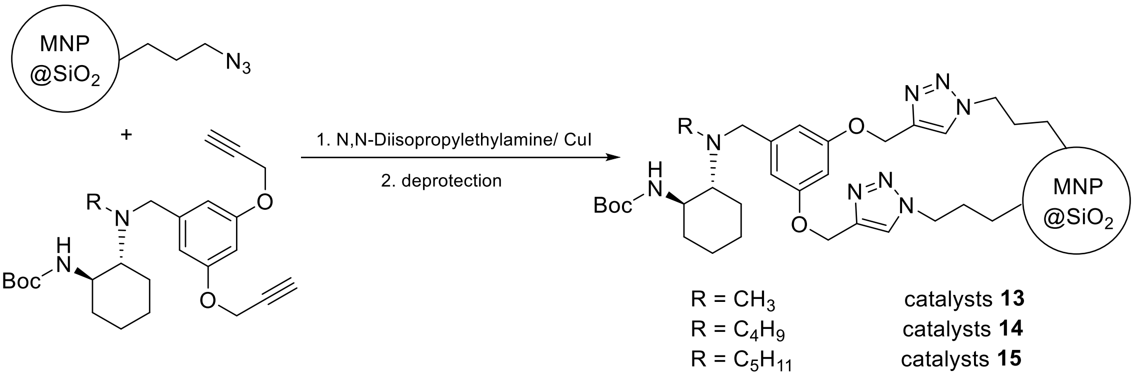
In 2020 Li *et al.* (2020) described a method for modifying the zeolite Y-supported Cu(I) microenvironment from hydrophilic to superhydrophobic by polydimethylsiloxane coating. This superhydrophobic material prevents H_2O adsorbing the micropores and consequently stabilizes the metal centers. The data exhibited that this metal catalyst is stable in highly humid conditions and shows outstanding adsorption desulfurization ability for water-including model fuel.

Metal-organic frameworks (MOFs) that are zeolite-like materials have been known as an important candidate for many uses such as catalysis (Dandan *et al.* 2019). One of the most attractive fields in MOFs is tuning their hydrophobicity by the introduction of various organic linkers. Oozeerally and coworkers (2021) conducted the preparation of UiO-66 by Naphthalene-dicarboxylate linkers to induce hydrophobicity. This catalyst improves the reaction selectivity in the isomerisation of glucose towards fructose by enhancing the hydrophobicity of the UiO-66 framework.

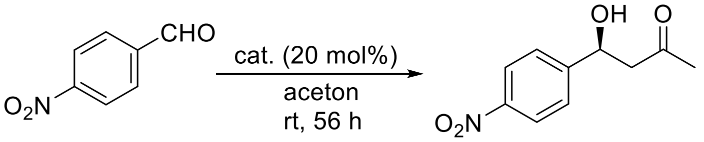
2.3 Magnetic nanoparticles

In recent two decades, remarkable attempts have been made in the improvement of synthesis and use of magnetic nanoparticles (MNPs), in various fields (Ince *et al.* 2021, Girgis *et al.* 2015, Kurtinaitienė *et al.* 2016). A wide range of synthesis conditions, and surface functionalization of MNPs are reported for tuning their size, shape, stability, physicochemical properties, and their biological performance (Evgeny 2020).

In 2019, Esmaeilnezhad and co-workers prepared 80 nm oleylamine coated magnetic iron oxide nanoparticles by

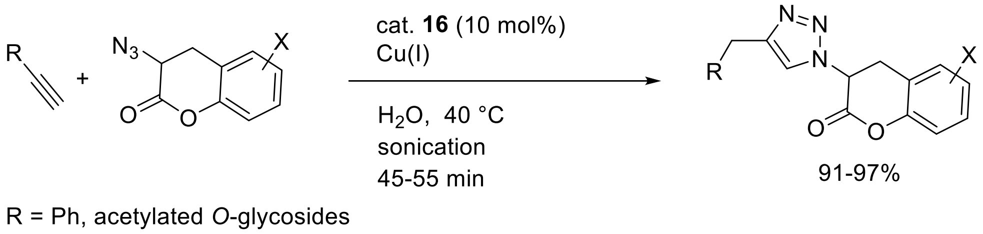


Scheme 8 Synthesis of silica-coated magnetic nanoparticles-based chiral cyclohexyl-1,2-diamine



cat.	yield (%)	ee (%)
13	91	85
14	89	89
15	97	94

Scheme 9 enantioselective catalytic aldol reaction



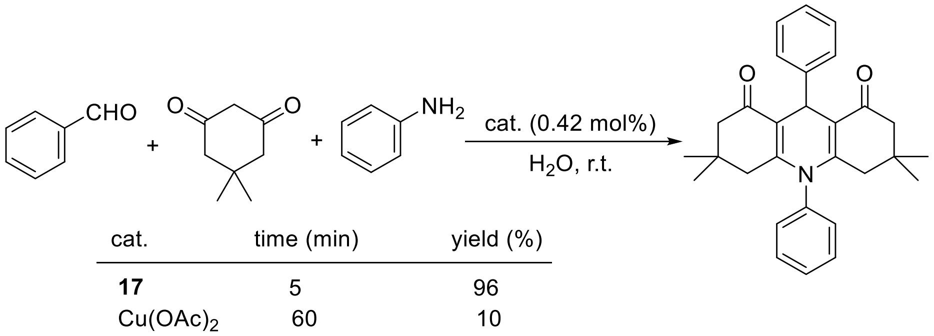
Scheme 10 catalytic synthesis of triazole derivatives

solvothermal decomposition of Fe(acac)$_3$ in oleylamine (Esmaeilnezhad *et al*. 2019). It was shown that due to better dispersion of hydrophobic magnetic nanoparticles in crude oil, these nanoparticles are an ideal candidate for the recyclable catalyst of the Toe-to-Heel Air Injection.

Tai and coworkers have designed silica-coated magnetic nanoparticles (MNP@SiO$_2$)-based chiral cyclohexyl-1,2-diamine using the copper-catalyzed azide-alkyne [3 + 2] cycloaddition reaction (Scheme 8) (Angamuthu and Tai 2019). These magnetic organocatalysts, catalysts **13**-**15** were then studied in direct aldol reaction (Scheme 9). Their efficiencies were compared for yield and enantiomeric excess (ee). Catalysts **13**-**15** having methyl, butyl, and pentyl substitution, respectively give good to high enantioselectivity (85, 89, and 94%, respectively). Apparently, ee can be enhanced by introducing a longer lipophilic chain at the tertiary amine on the cyclohexyl-1,2-diamine to growth its tendency to the hydrophobic substrate. Alkyl chain at nitrogen atom having the longest lipophilic substitution attained better yield and ee. It appears lipophilic chain length will effect rigidity toward the substrate.

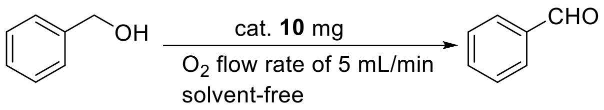
Recently, Jain and coworkers have developed the use of nanomagnetic Fe$_3$O$_4$ supported cyclodextrin (catalyst **16**) as a nanoreactor in the copper-catalyzed synthesis of 1,4-disubstituted-1,2,3-triazoles *via* click reaction under ultrasonication in water (Scheme 10) (Jain *et al*. 2019). Supporting the surface of magnetic nanoparticles with cyclodextrin (CD) avoids its agglomeration. On the other hand, CD affords a hydrophobic cavity for organic reactants, azides, and alkynes, but its hydrophilic outer surface makes the process practical in aqueous phase providing high yield of desired triazole derivatives. Finally, it is found that cyclodextrin is critical for the reaction progress in water by forming a host-guest complex between lipophilic reactants and its hydrophobic cavity and no reaction takes place in the absence of CD.

Another magnetite-based catalyst **17** has been prepared by Kazemnejadi *et al*. (2021) via immobilization of saponin on the surface of Fe$_3$O$_4$ nanoparticles then doped with Cu(II) ions. This supported catalyst performed the synthesis of quinazoline and acridine derivatives in water at room temperature within 10-65 min. It is interesting to note that lipophilic glycone moieties in the saponin can lead to



cat.	time (min)	yield (%)
17	5	96
$Cu(OAc)_2$	60	10

Scheme 11 One-pot synthesis of acridine



cat.	Pd loading (%)	coversion (%)	yield (%)	TOF (mol/h.mol)
18	2.68	20.77	4.67	6288.76
19	2.64	7.19	1.90	2147.28

Scheme 12 Pd-based catalyzed aerobic oxidation of benzyl alcohol

diffusion of hydrophobic reagents into the active center of catalyst and synthesis of desired products in excellent yields (Scheme 11).

2.4 Carbon materials

Environmental catalysis plays a crucial role in air and water contamination control, and the catalytic removal of pollutants (Adel Niaei and Rostamizadeh 2020). However many studies have proved that the effectivity and stability of environmental catalysts are highly dependent on moisture and humidity.

Today catalytic combustion is the essential method for the removal of Volatile organic compounds (VOCs) as major air pollutants. The main challenge in catalytic combustion of VOCs is to take place at low temperatures under humid conditions (Lamonier 2016). Catalytic activity can be decreased due to adsorption of the produced water vapor in the combustion process on the catalyst. Along this line, it was shown that low-temperature removal of toluene in highly humid conditions can be achieved using granular activated carbon-supported nano‑gold/metal oxides because of the hydrophobic property of activated carbon (Minh *et al.* 2018). In separate studies, Trung *et al.* (2020) described the use of other hydrophobic combustion catalysts, nano-sized noble metal on the ceria/granular carbon and nano-sized noble metal (Au, Pd, Au-Pd) supported on granular carbon (Trung *et al.* 2021).

In order to the destruction of hazardous organic compounds in wastewaters, Fe-Based MOFs particularly MIL-Fe have exposed good catalytic performance in Fenton-like process (Ahmad *et al.* 2020, Hu *et al.* 2019). Along this line, it has been demonstrated nanocomposite of MIL-101-Fe and graphene aerogel, compared to MIL-101-Fe, showed much enhanced catalytic efficiency in Fenton-like reaction for the removal of phenol in water, and also exhibited much-improved stability in humid air as well as easier recovery of reactivity under mild condition (Zhang *et al.* 2020). This performance and stability were attributed to the weakly hydrophobic nature of the graphene aerogel host. Similarly, resulted nanocomposite from the incorporation of TS-1 into MIL-101-graphene hydrogels, displayed high performance for the biphasic reaction of 1-octene epoxidation with hydrogen peroxide (Wu *et al.* 2021).

Also, the hydrophobicity of carbon materials was investigated in the synthetic application of nanocatalysts. Guo and co-workers prepared a porous carbon frame (PCF) using the calcination of black solid block (Guo *et al.* 2018). The phosphorus-doped alloy PCF supported palladium nanoparticle (catalyst **18**) is produced by sodium hypophosphite as reductant and the P source, and is applied in aerobic oxidation of benzyl alcohol (Scheme 12). Catalyst **18** presents better catalytic activity compared to the same catalyst **19** prepared by sodium borohydride as a reductant. The introduction of phosphorous increases the hydrophobicity of support which resulted in facilitating the adsorption of the benzyl alcohol as hydrophobic reagent and desorption of benzaldehyde as the product. Temperature-Programmed Desorption of CO_2 and NH_3 on catalysts **18** and **19** indicate that catalyst **18** had less oxygen-containing functional groups such as carboxyl and lactones, and that means that catalyst **18** is more hydrophobic.

Ballotin *et al.* (2020) synthesized amorphous nano-structured amphiphilic carbon using sulfuric acid and bio-oil by a simple thermal decomposition method. When the nanostructured carbon was added to a biphasic mixture of glycerine and acetone for the solvent-free ketalization stayed at the interface of the two phases. After stirring, it was detected the formation of stable emulsion promoted by the hydrophobic character of nanostructured carbon and hydrophilic properties of supported sulfonated groups. The amphiphilic carbon promoted the formation of emulsion from the biphasic glycerine/ acetone, which had a key role in the reaction interface and yield.

A particular aspect of some enzymes was that hydrophobicity, at least partly, could improve the catalytic activity, stability, or selectivity of the enzyme (Rodrigues *et al*. 2019, Manoel *et al.* 2015). In 2020, Szelwicka *et al*. described the transformation of α-angelica lactone to alkyl levulinates in toluene using multi-walled carbon nanotubes (MWCNTs)/ polytetrafluoroethylene (PTFE) hybrid-supported lipase B (Szelwicka *et al*. 2020). This catalyst was prepared by physical adsorption of PTFE and MWCNTs in the presence of non-ionic surfactants continued by the immobilization of Lipase B from *Candida Antarctica* via interfacial activation. The improvement of the performance of the enzyme after supporting on the hydrophobic support MWCNTs/PTFE was detected, probably because of interfacial activation or lowering agglomerates resulted in better homogeneity.

In a separate study, Chen *et al*. (2020) described the effect of the hydrophobicity of reduced graphene oxide (rGO) on the catalytic efficiency of Candida rugosa lipase in the glycerolysis reaction. The hydrophobic surface of rGO resulted in the distortion of the adsorbed lipase into configurations, in which the catalytic center of the enzyme was accessible from its side. The improvement in hydrophobicity of the surface leads to increase lipase activity because of the opening of the helical lid present on lipase.

2.5 Polymers

Polystyrene and its derivatives have progressively attracted some attention as a reinforcing material in hydrophobic matrices due to its low cost, ready availability, and chemical stability (Yüce *et al*. 2005, Yüce *et al*. 2008). Also, polystyrene is one of the most common polymeric supports used in the preparation of solid catalysts (McNamara *et al*. 2002). Wang *et al*. (2016) immobilized $H_5PMo_{10}V_2O_{40}$ into N,N-dimethylhexadecylamine functionalized chloromethylated polystyrene ($PMoV_2$@PS) by electrostatic interaction. The TEM and SEM images of the catalyst revealed irregular porous structure which matches well with the results obtained by porosimetry analysis. The catalytic performance of $PMoV_2$@PS was investigated in the direct hydroxylation of benzene to phenol with H_2O_2. The hydrophobic character of polystyrene-based support facilitates adsorption of nonpolar benzene and desorption of polar phenol, resulted in an enhancement in selectivity and yield of phenol.

The major impact of hydrophobicity when having in hand ester of fatty acid and their competition with H_2O for the adsorption on catalytic acid site has been also investigated in the design of the catalytic system for biofuel production. Indeed, H_2O molecules formed during esterification unavoidably can poison acid sites, resulted in the reduction of yield in the desired esters.

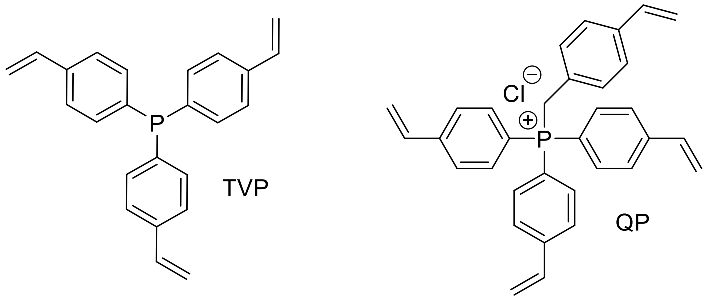
Wu *et al.* (2017) prepared **s**uper-hydrophobic solid strong acid (PDVB–$HOSO_2CF_3$) by sulfonation of nanoporous polydivinylbenzene (PDVB) by trifluoromethanesulfonic acid. BET surface area and pore volume were calculated to be 662 m^2/g and 1.20 cm^3/g, respectively and a typical nitrogen adsorption/desorption type IV profile was obtained. PDVB–$HOSO_2CF_3$ displayed excellent catalytic performance in esterification, acylation, and transesterification especially the production of biodiesel. The hydrophobicity of solid acid catalyst in these reactions is crucial since acid sites can be deactivated with water by-products.

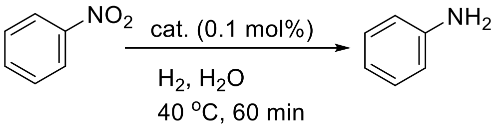
A same strategy has been applied also in the design and synthesis of a pyridinium-based acidic ionic liquid supported on poly-4-vinylpyridine (P4VP) core anchored in polystyrene shell based on the micellization of PS-*b*-P4VP (Jiang *et al*. 2020). This core-shell nanomaterial has been used to catalyze the esterification and preparation of the biofuel with excellent yields.

Wang and co-workers prepared 13.5 nm-sized Fe_2O_3 nanoparticles at 120°C by the solvothermal method in ethanol followed by supporting on polystyrene fibers (Fe_2O_3/PS) by the γ-Ray irradiation (Wang *et al*. 2019b). The photocatalytic activity of this recyclable semiconductor-catalyst was tested in the degradation of 4-chlorophenol (CP) and 4-nitrophenol (NP) under visible light. Excellent performance was shown in degradation of CP and NP (91.3% and 86.2%, respectively) after 60 min by hydrophobic supported catalyst Fe_2O_3/PS, whereas only 30.0% of CP by nonsupported Fe_2O_3 which was due to the hydrophobicity of polystyrene fibers.

Even though apparently the support should afford easy recyclability of the catalyst, another vital subject in designing a supported catalytic system for scientific and industrial researches is hydrophobic–hydrophilic balance and textural property of support. The tunable hydrophilic-hydrophobic property of the phosphine-functionalized porous ionic polymer-supported has provided many opportunities to perform the reduction of nitrobenzene with H_2 in water (Lei *et al*. 2020). This polystyrene-based polymer P(QP-TVP) has been prepared via radical copolymerization of (4-vinylbenzyl)-tris-(4-vinylphenyl)-phosphonium chloride (quaternary phosphonium salt, QP) with tris(4-vinylphenyl) phosphine (TVP). Specific surface area and total pore volume were measured to be 830 m^2/g and 0.80 cm^3/g, respectively. Interestingly, P(QP-TVP) stabilized palladium nanoparticle catalyst **20**, gave consistently higher yields than those obtained over polyQP- or polyTVP-based catalysts (catalysts **21** and **22**) prepared for comparison (Scheme 13). It was proposed that the superior performance of **20** in comparison with **21** and **22** is presumably due to amphiphilicity (or tunable hydrophobicity) of P(QP-TVP). Wettability test of catalysts confirms hydrophilicity of **21**, hydrophobicity of **22,** and amphiphilicity of **20**.

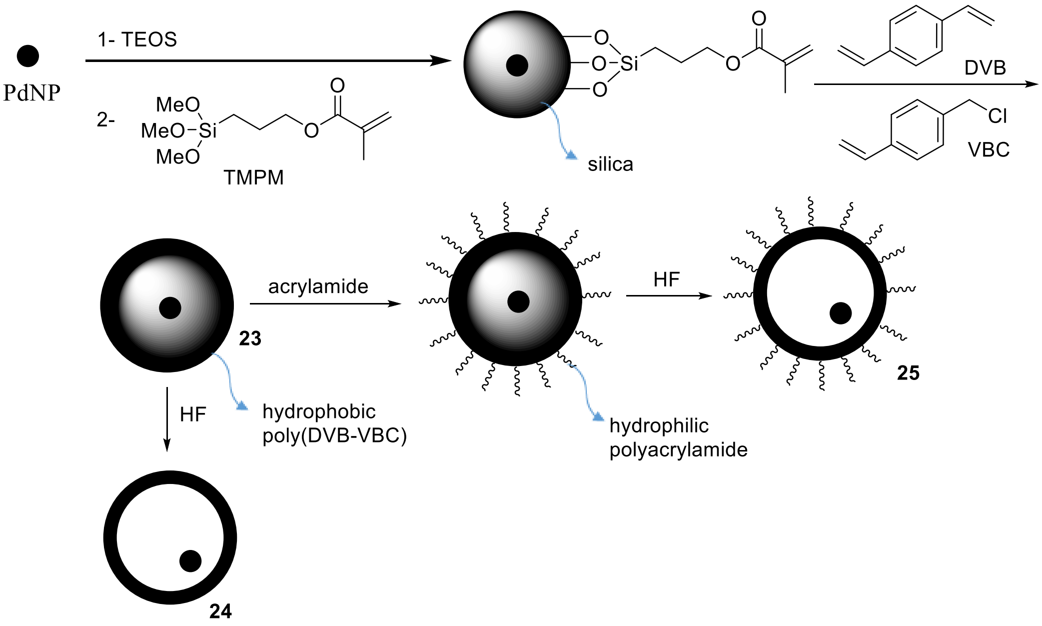
Yang *et al*. (2020) have performed a comparative study by using yolk-shell hybrid nanocomposites which encapsulate movable palladium nanoparticles in the polymeric hollow cavity (Scheme 14). Procedure for the synthesis of yolk-shell nanocatalysts has been started by the coating of palladium nanoparticles by Stöber silica followed





cat.	conv. (%)	sel. (%)	TOF (h^{-1})
20	98.6	100	986
21	64.5	100	645
22	33.7	99.1	334

Scheme 13 Pd-based catalyzed reduction of nitrobenzene

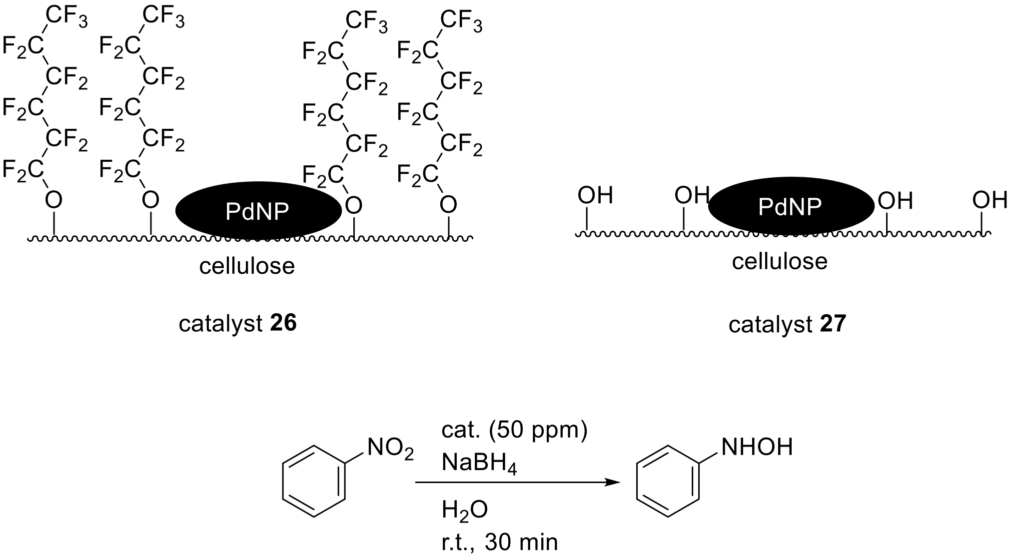


Scheme 14 Synthesis of yolk-shell nanocatalysts

by modification of silica with 3-(trimethoxysilyl)propyl methacrylate (TMPM) and formation of the second shell by polymerization with 4-vinylbenzyl chloride (VBC) and divinylbenzene (DVB) to give nanocomposite **23**. Selective removal of the silica shell from **23** by HF led to encapsulated movable palladium nanoparticles in a hydrophobic shell (catalyst **24**). The thickness of the polymer layer can also be controlled (15-24 nm) by monomers concentrations. Also, **23** was further modified by the polyacrylamide shell followed by etching by HF to give hydrophilic nano-rattles containing palladium nanoparticles **25**. These catalysts have been used in the reduction of NP and nitrobenzene (NB) in water by $NaBH_4$. It is interesting to note that hydrophobic catalyst **24** can improve the catalytic selectivity of hydrophobic substrate NB, but hydrophilic catalyst **25** is more suitable for the reduction of NP.

In recent decades, based on green chemistry principles cellulose has been broadly used in catalysis as support and stabilizer of metal nanoparticles (Kamel and Khattab 2021). But because of cellulose is a super-hydrophilic polymer its surface modification for controlling hydrophobicity and adsorption/desorption of chemicals is useful.

Cellulose-supported Pd nanoparticles with tunable hydrophobicity were prepared by perfluoro modification via grafting perfluoroalkyl iodide and followed by growing

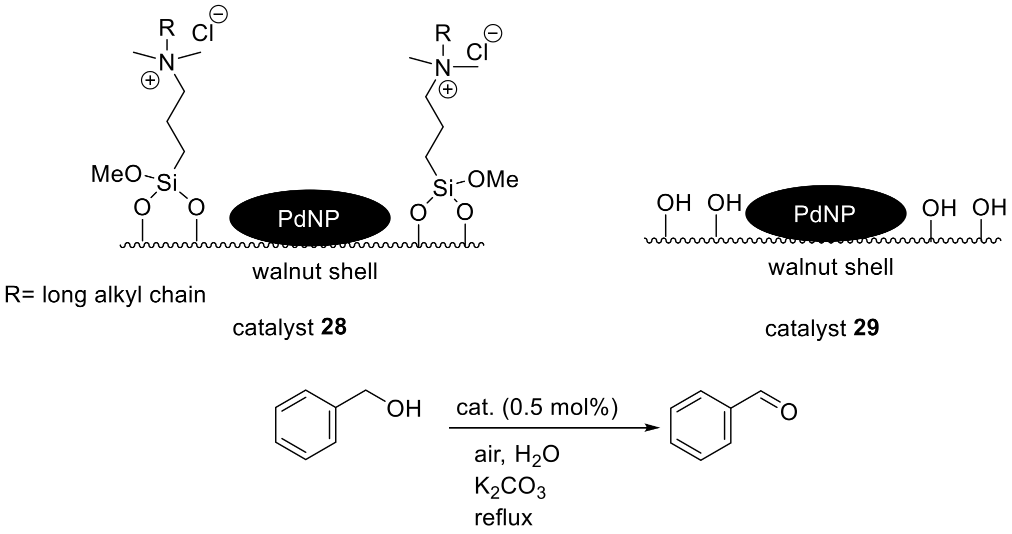


catalyst **26**

catalyst **27**

cat.	conversion	selectivity
26	98	95
27	43	75

Scheme 15 Selective reduction of nitrobenzene to PHA



catalyst **28**

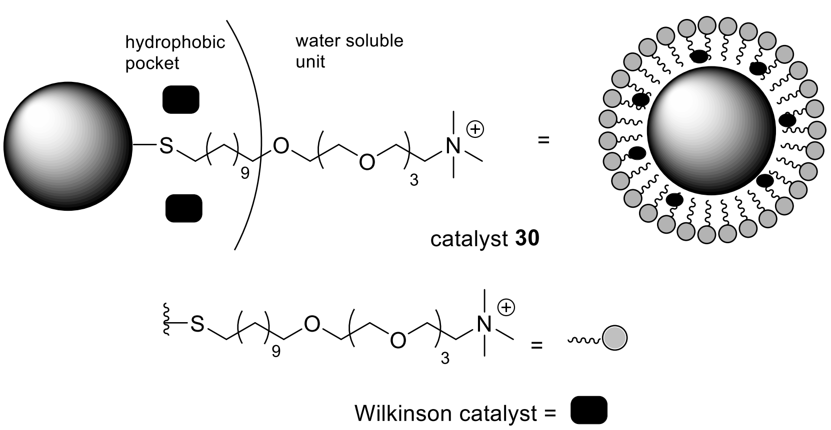
catalyst **29**

cat.	time (h)	yield (%)
28	8	99
29	24	22

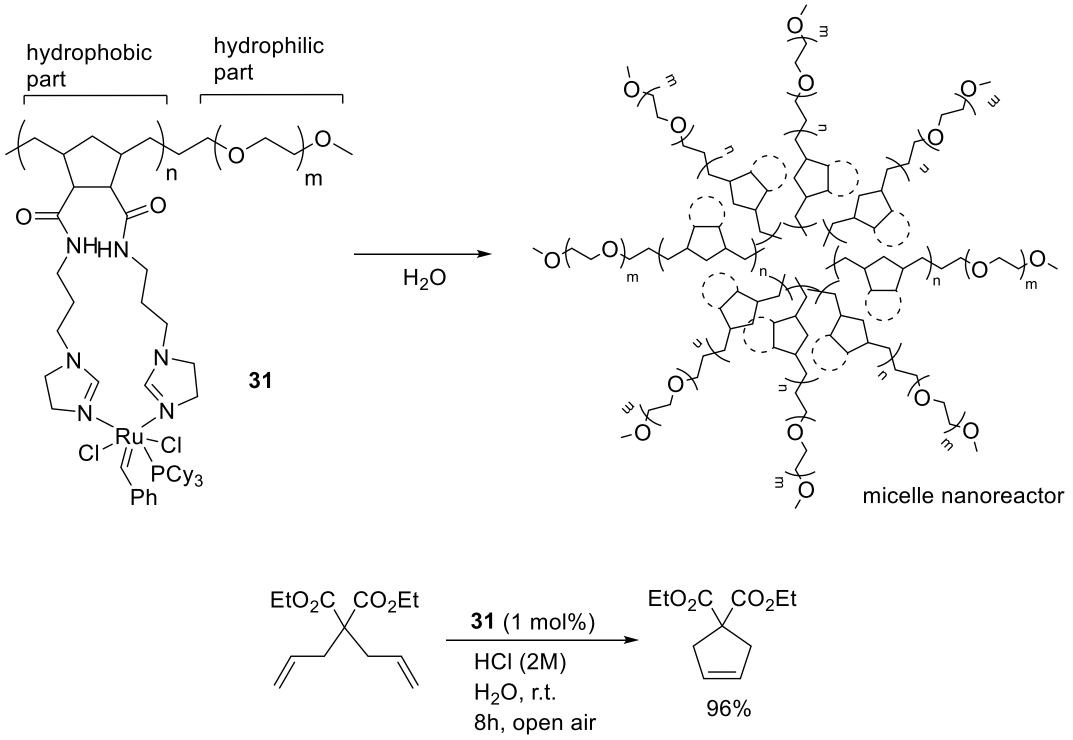
Scheme 16 Selective aerobic oxidation of benzyl alcohol

nanoparticles in situ to give catalyst **26** (Li *et al.* 2020). Catalyst **26** and non-modified cellulose-supported Pd nanoparticle **27** were used in the selective reduction of NB (Scheme 15). Interestingly, excellent conversion and selectivity could be attained by **26** at room temperature in aqueous media. Further studies showed that while comparable adsorption of NB and *N*-phenylhydroxylamine (PHA) on **27** were found, perfluoro-modified catalyst **26** with a more hydrophobic surface would assist the adsorption of NB but the adsorption capacity of **26** for PHA was much lower. The enrichment of NB on **26** will accelerate the reduction reaction. After PHA was synthesized, PHA could quickly desorb form **26**. This explains the slow rate of the conversion of PHA to aniline over **26**.

In recent years, agricultural waste biomass especially lignocellulosic ones (the most abundantly available natural polymer) such as walnut shell has increasingly attracted some attention in catalysis and synthesis of metal oxide



Scheme 17 AuNP- amphiphilic shell-based nanoreactor



Scheme 18 Amphiphilic polymer-based Ru catalyzed metathesis

nanostructures (Zamani *et al.* 2019a). Along this line, we have been reported the preparation of walnut shell stabilized copper nanoparticles as a recoverable and effective catalyst in the reduction of nitroarenes (Zamani *et al.* 2018a). Quite recently, we synthesized magnesium oxide nanoplates (Zamani *et al.* 2019b), high surface area aluminum oxide and boehmite (Zamani *et al.* 2019c), and cerium oxide nanoparticles (Zamani *et al.* 2018b) by the walnut shell as a sacrificial template. Also, we report the preparation of hydrophobic walnut shell by Zycosil, (a commercially available organo-silane compound, as hydrophobic agent) followed by immobilization of 5-18nm PdNPs to give catalyst **28** (Mousavi *et al.* 2020). The catalytic efficiency of **28** and non-hydrophobic walnut shell-supported PdNPs **29** were tested in aerobic oxidation of benzyl alcohol in water (Scheme 16). This alcohol was oxidized in the presence of **28** (0.5 mol%) in water at reflux condition in 8 h while this efficiency was not found for **29** even after 24 h. It is proposed that Zycosil may have improved the hydrophobicity/lipophilicity and adsorption of lipophilic reagents and desorption of water in **28**, which considerably improves the catalytic efficiency.

2.6 Amphiphilic polymer-based nanoreactors

Amphiphilic polymer-based nanoreactor systems provide a green, safe, and environmentally friendly methodology for the selective synthesis of organic chemicals (Harrison and Tang 2021). Recently Jeong and co-workers (2017) have shown that gold nanoparticles (AuNPs) can solubilize hydrophobic Wilkinson catalyst for hydrogenation of 4-vinylbenzenesulfonate. 2 nm AuNPs were applied as the scaffold for the catalytic system **30**, with the aim of formation nanoreactor scaffold features three essential elements: (1) a hydrophobic alkyl segment to create hydrophobic pocket for catalyst encapsulation, (2) a tetraethylene glycol unit and (3) a trimethylammonium head to provide water solubility (scheme 17). This supramolecular-based system, afford a nanoreactor to solubilize and stabilize hydrophobic Wilkinson catalyst while preserving catalytic activity and reusability. **30** catalyze the reduction of sodium 4-vinylbenzenesulfonate in water under hydrogen at room temperature. The recycling test of the system was effectively achieved in five runs that has proved the stability of 30 through supramolecular stabilization and tuning hydrophobic pocket.

Öztürk *et al*. (2018) developed a relatively simple approach to facilitate catalyst reusing by immobilizing the ruthenium complex onto block copolymer micelles **31**. Amphiphilic polymers bearing hydrophobic polynorbornene, imidazole side chain, and polyethylene glycol moiety (to achieve water solubility) as the self-assembly agent provide nanoreactor in aqueous media for Ru-catalyzed reactions (Scheme 18). TEM images indicated 85.95 nm-sized micelle structure-supported Ru. The catalytic performance of **31** was studied in the ring-closing metathesis reaction of diethyl diallyl malonate at room temperature in water under air. The diffusion of the olefinic substrate inside the hydrophobic core of micelle led to a very efficient catalytic system for metathesis reactions.

3. Conclusions

Due to increasing environmental and economic issues, ever-growing attention has been focused on the advancement of new improved efficient, selective, and reusable catalytic systems. Because of water usually is a by-product of organic processes hydrophobicity has been essential in the efficiency and stability of catalysts. On the other hand, water as a solvent is not only a green and cheap solvent but also has unique properties that so-called “hydrophobic effect”. This is the affinity for lipophilic molecules with hydrocarbon ingredients to minimize contact with the aqueous phase and to aggregate instead with other hydrocarbon molecules in water. The hydrophobic effect has now been applied to mimic biological chemistry and to offer notable selectivity and stability in catalytic chemistry. But the presence of water in the form of by-product or solvent, usually leads to the deactivation and poisoning, further restricting their recoverability. Therefore, the designing and employing of hydrophobic catalysts is crucial to assist the adsorption of lipophilic reagents and desorption of water, which make them to be used as effective, stable, and reusable catalysts in the presence of water.

The present article reviews recent reports on the development of various nanocatalysts with tunable hydrophobicity and studies in their use in different organic reactions and also environmental catalysis. Nanocatalysts with tunable hydrophobicity contain zeolites, MOFs, functionalized mesoporous silicas, polymers, composites, graphene, and yolk-shell nanostructures. Various nanocomposites and nanostructures lead to samples with different grades of hydrophobicity.

Commonly, the hydrophobicity of zeolites and mesoporous silica can be tuned by post-modification. The hydrophobicity of zeolites can be adjusted by dealumination, while less hydrophilic silicas can be obtained by functionalization, mainly with alkoxysilanes. Much attention has been paid to the improvement of polymer nanocomposites, such as polystyrene-based catalysts, because of their remarkable hydrophobicity. Also, carbon nanomaterials and perfluoroalkyl functionalization show suitable hydrophobicity and enhance catalyst stability and reusability. Control of hydrophobicity in nanocatalysts on an industrial and laboratory scale is a great challenge that needs considerable further research.

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