



## **SYNTHESIZED COMPOUNDS THROUGH DIFFERENT SPECTROSCOPIC TECHNIQUES**

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### **ABSTRACT**

Catalysis plays an important role in sustainable chemistry, enabling the development of more efficient processes by minimizing the consumption of energy and reducing the generation of by-products. The design of efficient catalysts is a key point in this respect, where spectroscopy confers fundamental knowledge at the molecular scale. Among the different spectroscopies, infrared (IR) spectroscopy is of great interest, enabling information about the nature of active species and their action mechanism, leading to precise structure-activity correlations, which are key points in the design of new catalysts. Moreover, the dynamic behavior of the catalysts under working conditions can be also monitored by IR spectroscopy, where structural modifications of working catalysts have strong repercussions in catalysis. In this chapter, interesting examples will be discussed, related to industrial relevant processes, like Fischer-Tropsch synthesis, ethylene oligomerization, synthesis of aniline from nitro compounds, and the dehydration of aldoximes to nitriles.

**Keywords:** - Catalysis, synthesis, Spectroscopy, Catalysts, Glycerol

### **I. INTRODUCTION**

One of the greatest challenges in the current chemical industry is the development of high-efficient processes with increased selectivity and reduced generation of by-products. This has motivated extensive research in the last years focused on the use of alternative renewable feedstocks and on the development of less energetic reaction pathways or radically new chemical processes. Catalysis plays an important role in defining new eco-efficient processes, where improvements in catalyst design and in catalytic reactor engineering are key elements that have to be linked to each other. The rational development of catalysts with enhanced catalytic performance relies on a fundamental knowledge of the catalytic process encompassing the

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reaction mechanism, rate-limiting reaction step, and the nature of active sites of the catalyst, where spectroscopy and theoretical studies are key aspects.

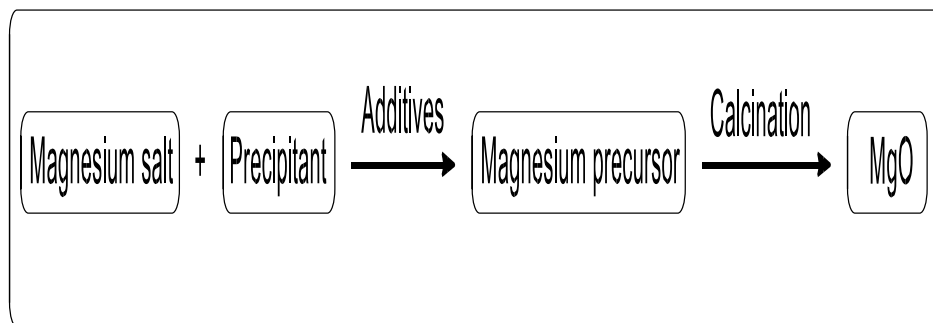
Spectroscopic techniques employ light to interact with matter and thus probe certain features of a sample to learn about its consistency or structure. Light is electromagnetic radiation, a phenomenon exhibiting different energies, and dependent on that energy, different molecular features can be probed. The basic principles of interaction of electromagnetic radiation with matter are treated in this chapter. There is no obvious logical dividing point to split the applications of electromagnetic radiation into parts treated separately. The justification for the split presented in this text is purely pragmatic and based on 'common practice'. The applications considered in this chapter use visible or UV light to probe consistency and conformational structure of biological molecules. Usually, these methods are the first analytical procedures used by a biochemical scientist. The applications covered in Chapter 13 present a higher level of complexity in undertaking and are employed at a later stage in biochemical or biophysical characterization.

## **II. ALKALINE EARTH METAL OXIDES CATALYZED TRANSESTERIFICATION OF GLYCEROL**

Heterogeneous base catalysts possess strong basic sites at the solid surface which can effectively increase the reactivity of glycerol. Metal oxides, as the most important heterogeneous bases, tend to exhibit excellent catalytic performance in the transesterification of glycerol with dialkyl carbonate to glycerol carbonate, especially for alkaline earth metal oxides. Compared to other metal oxides, alkaline earth metal oxides not only possess strong basicity, but also have better stability.

### **MgO Catalyzed Transesterification of Glycerol**

Magnesium oxide with different sorts of morphologies is conventionally prepared from the thermal decomposition of various magnesium precursors (Figure 1). The magnesium salt, precipitant, additive, preparation condition, and calcination temperature all have significant effects on the physical and chemical properties of MgO. More importantly, the catalytic performance of MgO is proved to have a close relationship with the morphology, surface area, particle size, crystallinity, and the concentration of basic sites of MgO catalyst.



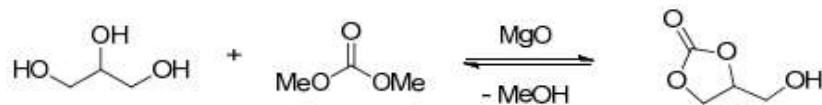
**Figure 1. General method for preparation of magnesium oxide.**

With commercially available MgO selected as a catalyst, transesterification of glycerol and dimethyl carbonate was studied (Table 1, entries 1–3). Research shows that the transesterification of glycerol can conduct DMF in the presence of sub-equivalent commercial MgO catalyst, providing glycerol carbonate with a low yield. However, in Wang and Yu’s research, transesterification can be conducted much more smoothly with the commercial MgO free of solvent, producing the product in a moderate yield. In order to further enhance the performance of the catalytic activity, a series of preparation methodologies of MgO were developed.

In 2014, Lee and co-workers disclosed the surfactant-assisted syntheses of MgO catalyst and the applications in the transesterification of glycerol to glycerol carbonate. The catalyst was prepared from the reaction of  $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  and the surfactant Pluronic F127 (a triblock copolymer of ethylene oxide/propylene oxide/ethylene oxide) in the presence of nitric acid (Table 1, entry 6). The results indicated that a much higher yield of glycerol carbonate was obtained in 75.4% yield than the ones without any modification of catalysts with surfactant. According to the titrating tests and  $\text{CO}_2$ -TPD experiments of the catalyst, the high catalytic activity of MgO is closely related with the higher basic site concentration of the surfactant-assisted MgO catalyst.

Besides, the catalyst could be easily recovered after centrifuging and reused after activating the catalyst at  $400\text{ }^\circ\text{C}$  in the nitrogen atmosphere and calcining to remove glycerol carbonate residue and avoid the decrease of catalytic activity. The yield of glycerol carbonate could be maintained at 68% in the 5th reuse.

**Table 1. Mixed oxides catalyzed transesterification of glycerol.**



Entry	Catalyst		Transesterification Conditions			Yield (%)	Sel. (%)
	Preparation Conditions	Morphology	Cat./Gly. (wt. Ratio)	DMC/Gly. (mol Ratio)	T/°C; t/h; Sol.		
1	Commercial MgO	-	0.54	5:1	100; 1; DMF	10.0	-
2	Commercial MgO; calcined at 400 °C	-	0.54	5:1	100; 1; DMF	9.0	-
3	Commercial MgO	-	0.04	4:1	75; 2; none	61.6	-
4	Mg(NO <sub>3</sub> ) <sub>2</sub> ·6H <sub>2</sub> O; calcined at 680 °C	Flake like	0.05	2:1	90; 0.5; none	11.1	92.5
5	Mg(NO <sub>3</sub> ) <sub>2</sub> ·6H <sub>2</sub> O, KOH; calcined at 680 °C	Irregular	0.05	2:1	90; 0.5; none	16.0	89.8
6	Mg(NO <sub>3</sub> ) <sub>2</sub> ·6H <sub>2</sub> O, surfactant, HNO <sub>3</sub> ; calcined at 680 °C	Sphere like	0.05	2:1	90; 0.5; none	75.4	98.8
7	Mg(NO <sub>3</sub> ) <sub>2</sub> ·6H <sub>2</sub> O, Na <sub>2</sub> CO <sub>3</sub> , 50 °C; calcined at 550 °C	Rod like	0.03	3:1	70; 1; none	<6.5	-
8	Mg(NO <sub>3</sub> ) <sub>2</sub> ·6H <sub>2</sub> O, Na <sub>2</sub> CO <sub>3</sub> , 70 °C; calcined at 550 °C	Spherical	0.03	3:1	70; 1; EtOH	<6.5	-
9	Mg(NO <sub>3</sub> ) <sub>2</sub> ·6H <sub>2</sub> O, Na <sub>2</sub> CO <sub>3</sub> , 70 °C; calcined at 550 °C	Flower like	0.03	3:1	70; 1; EtOH	< 6.5	-
10	Mg(NO <sub>3</sub> ) <sub>2</sub> ·6H <sub>2</sub> O, Na <sub>2</sub> CO <sub>3</sub> , 80 °C; calcined at 550 °C	Nest like	0.03	3:1	70; 1; EtOH	< 6.5	-

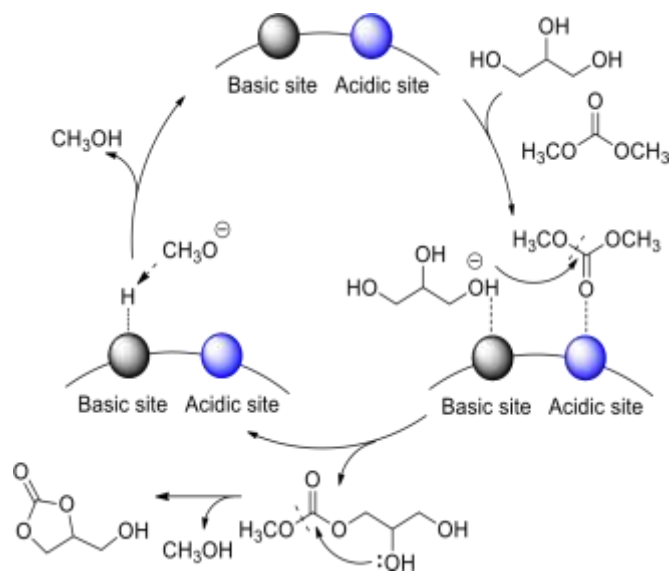
Entry	Catalyst		Transesterification Conditions			Yield (%)	Sel. (%)
	Preparation Conditions	Morphology	Cat./Gly. (wt. Ratio)	DMC/Gly. (mol Ratio)	T/°C; t/h; Sol.		
11	Mg(NO <sub>3</sub> ) <sub>2</sub> ·6H <sub>2</sub> O, Na <sub>2</sub> C <sub>2</sub> O <sub>4</sub> , 30 °C; calcined at 550 °C	Trapezoidal	0.03	3:1	70; 1; EtOH	93.0 <sup>2</sup>	-
12	MgO@ZIF-8: Mg(NO <sub>3</sub> ) <sub>2</sub> ·6H <sub>2</sub> O, ZIF-8, NaOH; calcined at 370 °C in argon	-	0.04	4:1	75; 2; none	70.0	-

<sup>1</sup> Gly. = glycerol; Sel. = selectivity; Sol. = solvent. <sup>2</sup> 99% yield after 3 h reaction.

Inspired by the previous work, Zhang and co-workers developed a series of micro-sized MgO catalysts with different morphologies and explored their catalytic performances in various organic syntheses in the past few years. As expected, MgO catalysts with rod-like, spherical, flower-like, nest-like, and trapezoidal morphologies were prepared via the precipitation of Mg(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O and precipitants Na<sub>2</sub>CO<sub>3</sub> or Na<sub>2</sub>C<sub>2</sub>O<sub>4</sub> varying from 30–80 °C within 3 min of stirring and further calcination (Table 1, entries 7–11). Recently, the trapezoidal MgO catalyst was successfully applied to the transesterification of glycerol and dimethyl carbonate, providing glycerol carbonate in more than a 99% yield. However, MgO with other morphologies could not perform well in the

transesterification. Compared to other morphologies of MgO, trapezoidal MgO possesses a bigger crystallite size, lower specific surface area, weaker surface basicity, and less Mg atom vacancies. Therefore, the perfect catalytic performance of MgO was attributed to the unique physicochemical property and morphology of the catalyst.

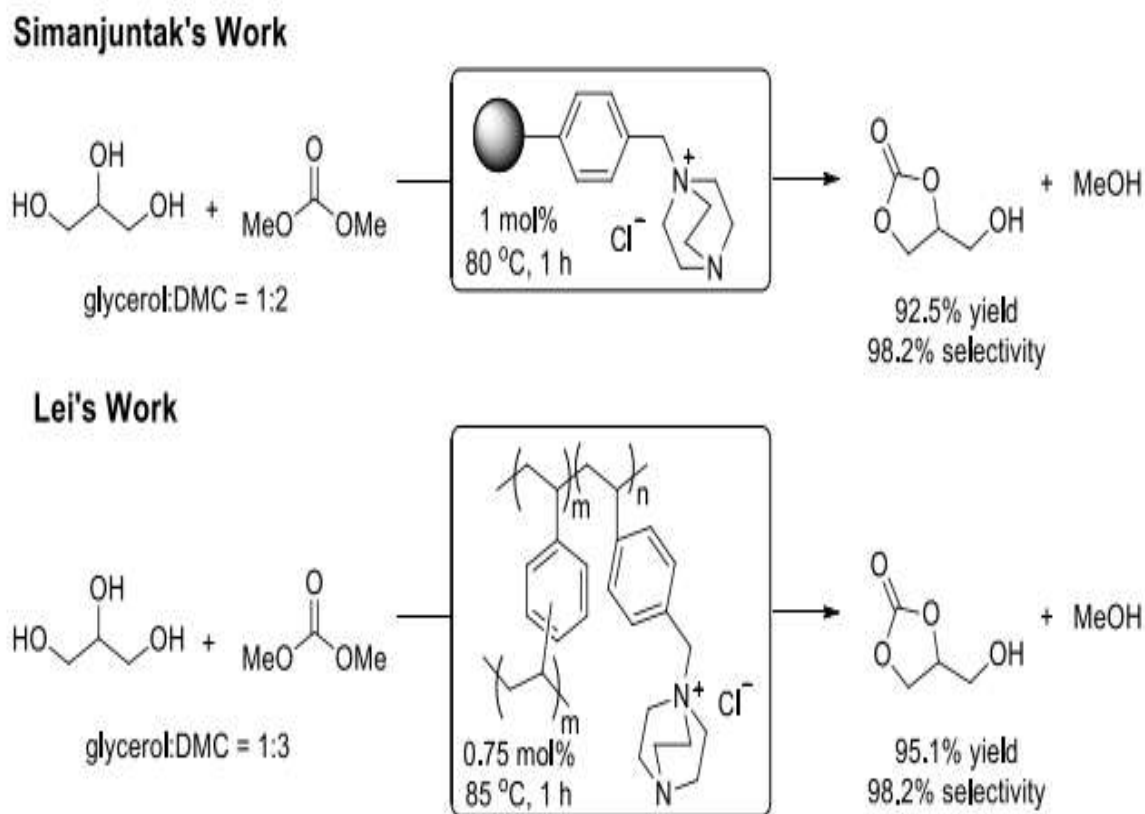
In the past few years, metal–organic frameworks (MOFs), as new microporous materials, have made great progress in heterogeneous catalysis. Very recently, Wang and Yu synthesized MgO-loaded zeolitic imidazole framework-8 (designated as MgO@ZIF-8) catalysts with various MgO loadings through wet-impregnation and calcination (Table 1, entry 12). This MgO material maintained the ZIF-8 structure and possessed physical property of high surface area and regular porosity, and decent thermal/chemical stability. The catalytic performance of MgO@ZIF-8 in transesterification had a certain enhancement compared to MgO, ZIF-8, and the physically mixed counterparts. An acid–base bifunctional catalytic process was proposed by Wang and Yu et al. (Figure 2). The higher catalytic activity could be attributed to the bifunctional sites on the surface of MgO catalyst. The low-coordinated zinc atom and NH groups of imidazole provided acidic sites to activate dimethyl carbonate, meanwhile MgO and nitrogen atoms in imidazole provided basic sites to activate glycerol by abstracting proton to generate glyceroxide ion. Results also showed that more basic sites were generated on the ZIF-8 surface with the incorporation of MgO nanoparticles and the basic sites play much more important roles in the catalytic transesterification.



**Figure 2. Plausible reaction mechanism for bifunctional catalysis in the transesterification of glycerol, (reprinted with permission from Reference, Elsevier).**

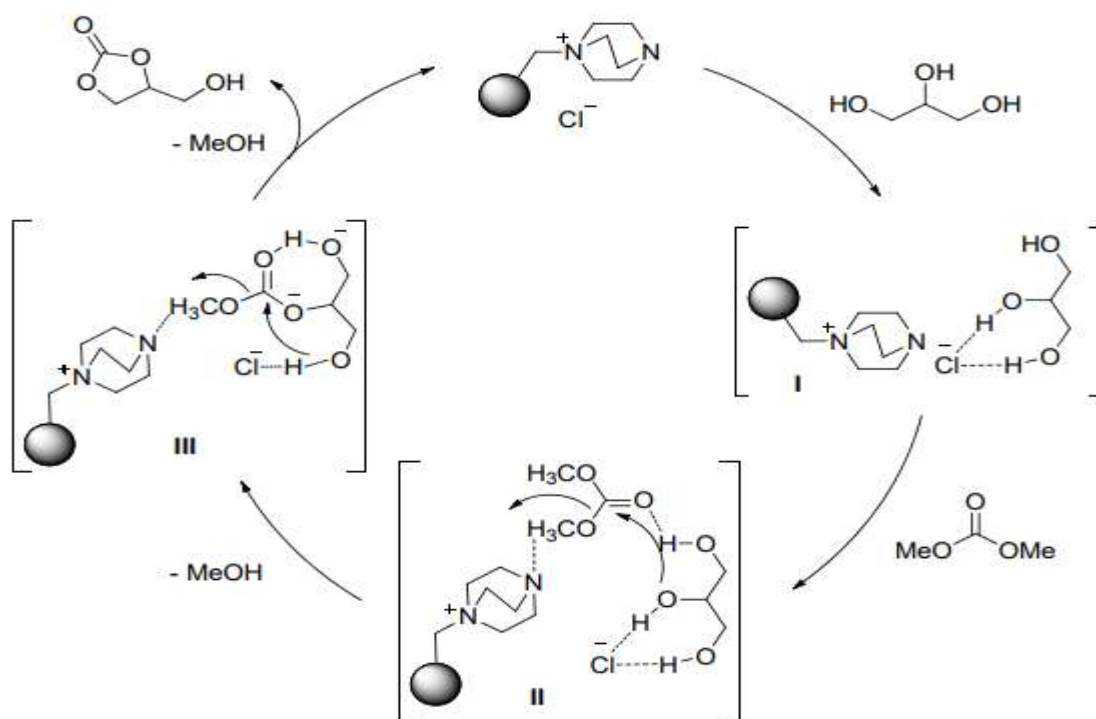
### III. Heterogeneous Organocatalysis for Transesterification of Glycerol

Organocatalysis has been rapidly and widely developed in the past few decades. With the exception of inorganic base, amines as organic bases are often chosen as catalysts in transesterification, and DABCO (1,4-diazabicyclo(2.2.2)octane) has proved to be a highly active and efficient homogeneous organic catalyst for the transesterification of glycerol with DMC to afford glycerol carbonate. As a homogeneous catalyst, DABCO is still confronted with problems of catalyst recovery and reusability. Therefore, Kim and Lee et al. synthesized a series of heterogeneous polyamine-anchored Merrifield resin catalysts and the DABCO-anchored catalyst exhibited excellent activity and selectivity (Figure 3). The resin catalyst can easily be recovered after simple manipulation and directly reused without any loss in yield and selectivity. Subsequently, Lei and co-workers reported an organ catalytic transesterification of glycerol with DMC using a bifunctional and robust catalyst with a DABCO-embedded porous organic polymer structure. With this excellent solubilization capacity polymer catalyst, comparative results were achieved in both activity and selectivity. Besides, the improvement of catalyst can easily be achieved in chemistry through the modification of polymer precursors.



**Figure 3. DABCO-derived heterogeneous catalysis in the transesterification of glycerol**

According to the results of the computational calculation and experiments, Simanjuntak and co-workers proposed a plausible mechanism for the DABCO-anchored Merrifield resin-catalyzed transesterification of glycerol (Figure 4). The high activity and selectivity of the reaction could be attributed to the following respects: 1) glycerol could be activated via the formation of strong hydrogen bonds with the chloride anion of catalyst (I); 2) hydrogen bonding interactions of DMC with the nitrogen atom and the remaining hydroxyl group of glycerol (II); 3) electrostatic interaction of contact counter ions in catalyst (III) which would effectively promote the intramolecular cyclization in the activity and selectivity of the reaction.



**Figure 4. Plausible mechanism of DABCO-anchored Merrifield resin-catalyzed transesterification of glycerol, (reprinted with permission from Reference, Elsevier, 2015)**

*N*-heterocyclic carbene (NHC), as an active organic base catalyst, has been used as an efficient homogeneous organ catalyst for the transesterification of glycerol with DMC for a long time. Considering the facile recovery and reusability of catalyst, NHC was immobilized on silica-supported mesostructured cellular foam (MCF) with hydrogen carbonate as protecting group by Buijninix and co-workers.

#### IV. CONCLUSION

With the increasing demand for the clean energy of biodiesel, glycerol as the main byproduct is confronted with a saturated state of the market. Glycerol carbonate, as one of the promising downstream products, is gaining widespread concern. This review has documented recent

advances in heterogeneous catalysis in the transesterification of glycerol to glycerol carbonate. The heterogeneous catalysts are focused on alkaline-earth metal oxides, hydrotalcites, zeolites, clinoptilolites, organic base catalysts, etc. Heterogeneous base catalysts, especially for alkaline-earth metal oxides, possess strong basic sites and exhibit excellent catalytic performance in transesterification. Mixed oxides are particularly preferred for transesterification due to their higher contents of acidic and basic sites, which are essential for the reaction.

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