

Editorial

# Metal-Based Catalysts in Organic Synthesis

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The role of catalysts is extremely important for various organic transformations and the synthesis of organic compounds. In the last two decades, a significant growth has been observed in the areas of catalytic processes with the development of several catalytic methods e.g., transition metal catalysis, organocatalysis, photocatalysis, electrocatalysis and biocatalysis [1,2]. Metal based catalysts are a widely used catalytic system and have notable contribution towards the synthesis of organic compounds. They can be simple metal salts, metal oxides or metal complexes which can exhibit high catalytic activity. They have diverse applications as catalysts under homogeneous, heterogeneous or onto solid support conditions, from academic to industrial research laboratories for the transformation of organic compounds [3]. Several techniques have already been explored, such as the use of microwave irradiation, ultrasound, light assisted or the use of ionic liquid or a supercritical CO<sub>2</sub> medium to drive the catalytic reaction energy efficiently. The development of new, sustainable and energy efficient catalytic processes is a great challenge for the synthesis of organic compounds.

This special issue is dedicated to contemporary progress of new metal-based catalytic systems for the synthesis of organic compounds. Four research articles address four different areas of metal-based catalytic processes towards the development of organic synthesis.

The first article deals with the catalytic carbocation of 2-alkynylamines, 1-alkynylphosphine and -phosphine sulfides [4].

The EtMgBr and Ti(O-*i*Pr)<sub>4</sub>-catalyzed reaction of the mentioned compounds with Et<sub>2</sub>Zn has been studied in various solvents, such as diethyl ether, methylene chloride, hexane, toluene, benzene, and anisole. Selective formations of 2-alkenylamines and 1-alkenylphosphine oxides from 2-alkynylamines and 1-alkynylphosphines are obtained after oxidation with H<sub>2</sub>O<sub>2</sub> in diethyl ether, whereas a mixture of stereoisomers is formed in other solvents. In 1989, Kulinkovich et al. first reported the formation of a titanacyclopropane complex upon the reaction of ethylmagnesium bromide with titanium (IV) alkoxides [5]. In this work, the reaction of (cyclopropylethynyl) diphenylphosphine sulfide was non-regioselective and produced a mixture of 1-alkenylphosphines regioisomers. This study shows a useful pathway for the transformations of functionalized acetylene derivatives using metal complex catalyzed organozinc synthesis. A proposed mechanism of Ti-Mg-catalyzed carbocation of substituted 1-alkynylphosphine sulfides with Et<sub>2</sub>Zn is also illustrated.

The second article describes the catalytic performances of a series of transition metal (Fe, Co, Ni, Cu, Ce)-modified titanium silicalite-1 (M-TS-1) catalysts towards the ammoxidation of methyl ethyl ketone (MEK) [6]. Ultrasonic impregnation method was applied for the preparation of transition metal-modified TS-1 [7]. The nickel-modified TS-1 catalyst exhibits good conversion and high selectivity of methyl ethyl ketoxime (MEKO) with H<sub>2</sub>O<sub>2</sub> as the oxidant. It also shows efficient recyclable properties [6]. The nickel modification changes the electron environment of the Ti active site and optimizes the adsorption capacity for H<sub>2</sub>O<sub>2</sub> activation. It also helps to reduce the surface acidity of the catalyst and prevents the further oxidation of oxime.

The third article reports the use of Pd nanoparticles and a mixture of CO<sub>2</sub>/CO/O<sub>2</sub> towards the carbonylation of aniline to *N,N'*-diphenylurea [8]. PdCl<sub>2</sub>(2,4Cl<sub>2</sub>Py)<sub>2</sub>, PdCl<sub>2</sub>(4MePy)<sub>2</sub>, PdCl<sub>2</sub>,

palladium nanoparticles (PdNPs), and palladium-based nanostructural material (PdNM) are studied as pre-catalyst for the carbonylation of aniline. The highest conversion and selectivity of aniline to *N,N'*-diphenylurea is reported for PdNPs with the mixture of CO/O<sub>2</sub> and CO<sub>2</sub> as the carbonylating agent. The proposed catalytic cycle shows that Pd(0) stabilized by pyridine ligand is the active species for the carbonylation reaction. This hypothesis attributes the efficiency of PdNPs over Pd(II) complexes.

The last article by Roy Barman et al. elucidates the comparison of catalytic activities towards the oxidation of cyclohexane with Fe(III) complexes under different energy stimuli (microwave irradiation, ultrasound and conventional heating) [9].

The oxidation of cyclohexane to cyclohexanol and cyclohexanone has a high industrial significance for the manufacture of Nylon-6,6 [10]. Three different Fe(III) compounds derived from *N'*-acetylpyrazine-2-carbohydrazide (H<sub>2</sub>L) have been reported and their catalytic activities are compared in three different energy stimuli. The iron complex [Fe(HL)(NO<sub>3</sub>)(H<sub>2</sub>O)<sub>2</sub>]NO<sub>3</sub> (1) shows the highest catalytic activity under optimized microwave irradiation conditions compared to [Fe(HL)Cl<sub>2</sub>] (2) and [Fe(HL)Cl(μ-OMe)]<sub>2</sub> (3) [9].

This special issue is versatile in terms of catalytic reactions and their applications. This collection will bring much interest to the researchers in the field of catalysis.

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**Conflicts of Interest:** The authors declare no conflict of interest.

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