

## Utility in organic synthesis and characterization of nanoparticle-based catalysts

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Various organic transformations are facilitated by catalysts. Even though different research groups are focusing on the homogeneous catalysts, their reusability is the prominent challenge. To overcome this challenge, researchers are exploring nano-sized catalysts, thereby trying to incorporate the useful characteristics of homogeneous catalysts into heterogeneous ones. Rational design of the nanoparticle-based catalysts is extremely important, as well as the interpretation of their structure-function relationship. In the various nanoparticles (NPs)/catalysts, the characterization is carried out using transmission electron microscopy (TEM), X-ray diffraction (XRD), X-ray absorption spectroscopy and X-ray photoelectron spectroscopy (XPS/ESCA). The size of the NPs using TEM and XRD analysis has been found to be in the range of 5 nm. The crystalline nature, analyzed using XRD, confirms the face-centred and body-centred structure for a variety of nanostructures at ambient conditions. In the study of nanocomposites, the morphology and facet design are investigated using scanning electron microscopy (SEM). Herein, we present a selective discussion of various organic syntheses involving heterogeneous nanoparticle-based catalysts and the techniques used for their characterization.

**Keywords:** Organic synthesis, heterogeneous catalysis, nanoparticle-based catalysts, TEM, XRD analysis.

### INTRODUCTION

Chemical synthesis employed in different industries, be it for pharmaceuticals or utility chemicals, involve catalytic reactions. Right from the Haber's synthesis of converting the almost non-reactive dinitrogen molecule to extremely useful ammonia, the effectiveness of catalysts is a proven fact. The recyclable characteristics of catalysts enable them to be an essential part of Green Chemistry. Most of the established industrial processes involve different heterogeneous catalysts, which means that the catalysts are in a different phase from the reactants and hence, easily separable. But the main drawbacks of heterogeneous catalysts were that the reaction mechanism could not be defined properly and fine-tuning of those catalysts was almost impossible. So, the researchers tried to design specific homogeneous catalysts, which can be easily modified to suit the different chemical reactions involved. Another favorable fact was that having known the exact chemical structure of the homogeneous catalysts, predicting the reaction mechanisms was less complicated. Here the main obstacle was the separation of the catalyst from its homogeneous mixture with the reactants and products, thereby affecting the recyclability of the catalysts. In order to incorporate the favorable properties of both the heterogeneous and the homogeneous catalysts, different research groups

started investigating catalysis facilitated by metal nanoparticles (NPs). These NPs, of dimensions between 1-10 nm, could catalyze chemical transformations at par or even better than the metal complexes [1]. One of the most beneficial aspects of NPs is the greater surface-to-volume ratio of the metal NPs than the ordinary metallic heterogeneous catalysts. In addition, the metal atoms are less coordinated to other species, thereby providing greater number of active sites for the catalytic reactions than homogeneous catalysts. Isolation of the catalytic metal NPs is also very convenient, thereby increasing their recyclability [2, 3].

The fundamental studies of the heterogeneous catalysts were carried out using *in situ* characterization techniques, as well as external techniques. In these techniques, the structures of catalytic nanocrystals were studied. These investigations included the study of crystal phases and morphology along with size, shape and orientation, surface and structural features [4-6].

#### *Organic transformations catalyzed by metal NPs and their characterization*

The carbon-carbon or the carbon-heteroatom bond formation reactions are ubiquitous reactions, utilized in the production of various essential chemicals. But these bond formations often need the boost from different catalysts. Initially, the emphasis was on the development of homogeneous catalysts which could effectively facilitate the organic trans-

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formations, and be recycled a number of times.

Gradually, certain beneficial aspects of the heterogeneous catalysts shifted the investigations towards catalysis by metal nanoparticles. Many carbon-carbon cross-coupling reactions could be effectively carried out by nano-scale metal particles, embedded on a suitable support. Not only the metal NPs, but also the characteristics of the support, such as degree of hydroxylation, the size and nature of the crystals, etc., had profound effect on the C-C cross-coupling reactions.

One of the first reports of palladium NP-catalyzed Suzuki-Miyaura cross-coupling reactions involved the reaction between phenylboronic acid and aryl halides. Reetz and co-workers utilized not only aryl bromides, but also activated aryl chlorides to carry out the SM coupling reaction in presence of palladium nanoparticles [7, 8]. The same group had also successfully utilized these catalysts in Mizoroki-Heck cross-coupling reactions. In order to understand the mechanism of such reactions, detailed structural characterizations of the catalysts were carried in addition to those of the intermediates. This led El-Sayed and co-workers to report that the edge and the vertex atoms of palladium NPs act as active sites for this type of catalysis [9].

In 2011, Cai *et al.* reported palladium-based NPs supported on fluorosilica gel. The fluorine-substituted alkyl chains were able to adhere to the Pd-NPs through non-covalent bonding, thereby stabilizing the NPs and enabling these species to act as efficient catalysts for C-H functionalization reactions [10]. Arylation at the C2 positions of indoles could be successfully carried out in presence of 0.1 mol % of the heterogeneous catalyst. Specifically, it was observed that N-alkylated indoles exhibited better conversions than the non-alkylated substrates. In addition, a comparison between the aryl halides showed that aryl iodides were more efficient than the chlorides or bromides, as the arylating agent. In all these investigations, the Pd-NPs could be easily separated from the reaction mixture through centrifugation and decantation, thereby generating recyclable catalysts [11]. Another research group, Cao and co-workers reported the use of similar perfluorinated alkane-functionalized molecular organic frameworks (MOF), which could encapsulate Pd-NPs, and thereby act as efficient catalysts for C-H functionalization reactions. NU-1000 MOF [ $Zr_6(\mu^3-OH)_8(OH)_8(TBAPy)_2$ ], where TBAPy = 1,3,6,8-tetrakis(p-benzoate)pyrene was reacted with perfluorinated alkanic acids and this moiety was utilized to encapsulate the palladium nanoparticles. It is worth noting that the C2-H could be arylated in

indoles and the reaction could be effectively carried out in the greenest solvent, which is water [12]. In many reports, the measurement of the yield, size and concentration of metal nanoparticle catalyst such as fluorosilica gel perfluoro-tagged palladium nanoparticles was carried out using techniques like inductively coupled plasma atomic absorption spectroscopy (ICP AAS), XRF and TEM. Also, the degradation due to catalytic activity at the reaction temperature was also studied using XRD for metal nanoparticle catalysts [4].

Among the different transition metals, gold-catalyzed organic transformations are widely explored by various research groups [13-15]. In particular, Au-NPs are found to be quite efficient catalysts and these are also observed to be structure-sensitive in nature. The structural sensitivity of the intrinsic Au nanocatalysts is studied through high resolution transmission electron microscopy (HRTEM), X-ray photoelectron spectroscopy (XPS) and X-ray absorption near edge spectroscopy (XANES) characterization. A correlated spectrum obtained of Au 4f XPS and Lm-edge XANES indicates the bulk Au like electronic structure for the Au nanoparticles supported on SiO<sub>2</sub> larger than 3 nm whereas the particles below 3nm showed structures deviating from the Au bulk structure. This characterization has shown how the controlled synthesis of the catalyst has affected the surface and interface design. *In-situ* diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) measurements were also conducted to analyze the CO adsorption on the low-coordinated Au atoms on Au nanoparticles supported on SiO<sub>2</sub>. DRIFTS measurement showed that CO adsorption was proportional to the concentration of Au (3-4 nm) nanoparticles. This observation was logical, as the catalytic oxidation of CO occurs when it is adsorbed by the Au nanoparticles. Moreover, the low-coordinated Au atoms on Au/SiO<sub>2</sub> act like an active site at room temperature. For the larger-sized Au NPs (>4.5 nm) the CO adsorption was lower mainly due to size effects and smooth surfaces. Lower adsorption was also observed for the size below 3 nm reasoning the structure effects [5, 6]. In these investigations, Au NPs supported on TiO<sub>2</sub>, Fe<sub>2</sub>O<sub>3</sub> and Co<sub>3</sub>O<sub>4</sub> have been extensively studied showing rapid catalytic activity for size below 5 nm.

One of the very important organic transformation reactions includes the Fischer-Tropsch synthesis (FTS) reaction. It is a prominent method to obtain synthetic petroleum through the conversion of syngas, which can be obtained from coal or shale gas, in presence of a suitable catalyst [16]. Among the different metal-based catalysts, ruthenium

nanocatalysts have been successfully utilized in these types of reactions [17]. In the characterization study of Ru nanocomposite catalysts, the annular dark-field image obtained from scanning tunneling electron microscope shows the FCC structures and (311), (211) active planes of the Ru nanocomposite catalysts. The images and the diffraction pattern can be seen in detail in ref [5]. Different structures and the facets of the Cu<sub>2</sub>O nanocatalysts were also investigated using TEM. Cubic Cu, octahedral Cu, rhombic dodecahedra Cu NCs were observed.

An extensive analytical and structural characterization using nano X-ray computer tomography, electron tomography and TEM was reported by Spiecker and coworkers in 2021 [6]. Here the authors have explained the design and importance of Ga-Pd NP-based catalysts. For the samples above 100 nm the 3D structural characterization was carried out using FIB-SEM using slice and view method, for the samples below 100 nm the atomic probe tomography gave atomic resolution images. These Ga-Pd nanocatalysts had exhibited excellent activity in alkane dehydrogenation reactions.

In 2017, Kempasiddaiah *et al.* have reported an interesting green synthesis approach where biomass carbon-supported Pd heterogeneous catalyst is prepared for energy storage application [18]. In their report, they have used FESEM-EDX to study the surface morphology and its composition. The images revealed the porous nature of the synthesized materials. The TEM images showed a crystalline (111) plane and FCC nature of the Pd nanoparticles. Other tools of characterization, XRD, FTIR, ICP-OES, NMR, TGA, CHNS, were also employed to study the detailed structure and composition. Cyclic voltammetry, galvanostatic charge discharge (GCD) and electrochemical impedance spectroscopy (EIS) were used for electrochemical analysis.

Metal oxide nanoparticles in a biomass-based solvent like glycerol have been studied because of their wide applications. Chahdoura *et al.* have reported such synthesis of copper (I) oxide nanoparticles which were stabilized by poly vinylpyrrolidone in neat glycerol (under hydrogen atmosphere) [19]. TEM characterization showed particle size of NPs in the range of 3-6 nm along with formation of aggregates. XRD analysis, XPS and IR spectroscopy were also carried out to study the structure of the NPs.

In 2021, Pamidimukkala and Shaikh reported the catalytic utility of palladium-based nanocatalysts in a carbon-carbon cross-coupling reaction, like Suzuki-Miyaura reaction. The Pd-NPs were supported on magnetic chitosan. While the inherent

magnetic property of these nanocatalysts allowed easy separation, the characterizations were carried out using a wide variety of spectroscopic methods, including infrared spectroscopy (IR), transmission electron microscope (TEM), and some methods based on X-ray, such as X-ray powder diffraction (XRD), X-ray absorption near edge structure (XANES) spectroscopy and X-ray photoelectron spectroscopy (XPS). The thermal behavior of the catalysts was analyzed using thermogravimetric analysis. The catalysts exhibited remarkable activity in Suzuki reaction, in which the catalyst loading was 0.0055 mol% and over 99 % yield was obtained.

#### *Significance and future scope of NP-based catalysts*

In order to efficiently follow the basic principles of Green Chemistry, catalysts are essential as opposed to stoichiometric reagents. In addition, the more recyclable a catalyst, the less wastage is produced and less resources are required. These factors ensure the importance of nanoparticle-based catalysts. Since researchers are now more aware of these facts, a wider group of nanoparticles are being investigated to find out specific catalytic applications. Hence, different characterization techniques are essential in both studying the NP-based catalysts and exploring their catalytic reactions.

#### *Conclusion*

Thus, we observed that owing to the excellent property of recyclability, the palladium-based nanocatalysts have been able to contribute effectively to the development of various organic reactions, which are industrially important. Different carbon-carbon cross-coupling reactions, like Suzuki-Miyaura, Sonogashira, Stille, etc., have been explored using Pd-NPs [20]. In addition, analysis of the newly designed catalysts is of prime importance, in order to fully understand the mechanism of the reactions involved and the catalytic process. Hence, heterogeneous nanoparticle-based catalysts have been extensively characterized using a wide range of spectroscopic methods.

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