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A REVEALING STUDY ON METALS AND METAL SALTS IMPREGNATED SILICA: AN EFFICIENT AND VERSATILE CATALYST IN GREEN CHEMISTRY

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ABSTRACT

In the present review, heterogeneous catalysis by silica and silica doped with metals or their salts is discussed to generate a brief overview of selective organic syntheses from the perspective of green chemistry. The metal catalysts were encapsulated in silica and they offer the advantages of easy availability, low cost, ease of processing, long catalytic lifetime, environmental friendliness, good to excellent yield of products, and recyclability. Such catalysts have gained worldwide acceptance. These impregnated silica-based supports are widely used in the preparation of various natural products or strong biological scaffolds or their precursors which have a wide array of pharmaceutical and industrial applications. Advancement in the medical world is also elaborated by employing these eco-friendly catalysts.

Keywords: Heterogeneous, Metal-Doped, Silica, Catalyst, Solid Support, Solvent-Free, Green Method.
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INTRODUCTION

For decades, catalysis has been essential in the manufacturing sector. Catalysts allow procedures to be carried out at the standard temperature and pressure found in industrial settings, reducing the need for costly and inefficient special processing equipment. They work well in a variety of reaction environments, including liquid, gas, and solid surfaces.[1] Heterogeneous catalysis, in which solid materials catalyse the reactions, has a number of benefits over homogeneous catalysis, including superior recyclability reuse of the catalyst and simple product separation. Solid-phase synthesis of peptides by Merrifield in 1960 was a groundbreaking achievement,[2] but the concept of solid-phase preparation of chemical molecules dates back to the 1940s. Extending this branch of solid-phase synthesis has attracted a lot of attention during the past two decades.[3-11] The use of solid acid catalysts has propelled organic synthesis towards the forefront of heterogeneous catalysis.[12] Clay and silica[13] are the most common bases for solid acid catalysts, with silica being the cheapest. Often found in its natural form as quartz, silicon dioxide (silica) has the chemical formula SiO_2. Silica is the primary component of sand in various geographical regions. Notable examples include opal, aerogels, silica gel, fused silica, and fumed silica. Additionally, silica is safe, fireproof, nonreactive, and stable under normal conditions of use. The stationary phase[14] in chromatography is silica gel. It is utilised as a sorbent for the dehydration of gases and fluids and as a catalyst support for various processes due to its enormous surface area (5-800 m^2 g^{-1}). As a result of its low acidity and high solubility, silica has found widespread use as a catalyst, accelerator, and reaction medium.[15,16] Heterogeneous catalysis always makes use of silica-based derivatives.

Few Instances of Simple Reactions Catalysed by Silica Support Only

Currently, several organic reactions have been reported to be performed efficiently under adequate conditions using reagents that have earlier been adsorbed on inorganic supports. This silica catalyst has been one of the most extensively used inorganic supports in organic synthesis.[17-19] In 2010, Besbes *et al.* reported that silica gel, performing as a Lewis acid, reacted with N-acyl-2,2-dimethylaziridines to produce allylamides, oxazolines, and amino alcohols (Scheme-1). All these compounds have pharmaceutical potentialities.[20]

Aboumessad and his co-workers (2015) developed a process of heating ethylene glycol in the presence of silica gel in a 150 °C autoclave for 24 hours, under autogenic pressure and promoting the formation of

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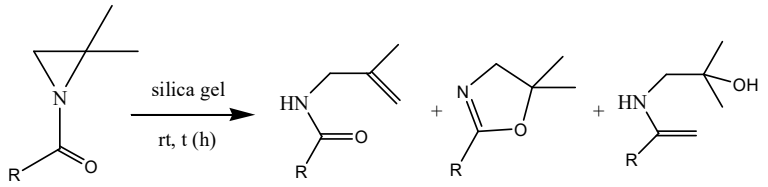
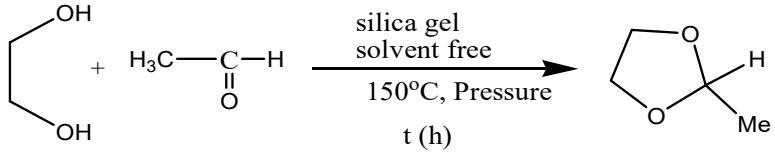
acetaldehyde in situ, which is bound by the ethylene glycol in the heterogeneous environment to form 2-methyl-1,3-dioxolane (Scheme-2).[21]



Scheme-1: Action of silica gel on N-acyl-2,2-dimethyl aziridines

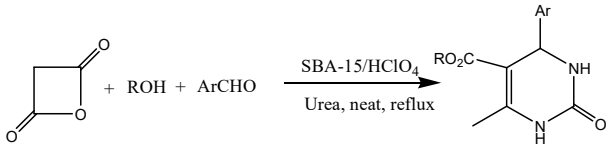


Scheme-2: Conversions of Ethylene Glycol Using Silica

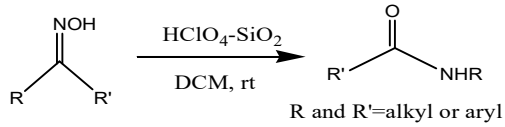
Silica Supported Acid Catalysts

Because of their unique properties, such as high efficiency due to large surface area, thermal stability and reusability, low harmfulness, greater selectivity, easy handling,[22,23] and high selectivity,[24] silica-supported acids like silicated polyphosphoric acid and silicated perchloric acid have attracted significant interest in modern organic synthesis. Recent research has revealed the success of using a silicated polyphosphoric acid catalyst for a number of different heterogeneous organic transformations, including Hantzsch condensation, Knoevenagel condensation, and Michael addition. However, silicated perchloric acid, prepared using mesoporous silica SBA-15, has been identified as an acid catalyst that can be readily used for a variety of organic reactions,[25-27] including anomeric deacetylation or debenzoylation, glycosylation reactions in carbohydrate chemistry, geminal diacylation of aldehydes, and Friedländer condensation, due to its stability in air and ease of removal *via* filtration. Some examples are depicted below (Scheme 3-4).

Silicated perchloric acid-mediated reactions[25-27]



Scheme-3: SBA-15/$HClO_4$ Catalysed Biginelli-Type Condensation[25]

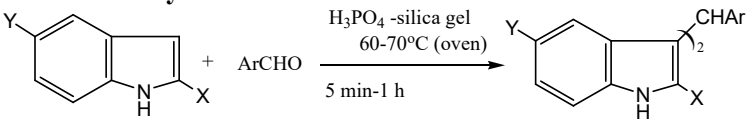


R and R'=alkyl or aryl

Scheme-4: Beckmann Rearrangement of Ketooximes[26]

Environmentally benign and inexpensive acids such as Phosphoric acid and *para*-toluene sulphonic acid (tosic acid) were also adsorbed on TLC grade silica gel allowing the successful synthesis of significant heterocyclic compounds with medicinal importance like symmetrical bis(indolyl)alkanes (Scheme-5) and substituted benzimidazoles (Scheme-6). The overall yield of the products was excellent.

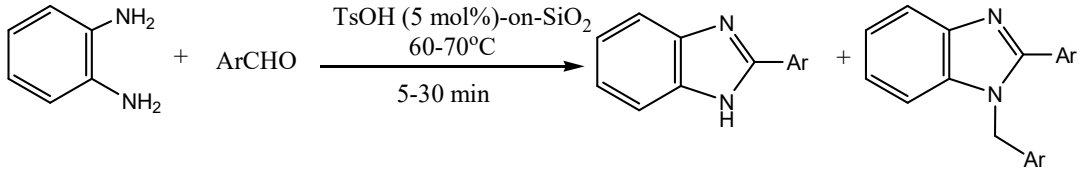
Phosphoric Acid-Silica Gel Catalysed Reaction[28]



X=H; Y=H X=H; Y=Br
X=H; Y=OMe
X=H; Y=NO_2 X=Me; Y=H

Scheme-5: Synthesis of Symmetrical Bis(indolyl)alkanes

Tosic Acid-Silica Gel Catalysed Reaction[29]

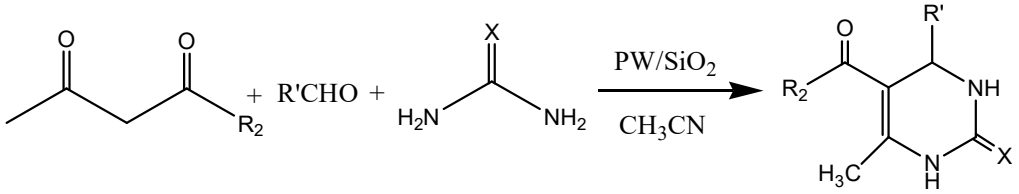


Scheme-6: Synthesis of Benzimidazoles

Strong Bronsted acidity, reaching into the super acidic zone, is characteristic of heteropolyacids (HPAs), and the acid-base property of HPAs is frequently diversified across a broad range by modifications in chemical composition. "The ionic structure of solid HPAs is different, consisting of very mobile elemental structural components such hetero-poly anions and counter cations (H^+, H_3O^+, H_5O^{2+}, etc.). Proton mobility is exceptionally high in this novel arrangement. Therefore, HPAs are both commercially and ecologically desirable due to their many advantages as catalysts.

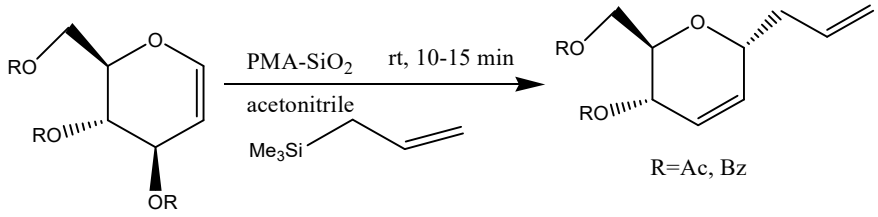
HPA-Encapsulated on Silica Catalysed Reaction[30]

Rafee *et al*. succeeded in the synthesis of dihydropyridine-2(1*H*)-ones (compounds with antihypertensive, antiviral, antitumor, antibacterial activities) and thiones catalysed by silica-supported Phosphotungstic acid ($H_3PW_{12}O_{40}$) (Scheme-7).[31]



Scheme-7: Synthesis of 3,4-dihydropyrimidinones or Thiones using PW/SiO_2[31]

Yadav and his research group developed the synthesis of 2,3-unsaturated glycopyranosides by Ferrier rearrangement using phosphomolybdic acid ($H_3PMo_{12}O_{40}$) embedded on silica gel as a mild, effective, and reusable catalyst (Scheme-8).[32] This review was written with the hope that it would stimulate more research into the catalytic behavior of metal or metal salt-doped silica in a variety of organic synthesis applications. The large body of literature was narrowed down to include only scholarly publications published after the year 2000. A small number of previous studies were included, however, with the intent of bolstering the discussion of relevance. The following discussion uses a few instances to illustrate the point.

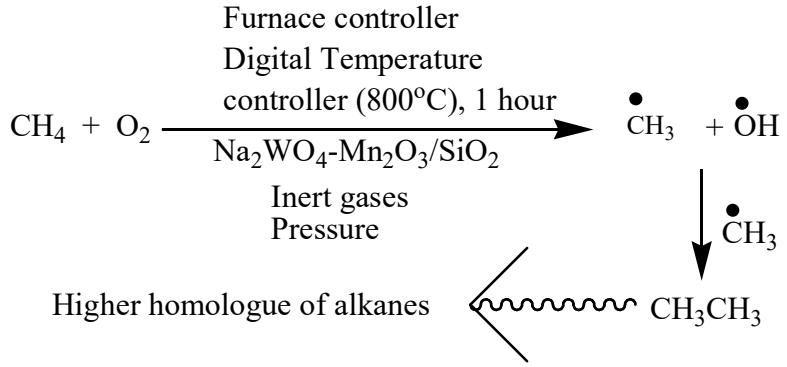


Scheme-8: Synthesis of 2,3-unsaturated Glycopyranosides using PMA[32]

Typical models of metal or Metal Salts Supported Silica Catalysed Reactions: Na_2WO_4-Mn_2O_3/SiO_2 Catalysed Oxidative Coupling of Methane[33]

With the addition of oxygen to value-added chemicals like ethane, ethylene, propane, propylene, and so on (Scheme-9), Nintao *et al.* demonstrated in 2021 that oxidative coupling of methane (OCM) is an effective technique for methane (an imperative green-house gas) transfiguration. The OCM reaction is exothermic, hence it typically takes place between 600 and 1000 degrees Celsius. Methane reacts with an oxygen atom on the surface of the catalyst, producing an intermediate hydroxyl radical and a product methyl radical. The result of the reaction between the two methyl radicals is an ethane molecule. The ethane is then oxidised to produce a C2+ hydrocarbon. Due to its large pore size and volume, broad

surface area, and excellent dispersion of active metal components, silica provides good catalyst support for the OCM reaction. The author has utilised this effective catalyst Na_2WO_4-Mn_2O_3/SiO_2 (NWM) to successfully accomplish the OCM reaction.[33]

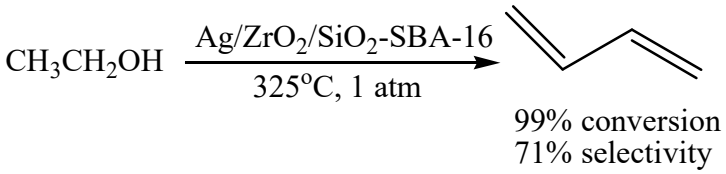


Scheme-9: Schematic Diagram of an OCM Reaction[33]

Methane and oxygen (in a volume ratio of 3.5:1) were utilised as the reactant gases, with a total feed rate of 50 mL/min, and the reaction was conducted at a high temperature of 800°C. The average response time was one hour. Gas chromatography (GC-14A, Shimadzu, Kyoto, Japan) equipped with a flame ionisation detector (FID) and a thermal conductivity detector (TCD) was utilised to examine the effluent gas.

Catalytic Performance of $Ag/ZrO_2/SiO_2$ Catalysts for the Production of Butadiene from Ethanol[34]

Scheme-10 depicts the ternary $Ag/ZrO_2/SiO_2$ catalyst system used by Dagle *et al.* (2018) for the one-step conversion of ethanol to butadiene. Under mild circumstances (325 °C, 1 atm, and 0.23 h^{-1}), 99% conversion and 71% selective butadiene synthesis were accomplished using a 1%Ag/4%ZrO_2/SiO_2-SBA-16 catalyst (SBA-16 is a kind of mesoporous silica). It was determined that SBA-16 was the most rational choice among several types of silica tested as catalyst supports, including silica gels, fumed silica, and mesoporous silica. It was hypothesised that the SiO_2 backing had a major effect on both conversion and selectivity.[34]



Scheme-10: Reaction Pathway for the Formation of Butadiene from Ethanol[34]

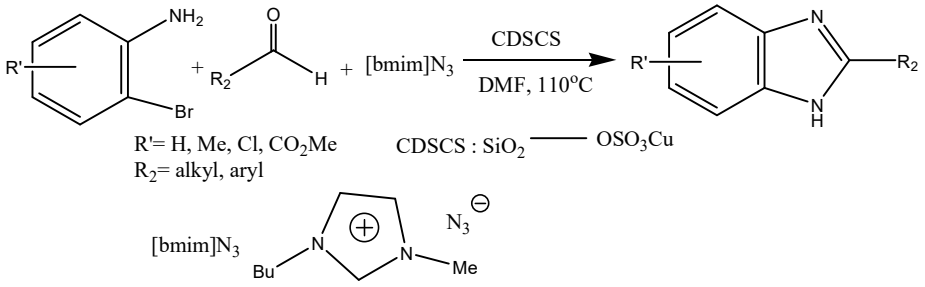
Oxidative Coupling of Methane Using Mg/Ti-doped SiO_2-Supported Na_2WO_4/Mn Catalysts[35]

In this study,[35] it was revealed that the preparation of α-cristobalite SiO_2 has been carried out by nucleation with Na_2WO_4, resulting in OCM-active Na_2WO_4. Although, Na_2WO_4 can be stabilised by α-cristobalite SiO_2, Mn oxides, and liquid Na_2WO_4 can be assimilated into the SiO_2 surface during the conversion of amorphous to α-cristobalite SiO_2 at high temperatures. In addition, the Na/W/Mn complexes were not completely immersed in the reactants. There may be a decrease in OCM activity due to a lack of Na_2WO_4 and Mn oxides. Thus, Mg and Ti doping to SiO_2 may compensate for the loss of accessible Na/W/Mn compounds, and amplify the quantity of Na/W/Mn compounds on the periphery of α-cristobalite SiO_2's surface, thereby refining the OCM activity by increasing the number of active sites on the support surface. The OCM activity of Na_2WO_4/Mn catalysts supported on Mg- and Ti-impregnated -α cristobalite SiO_2 was improved, leading to a 60.3% C2 selectivity and a 23.1% C2 yield at 800 °C. These values represent an increase of 18% in C2 selectivity and a 35% increase in C2 yield, respectively, compared to those of standard $Na_2WO_4/Mn/SiO_2$ catalysts.

Nano Catalyst Copper-Doped Silica Cuprous Sulfate as a Heterogeneous Catalyst for the One-Pot Synthesis of 1-H-2-Substituted Benzimidazoles[36]

Behrouz (2018) developed a simple, three-component synthesis (Scheme-11) of 1-H-2-substituted benzimidazole derivatives from easily accessible substrates using the highly competent heterogeneous

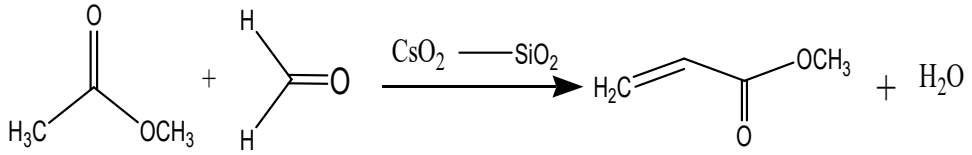
nano-catalyst copper-doped silica cuprous sulfate (CDSCS). Different 2-bromoanilines, aldehydes, and [bmim]N_3 react in DMF at 110 °C in the presence of CDSCS to produce the respective 1-H-2-substituted benzimidazoles in good to outstanding yields, according to this strategy. CDSCS is a low-cost nano-catalyst that can easily be recovered and reused for numerous reactions with little to no loss of activity. A brief summary of the factors that make this procedure appealing for the synthesis of structurally diverse benzimidazole derivatives would be as follows: the use of an environmentally acceptable and cost-effective heterogeneous catalyst; the use of [bmim]N_3 as a benign azide source; and the process's applicability in industrial synthesis.



Scheme-11: Synthesis of 1-H-2-substituted benzimidazoles using CDSCS

Aldol Condensation Reaction of Methyl Acetate and Formaldehyde over Cesium Oxide Supported on Silica Gel[37]

The organic monomer methyl acrylate (MA) is used extensively in the pharmaceutical industry. Recently, Wang *et al.* (Scheme-12) documented the aldol condensation of methyl acetate (Ma) and formaldehyde (FA) on cesium oxide supported on three different types of silica gel: A-type (A-silica), B-type (B-silica), and C-type (C-silica).[37] A-type amorphous silica gel has pores of around 2.5 nm in diameter, B-type amorphous silica gel has pores of approximately 4.5-7.0 nm in diameter, and C-type amorphous silica gel has macro-pores.[38,39] The Cs/silica catalysts in this investigation were prepared using A-, B-, and C-type silica gels as supports. Cs/B-silica appears to be more appropriate for industrial application than Cs/SBA-15 due to the lower cost of silica gel and higher performance.



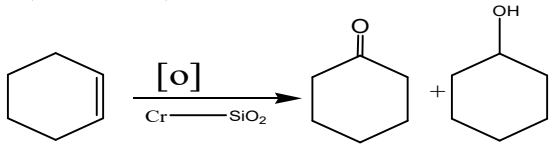
Scheme-12: Aldol Condensation Reaction of Methyl Acetate and Formaldehyde over Cesium Oxide Supported on Silica Gel[37]

Cu-Cr Impregnated Silica Catalyst from Rice Husk[40]

In his dissertation from 2014, Mitra[40] described a simple process for alkaline extraction of rice husk (RH) followed by acid precipitation to produce amorphous silica with a high specific surface area and minimal mineral impurities. The use of rice husk ash/char (RHA) has been demonstrated in the literature to yield silica in either an amorphous or high-purity amorphous form. Since RHA has been found to contain 60% silica or higher, it can be used as a commercial raw material in the manufacture of silica gels and powders (Kamath and Proctor[41]; Chakraverty and Kaleemulla[42]). Rice husk can be used as a substrate in the synthesis of a variety of silica compounds, from silica carbide and silicon nitride to amorphous silica and elemental silicon. It has been reported that mesoporous silica can be synthesised from rice husk with or without the addition of metals. Cu/RHA was calcined at 673K using the deposition-precipitation method, as reported by Chen *et al.*[43] Methanol was partially oxidised with the help of these catalysts, leading to the production of hydrogen gas. To oxidise styrene in the presence of hydrogen peroxide, Adam and Iqbal[44] showed how to dope rice husk silica with metallic Chromium. It has been demonstrated that chromium doped on mesoporous silica can efficiently convert cyclohexane to cyclohexanone and cyclohexanol (Scheme-13), two key intermediates in the synthesis of nylon-6 and nylon-66.

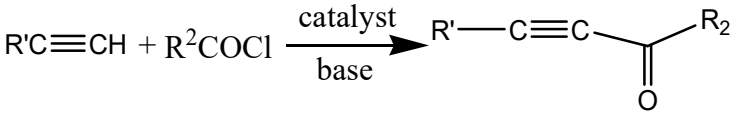
Metallic Palladium Deposited Over Donor-Functionalised Silica Gel Catalyst for the Synthesis of Alkynyl Ketones by Sonogashira Cross-Coupling Reaction[45]

In 2020, Semler *et al.*[45] have described the catalytic role of palladium catalysts deposited over silica gel bearing composite amide-donor functional superficial moieties in the well-known Sonogashira-type cross-coupling reaction of acyl chlorides with terminal alkynes, producing synthetically magnificent 1,3-disubstituted prop-2-yn-1-ones (Scheme-14).



Scheme-13: A Typical Example of a Cr-SiO_2 Catalysed Reaction

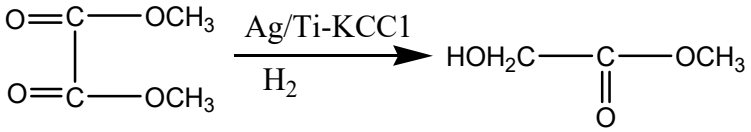
The researchers deposited cautiously Palladium catalysts over silica gel bearing simple amine ($\equiv Si(CH_2)_3NH_2$) and composite amide functional pendants equipped with various donor groups in the terminal position ($\equiv Si(CH_2)_3NHC(O)CH_2Y$, where, Y = SMe, NMe_2 and PPh_2). According to the report, the catalysts displayed noble catalytic activity in the reactions of aroyl chlorides with aryl alkynes under moderately mild reaction conditions even without the addition of copper co-catalyst.



Scheme-14: Sonogashira Cross-Coupling Reactions Mediated by Pd Catalyst Deposited Over Donor-Functionalised Silica Gel[45]

Role of Ti on Ag Catalyst Supported on Spherical Fibrous Silica in the Partial Hydrogenation of Dimethyl Oxalate[46]

In a recent report[46], Ouyang and his co-workers have developed an advantageous Ag catalyst doped on a novel, Ti-decorated spherical fibrous silica (Ag/Ti-KCC-1) *via* a simple methodology. Ag dispersion and the adsorption ability of the starting materials on the catalyst surface were seen to be enhanced by the addition of Ti, which was shown to limit the aggregation of Ag and promote the electron transfer from Ti to Ag. To improve the efficiency of the catalyst in the hydrogenation of dimethyl oxalate (DMO), a suitable amount of Ti additive was supplied to ensure equal adsorption of hydrogen and DMO on the catalyst surface. In the synthesis of pharmaceuticals, laboratory fine chemicals, and the perfume industry[47], methyl glycolate (MG) is a crucial substrate and reaction intermediary. This study reports the development of a family of hydrothermally produced spherical fibrous nano-SiO_2 (Ti-KCC-1) containing titanium at varying Ti/Si atomic ratios. A silver precursor was then successfully used for partial hydrogenation of DMO by being doped onto a solid Ti-KCC-1 support with a large surface area. This electron transfer from Ti to Ag reduces DMO coverage, but the substantial beneficial effect on boosting Ag dispersion may make up for the lower unit activity, resulting in increased catalytic activity overall. In conclusion, higher apparent catalytic activity was observed in the hydrogenation of DMO to MG (Scheme-15) when using the Ag-based Ti-decorated catalyst with the optimal Ti / Si ratio.

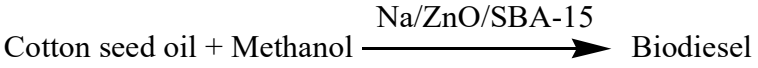


Scheme-15: Ag/Ti-KCC-1 Catalysed Partial Hydrogenation of Dimethyl Oxalate[46]

Na/ZnO Doped Mesoporous Silica Catalyst for Biodiesel Production by Transesterification of Native Cotton Seed Oil[48]

Malhotra and his group (2018) recently described in a research article, the role of Na/ZnO loaded SBA-15 in the process of transesterification from virgin cotton seed oil (Scheme-16) and the catalyst activity depending on its basic strength. The active species (Na/ZnO) was encapsulated on SBA-15 by an energy-efficient one-pot synthetic method under atmospheric conditions, without hydrothermal treatment, and following a wet impregnation method. The prepared heterogeneous catalyst was then utilised for biodiesel

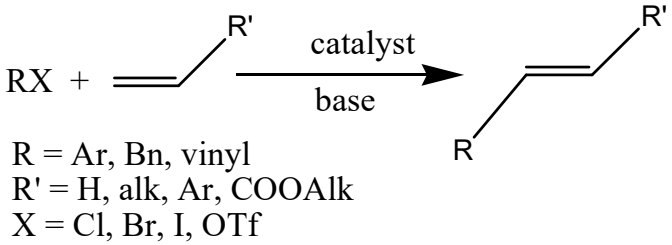
production *via* transesterification of virgin cotton seed oil with methanol. The effectiveness of the catalyst in the recycling process and its tolerance to high levels of free fatty acids were also assessed. SBA-15 is a thermally stable mesoporous material suitable as a great solid support with a large surface area to impregnate and entrap the active metals in the nano-channels of the mesoporous materials.



Scheme-16: Na/ZnO Doped Mesoporous Silica Catalyst for Biodiesel Production[48]

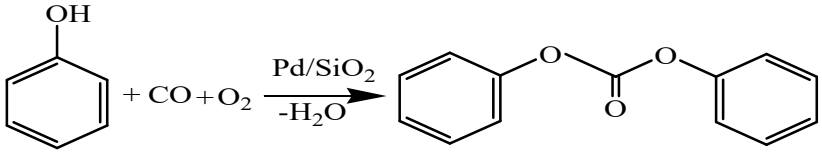
Silica-Supported Palladium Catalysts for Various Types of Organic Transformations[49]

Zhu *et al*.[50] placed Pd(0) catalysts onto anilino- and pyridylamino-modified silica gel, creating a range of recyclable, eco-friendly catalysts. When used for the Heck coupling of iodobenzene with styrene or acrylamide, these catalysts performed admirably. In another review of the literature, Clark and colleagues[51] used the reaction of aminopropylated silica with 2-pyridinecarbaldehyde to create a mesoporous silica gel that was tethered by iminopyridine groups. After being metalized with Palladium (II) salt, the solid supports proved to be highly effective heterogeneous catalysts for the Heck coupling of iodobenzene and methyl acrylate. Pd(0) immobilised on standard silica gel modified with $Si(CH_2)_3NH_2$ or $Si(CH_2)_3NH(CH_2)_2NH_2$ groups acts as an active and reusable catalyst in the Heck reaction of haloarenes (Scheme-17), as shown in a publication by Wang and co-workers.[52]



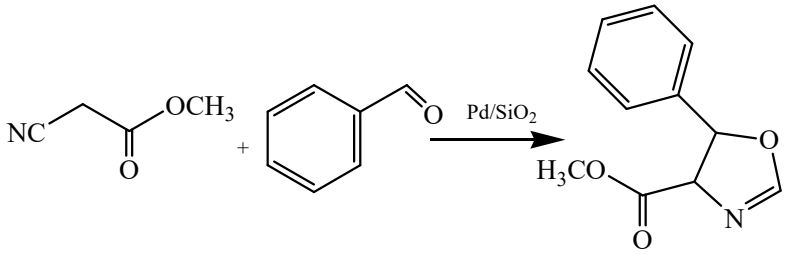
Scheme-17: The Heck Coupling Reaction[49]

One of the most important ways to synthesise diphenyl carbonate from inexpensive and easily accessible starting materials is through the oxidative carbonylation of phenol with carbon monoxide and oxygen (Scheme-18).[53,54] Catalysts for the aforementioned process were prepared by Li *et al*.[55] using the sol-gel method, where Pd complexes were impregnated on silica that had been functionalised by silylpropropylated 1,2-diaminocyclohexane.



Scheme-18: Oxidative Carbonylation of Phenol

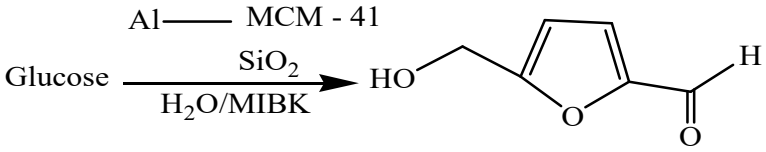
Catalysts for the aldol reaction between methyl isocyanoacetate and benzaldehyde, leading to 4-methoxycarbonyl-5-phenyl-4,5-dihydrooxazole (Scheme-19)[56], were prepared by immobilising Pd pincer complexes on silica *via* 3-(triethoxysilyl)carbamate groups. Five consecutive catalytic cycles were used to achieve a high level of trans-isomer selectivity (83-84%) and conversion (92-96%).



Scheme-19: Aldol Reaction of Methyl Isocyanoacetate and Benzaldehyde

Preparation of 5-hydroxymethylfurfural from Glucose using Aluminium Doped MCM-41 Silica as an Acid Catalyst[57]

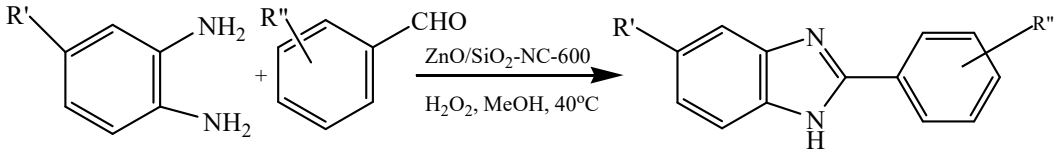
Aluminium-doped mesoporous MCM-41 silica catalysts were originally developed by Morales and colleagues[57] using a sol-gel approach based on the combined hydrolysis of tetraethylortosilicate (TEOS) and aluminum triisoproxide. As a surfactant, n-dodecylammonium chloride was utilized at room temperature before being calcined at 550 degrees Celsius. Two high-specific surface-area solids were synthesised containing Brönsted and Lewis acid sites and various Si/Al molar ratios (5 and 10). The reaction medium was a mixture of 30 catalysts by weight of glucose and water/methyl isobutyl ketone (MIBK). After 150 minutes of reaction time at 195 degrees Celsius, the yield of 5-hydroxymethylfurfural (HMF) was 36%, while the conversion of glucose was 87% (Scheme-20). Only fructose was detected as a byproduct of the process; neither levulinic acid nor furfural was produced. In addition, the glucose conversion was improved and a high yield of HMF was obtained in just 30 minutes when an aqueous solution of sodium chloride (20 wt.%) and MIBK was used as the reaction medium. This was because the partition coefficient between the organic and aqueous phases increased to 1.9. After three catalytic cycles, the activity was likewise successfully recorded.



Scheme-20: Preparation of 5-hydroxymethyl Furfural from Glucose[57]

Study of N-doped Carbons (derived from biomass) with Silica-supported Ultrasmall ZnO Nanoparticles as the Green Catalysts for the Synthesis of Benzimidazoles[58]

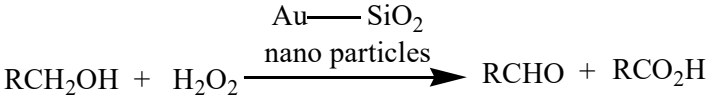
Under mild circumstances (Scheme-21), 2-arylbenzimidazoles were synthesised by Bai and his team in 2017 using ultrasmall ZnO nanoparticles anchored to N-doped carbons (made from chitosan) with silica support (ZnO/SiO_2-NC) as the catalyst. These catalysts performed exceptionally well and could be recycled six times with no discernible drop in activity or selectivity. High catalytic performance was achieved by using hydrophilic N-doped carbon derived from biomass chitosan and silica gel for uniform dispersion of ZnO nanoparticles in methanol and interaction with reactants.



Scheme-21: Synthesis of 2-aryl benzimidazoles under the ZnO/SiO_2-NC-600 Catalyst

Au Nanoparticles Impregnation in Hybrid Silica by Sol-Gel Method Leads to Improvement in Gold Oxidation Catalysis[59]

Sol-gel entrapment of gold nanoparticles in hybrid silica increases gold catalysis in the selective oxidation of alcohols using aqueous hydrogen peroxide as an environmentally friendly primary oxidant (Scheme-22), as detailed in the study outcome by Pagliaro *et al*. (2016).[59] It was also noted that the use of a nontoxic primary oxidant is crucial to the success of any heterogeneously catalysed gold-based alcohol oxidation process. Carbonyl and carboxyl compounds of gold are employed in the production of many pharmaceuticals, polymers, colorants, paints, detergents, perfumes, flavors, and other high-value functional products[60] because of the metal's lack of toxicity. Catalyst recyclability was significantly improved by the sol-gel-doped Au nanoparticles' remarkable physical and chemical stability.



Scheme-22: Oxidation of Alcohols[59]

Heterogeneous Nano-Catalyst Copper-Doped Silica Cuprous Sulfate (CDSCS) for [3+2] Huisgen Cycloaddition[61]

The usual method for making 1,2,3-triazoles[62,63] is the Huisgen 1,3-dipolar azide-alkyne cycloaddition. In order to catalyse this reaction (Scheme-23), Behrouz and colleagues[61] synthesised and characterised copper-doped silica cuprous sulfate (CDSCS). Cu (I)-catalysed 'Click' cycloaddition of organic azides with terminal alkynes demonstrated the catalytic efficacy of the nano catalyst CDSCS. The reaction media was a THF/H_2O (1:1, v/v) mixed solution, and it occurred at room temperature. In most cases, high yields of pure cyclised compounds were achieved in a swift reaction time. These substances share functional similarities with beta-adrenoceptor antagonists. According to the study authors, CDSCS is a reusable nano catalyst that is chemically and thermally stable.

R' = alkyl, alkoxy, aryloxy
R^2 = $ArOCH_2$, Ph, Me_2COH

Scheme-23: Synthesis of New β-blocking Analogues using CDSCS[61]

$MnTiO_3$ Triggered Low-Temperature Oxidative Coupling of Methane using TiO_2-doped Mn_2O_3-Na_2WO_4/SiO_2 Catalyst[64]

Oxidative coupling of methane (OCM)[65,66] is a distinguished method for the direct transformation of methane to ethane and higher alkanes (C2+ products). From the literature survey, many catalysts were reported for this process but among them, Mn_2O_3-Na_2WO_4/SiO_2 showed the highest conversion and selectivity, but only at a high temperature of 800° to 900°C, which created difficulty in industrial chemical processes. Here, Wang *et al.*[64] prepared TiO_2-doped Mn_2O_3-Na_2WO_4/SiO_2 catalyst by employing Ti-MWW zeolite as TiO_2 dopant and SiO_2 support, enabling OCM with 26% transformation and 76% C2-C3 selectivity. $MnTiO_3$ activates the low-temperature $Mn^{2+}\leftrightarrow Mn^{3+}$ conversion for O_2 activation and also catalyses along with Na_2WO_4 for selective conversion of methane to C2-C3. The Mn_2O_3-TiO_2-Na_2WO_4/SiO_2 catalyst was prepared in a ball mill. This catalyst can be converted in situ into $MnTiO_3$-Na_2WO_4/SiO_2, yielding 22% conversion and 62% selectivity at 650°C.

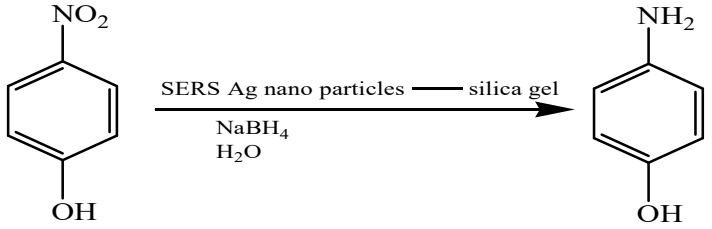
Study of Cr-Doped Silica and Ferric Oxide Gel Catalyst for the Conversion of *ortho*- to *para* Hydrogen[67]

Hydrogen is a well-studied element in the experimental and theoretical realms of molecular science due to its existence in monoatomic, diatomic, and triatomic systems. It can be used as rocket fuel[68,69] and automobile fuel[70–72] and is among the best cold neutron moderator materials.[73-77] Para and ortho hydrogen are the two spin states that can be found in molecular hydrogen. Energy levels of ortho- and para-hydrogen are temperature-dependent due to the difference in rotational energy level, with para-hydrogen predominating at low temperatures. The equilibrium temperature, 20 K (99.8% para-hydrogen), was attained through the typical transformation after a lengthy process. At present, two catalysts, iron (III) oxide (Fe_2O_3) and chromium (II) oxide doped silica ($CrO.SiO_2$), are utilised for the conversion of ortho- to para-hydrogen. The interaction of ortho- and para-hydrogen on the surfaces of the aforementioned catalysts was studied by Hartl and his research group[67] using neutron vibrational spectroscopy. Measurements of X-ray absorption fine structure and X-ray/neutron pair distribution function were used to analyse the catalytic surfaces.

Deposition of SERS Active Silver Nanoparticles on Silica Gel Photochemically and their Catalytic Role for the Reduction of Aromatic Nitro Compounds[78]

As a promising role has been shown in catalysis[79-82] and SERS (surface-enhanced Raman scattering) research[83], metallic nanoparticles, specifically silver, have been the focus of this work. In addition, silver nanoparticles may be studied and identified in solution because of their strong plasmon absorption capabilities in the visible spectrum. For immobilisation applications, Pal and colleagues[78] investigated impregnating silver (I) gelatin complex onto silica gel. Exposure to UV light helped secure the silver

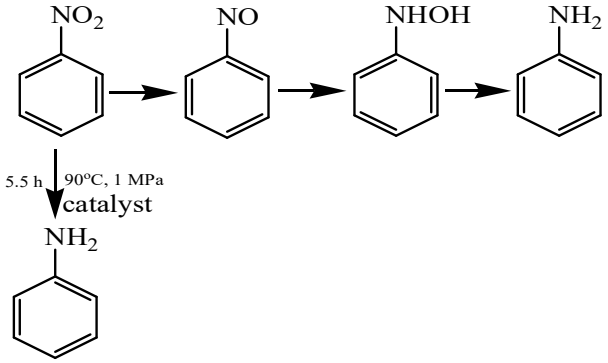
nanoparticles to the surface after the silica gel containing them had been deposited there. Silver particles on silica surfaces have been identified and characterised using standard techniques, including UV-visible spectroscopy, transmission electron microscopy, energy-dispersive X-ray analysis, and thermal analysis. Clusters of silver nanoparticles were found in the silica matrix, as evidenced by the unique SERS activity of the silver particles generated photochemically. The SERS activity of the silica matrix surface, thus, continues for a considerable amount of time (months). Catalytic reduction of nitro compounds (Scheme-24) was successfully carried out by the study group after they took their cue from the surface activity of the silica matrix. This was accomplished in aqueous, organic, and three different micellar media.



Scheme-24: Reduction of 4-nitro Phenol[78]

Reduction of Nitrobenzene to Aniline over Silica Gel Supported Nickel Catalysts

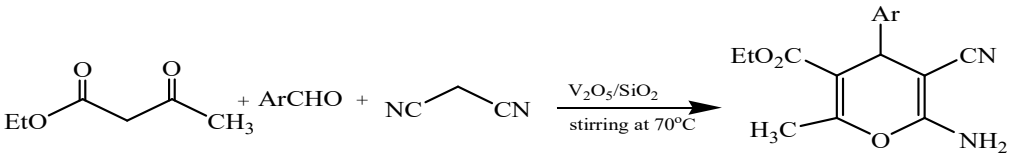
Hou and his research group[84] have developed a Ni catalyst with exceptionally uniform particle size distribution, with an average particle size of 3.7 nm. They were able to accomplish this by doping a nano-sized silica gel (20-100 nm) with an aqueous solution of $Ni(en)_3(NO_3)_2$. Furthermore, nitrobenzene was hydrogenated into aniline using this catalyst under risk-free reaction conditions (90 °C and 1.0 MPa). Hydrogenation of nitrobenzene was studied using commercial Raney Ni and Ni particles of varying sizes employed on nano-sized silica gel (Scheme-25). The reaction network and mechanism of nitrobenzene hydrogenation on a 3.7 nm Ni catalyst were discussed using investigations of product distribution and temperature dependence. Several unwanted intermediates did not develop in a linear fashion during the reaction, including nitrosobenzene, N-phenylhydroxylamine, azoxybenzene, azobenzene, and hydrazobenzene.



Scheme-25: Reduction of Nitro Benzene[84]

Synthesis of 4H-pyrans *via* a Multicomponent Reaction in a Solvent-Free manner with the use of Catalyst V_2O_5 Supported Silica[85]

Khatab *et al*.[85] have used a V_2O_5/SiO_2 catalyst, which is both efficient and safe for the environment, to successfully produce 4H-pyran derivatives. Using ethyl acetoacetate (EAA), malononitrile, and aldehydes, a series of molecules known as 2-amino-3-cyano-4H-pyran derivatives were synthesised in a single step (Scheme-26). Without any solvents and with constant stirring at 70 degrees Celsius and in the presence of a trace amount of V_2O_5/SiO_2 catalyst, the reactions were completed. Many oxygen-containing heterocyclic compounds base their construction on 4H-Pyran derivatives. To obtain 4H-Pyrans, a single-step reaction involving Knoevenagel-Michael cyclo-condensation was created. Their antibacterial, anticancer, antitubercular, pigment, antiviral, and spasmolytic properties,[86] in particular, have attracted a lot of attention from the pharmaceutical and scientific communities.



Scheme-26: Synthesis of Various 4H-pyrans *via* Multicomponent Reaction[85]

Advancement of Metal-Doped Silica Support in the Pharmaceutical Domain

In recent work, silica-coated Mn-doped Zinc Sulphide (ZnS) nanocrystals were employed for theranostic applications such as marking HeLa cells and delivering anti-cancer drugs. A significant amount of the fluorescent experiment's quantum yield was preserved due to the silica layer.[87]

In 2021, Kontonasaki *et al*. showed that calcium, magnesium, strontium, and cobalt-doped mesoporous silica nanoparticles can combine optimal textural features for periodontal tissue healing if the synthesis method and drug loading parameters are optimized.[88] Hao *et al*. (2021) created 5-aza-2-deoxycytidine and docetaxel-loaded nanoparticles out of manganese-doped mesoporous silica. To establish drug-loaded nanoparticle accumulation in tumors for cancer therapy, their investigation devised a dry cupping device and a method for the framework engineering of silica-based nanoplatforms for biodegradation amendment.[89] Zou's group (2022) has created lactoferrin-functionalised hollow mesoporous silica nanoparticles loaded with resveratrol to treat ischemic stroke. Lactoferrin-functionalised hollow mesoporous manganese-doped silica nanoparticles (LHMMSN) were developed to carry resveratrol (RES). With this technique, insoluble medicines can be transported across the blood-brain barrier and used to treat inflamed areas for anti-inflammatory, antioxidant, and neuroprotective effects. The anti-inflammatory and neuroprotective effects of LHMMSN-RES may explain why mice with a blocked middle cerebral artery recover their motor functions more quickly than controls.[90] Biodegradable manganese-doped silica nanoparticles (PMMSN) loaded with resveratrol (RES) were produced by Jiang and colleagues in the same year as a carrier of resveratrol, a complex plasma component. Research using both in vitro and in vivo models showed that PMMSN-RES successfully transported RES to the spinal cord, suppressed apoptosis, and controlled inflammation by counteracting the effects of oxidative stress. In mice with spinal cord injury (SCI), treatment with PMMSN-RES dramatically restored motor function, indicating a novel therapeutic strategy with clinical potential for SCI.[91] It's generally accepted that silver has antibacterial properties. Kawashita *et al*. used the sol-gel method to create silver-doped silica glass particles that are both colourless and chemically stable. Dental composite restoration was only one medical use that held out high prospects for the material's antibacterial properties.[92] Studies comparing the antibacterial activity of SiO_2 and Se-SiO_2 against gram-positive *Staphylococcus aureus* and gram-negative bacteria like *Escherichia coli* have been conducted using the disc diffusion technique. Particle size plays a dynamic role in determining the antibacterial activity of SiO_2 and doped Se-SiO_2 nanocomposite materials against Gram-positive and Gram-negative pathogenic organisms. Compared to pure Se-SiO_2, the antibacterial capabilities of Se-SiO_2 nanocomposite materials are greatly improved. The evaluation of Se-SiO_2 nanocomposite material and its high value of the electron-hole charge separation through low band gap energy has projected significant antibacterial activity and medical use.[93,94] In order to ensure robust osseointegration between the host bone and implants, bioactive glasses based on silica are a family of reactive biomaterials with desirable features (such as bioactivity, osteoproduction, and angiogenesis). Stan and his group were the first to demonstrate the potential of thin silica-based implant-type coatings with double addition of possibly antibacterial Cu and Ga agents by using preliminary mechanical and in vitro biological behavior. As Cu and Ga co-substituted silica-based bioactive glass films showed promise in preventing metallic endo-osseous implants from post-operative microbial infection, more investigation into their mechanical and in vitro biological effects is necessary.[95] A significant obstacle to better patient outcomes in cancer treatment is the difficulty in precisely diagnosing the tumor. Insufficient sensitivity and resolution are common limitations of single-imaging-modality deployment. Here, it was demonstrated that monodisperse iron oxide nanoparticles coated with fluorescent silica nano-shells can be used for simultaneous fluorescence and magnetic resonance imaging of malignancies. Iron oxide nanocrystals were encased in silica shells containing Rhodamine B isothiocyanate by the reverse microemulsion method. The size distribution of the core-shell nanoparticles

was then confirmed using transmission electron microscopy and dynamic laser scattering. The nanoparticles with a dye-doped silica shell were characterised by their fluorescence using photoluminescence spectroscopy. In the trials, the core-shell nanoparticles were shown to be easily dispersible in water and to cause minimal cellular damage. The enhanced permeability and retention effects of the synthesised nanoparticles were demonstrated, in vivo fluorescent imaging and ex vivo tissue analysis, to particularly target cancers. This novel dual-modality nanoparticle method ensures superior tumor imaging.[96]

CONCLUSION

After introducing silica as a practical, solid heterogeneous catalyst, a selective number of reactions catalysed by silica supports were discussed in the first section of this review. In the review's second section, we looked at the various types of reactions that can be catalysed by a silica support impregnated with metals or metal salts. Exemplary studies were presented that were found to be relevant to the scientific literature, with an emphasis on the synthetic procedures employed to generate them and the effect they had on the properties of the heterogeneous solid catalyst. The principles of green chemistry were demonstrated by illustrating the syntheses of various organic pharmacophores, biologically important compounds, and natural products with medicinal importance, using a wide variety of metals or combinations of metals, metal salts, and nano metal salts doped into various silica solids as versatile catalysts. Doped silica has a number of important medical applications, and these were covered as well. This review is important, and it will be useful in the future for learning more about the processes catalysed by metal-impregnated silica supports.

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CONFLICT OF INTERESTS

The author declares that there is no conflict of interest.

AUTHOR CONTRIBUTIONS

The Author contributed significantly to this manuscript, participated in reviewing/editing, and approved the final draft for publication. The research profile of the author can be verified from her ORCID ID, given below:

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