# IN THE NAME OF GOD


**Faculty of Science**

**M.Sc. Thesis in Organic Chemistry**

# NEW APPLICATION OF ALUMINUM TRIS (DODECYLSULFATE) TRIHYDRATE AS A LEWIS ACID-SURFACTANT-COMBINED CATALYST IN WATER

**By**

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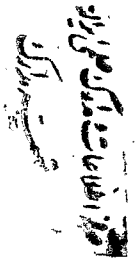

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**BY:**

Asma Riazi

**THESIS**

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*Dedicated to:*

*My Parents and my brother, Dr. Ehsan Riazi*

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## Abstract

**New applications of aluminum tris(dodecylsulfate) trihydrate as a Lewis acid-surfactant- combined catalyst in water**

**By:**

**Asma Riazi**

In this thesis we have focused our attention on three important transformations in organic synthesis in water in the presence of aluminum tris(dodecylsulfate) trihydrate as a potential Lewis acid surfactant combined catalyst (LASC). We have studied the ring opening of epoxides with different nucleophils, the three compounent Biginelli reaction and Michael reaction with carbon nucleophiles such as α-nitro ethyl acetate, malononitrile and etc. Reactions proceeded with excellent yields in mild conditions.

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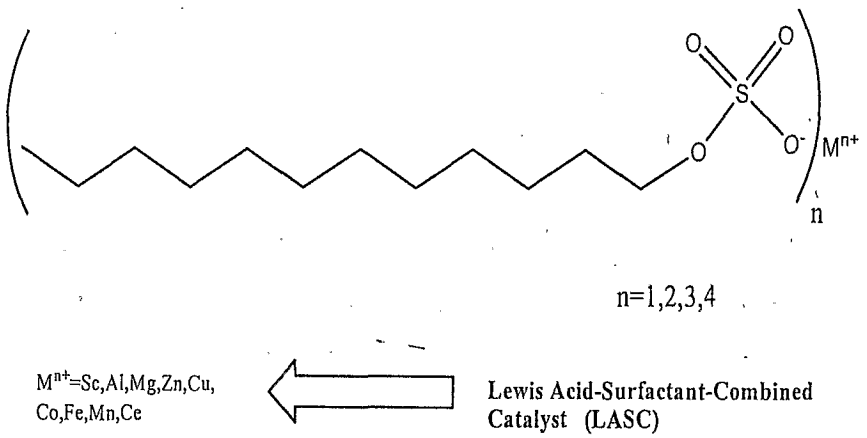
## 1.1. Introduction:

Although today's environmental consciousness imposes the use of water as a solvent on both industrial and academic chemists but organic solvents are still used instead of water for mainly two reasons. First, most organic substances are insoluble in water, and as a result, water does not function as a reaction medium. Second, many reactive substrates, reagents, and catalysts are decomposed or deactivated by water. Our goal is to develop a novel catalytic system which enables the use of water as a solvent for a wide range of reactions of organic materials.[1] The first drawback in the use of water (the solubility problem) may be overcome by using surfactants, which solubilize organic materials or form colloidal dispersions with them in water.[2] Indeed, surfactants have been occasionally used in organic synthesis. One very successful example is emulsion polymerization.[3] Some late transition metal-catalyzed reactions in water have been also conducted in the presence of surfactants or surfactant-like ligands.[4] In many other cases, however, large quantities of surfactant molecules in compare to the reaction substrates are needed for the desired reactions to proceed efficiently, and thus, the systems are impractical even if water can be used as a solvent.[5] From the viewpoints of practicability and applicability, the surfactant-aided organic synthesis is still at the preliminary stage. In the course of investigations to circumvent the second drawback in the use of water (the decomposition problem), Kobayashi and co-workers studied Lewis acids that work in aqueous media. To avoid the use of cosolvents, which are often required for best efficiency, the effect of anionic surfactants such as SDS on Lewis-acid-catalyzed aldol reactions and allylation reactions in water was investigated. These reactions, too, benefited greatly

from the addition of surfactants. Taking this concept one step further, Kobayashi and co-workers developed a new type of Lewis acids in which the active metal cation carries long anionic hydrocarbon sulfate or sulfonate ligands (Figure 1) that gave them ability of micellar aggregates in water. These so-called Lewis acid- surfactant combined catalysts (LASCs) have been successfully employed in aqueous Diels-Alder reactions, aldol reactions, Mannich-type reactions, and allylation reactions.[7] Recently, in our laboratory, Firouzabadi et. al have also introduced aluminum tris(dodecyl sulfate) trihydrate [$Al(DS)_3.3H_2O$] as another Lewis acid-surfactant- combined catalyst (LASC) for Michael addition of indoles and pyrroles to α, β-unsaturated electron-deficient compounds,[8] ring opening of epoxides with aromatic amines and synthesis of thiiranes from epoxides in water.[9]




**(Figure 1)**

## 1.2. A Brief literature review on organic chemistry in water:

Water plays an essential role in life processes, however its use as a solvent has been limited in organic synthesis. Despite the fact that it is the cheapest, safest and most non-toxic solvent in the world, its presence is generally avoided through the

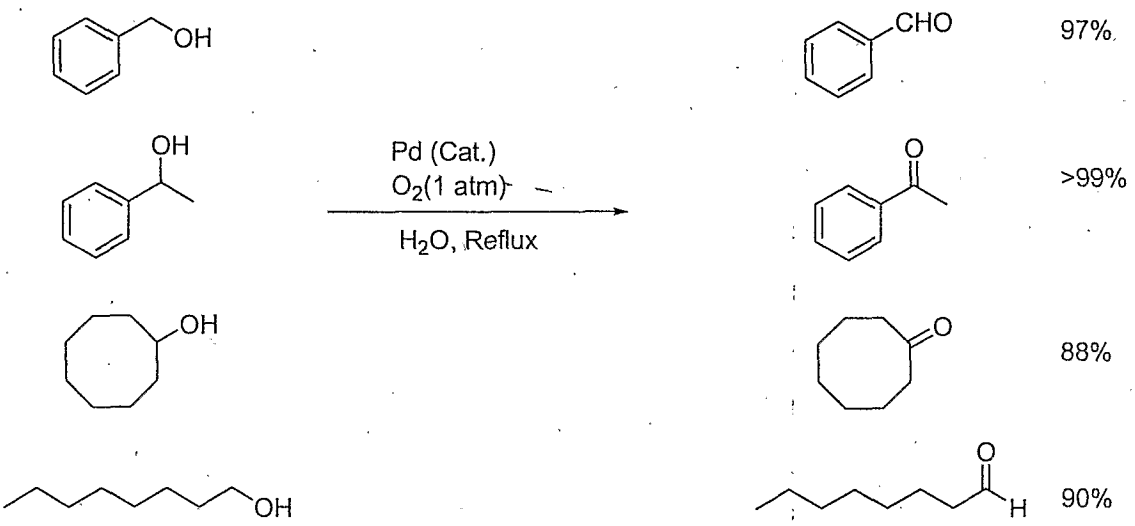
dehydrative drying of substrates and solvents. The use of water as a medium for organic reactions is therefore one of the latest challenges for modern organic chemists.[10] The types of organic reactions in water are broad including pericyclic reactions, reactions of carbanion equivalent, reactions of carbocation equivalents, reactions of radicals and carbenes, transition-metal catalysis, oxidations-reductions. Aqueous organic reactions have broad applications such as synthesis of biological compounds from carbohydrates and chemical modification of biomolecules.

### 1.2.1. Oxidations

Oxidative transformations of functional groups are fundamental processes in organic chemistry, being used in both laboratory synthesis and in the manufacturing of bulk chemicals.[11] The search for new, modified, and improved procedures is intensifying, driven mostly by the need for cleaner selectivity and higher efficiency, and by economic and environmental constraints. In the last few years, there has been a strong emphasis on the use of so-called "Green Chemistry" in an effort to protect the environment from pollutants.[12,13] Stoichiometric oxidation with metal oxidants, such as silver oxide, manganese oxide, nickel peroxide, and chromium and copper compounds, are generally used for the selective transformation of functional groups.[14] These reagents however are corrosive and contain toxic heavy metals in their reduced form. The disposal of these metal oxidants is undesirable from both an economic and environmental point of view. Therefore, research has been directed towards finding ways to use these metals in catalytic amounts. As a result, great effort has been made to develop new and improved catalytic processes. An ideal catalytic oxidation reaction should take place at room temperature in an environmentally friendly solvent system, for example, in water with a green co-oxidant such as oxygen (air) or the extensively studied hydrogen peroxide.[15]

### 1.2.1.1.Oxidation of alcohols in water

Transition-metal-catalyzed aerobic oxidation of alcohols[16] is one of the typical examples. Although many highly efficient aerobic alcohol oxidation systems either catalyzed by transition-metal catalysts (mainly copper,[17] palladium, [18,19,] or ruthenium[20]) alone or in combination with nitroxyl radical 2,2,6,6-tetramethyl-piperidyl-1-oxy (TEMPO)[21,22] have been developed, only a few examples of catalytic aerobic oxidations of alcohols in water have been reported to date. For example, catalytic oxidation of alcohols can be achieved in water by molecular oxygen by using a novel amphiphilic resin-dispersion of palladium nanoparticles (ARP-Pd). In the presence of the nano-palladium catalyst, primary alcohols give the corresponding aldehyde products and secondary alcohols give the corresponding ketones in water (Scheme 1.1). ARP-Pd can be reused with negligible loss of catalytic activity after several runs.[23]




**(Scheme 1.1)**