

# Original Article: The Use of Silica@Zn<sup>+2</sup> as a catalyst in Diels-Alder reactions



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## ABSTRACT

In this study, the application of the Diels-Alder cycloaddition reactions between methyl acrylate and cyclopentadiene has been studied using a silica-supported catalyst with various concentrations of Zn<sup>2+</sup> ion (Silica@Zn<sup>+2</sup>) as Lewis acid catalyst without using the solvent. The effective role of silanol groups in increasing the stereoselectivities of products was also studied.

## Introduction

The Diels-Alder reaction is applied to provide C-C bonds to afford molecules with a double bond and two formed C-C single bonds [1, 2]. This reaction leads to six-membered rings and the challenge is to control the regioselectivity and stereochemistry [3]. Typically, the reaction leads under mild

reaction conditions with dienes and dienophile structures, with external thermal energy or pressure. There are various processes to grow the rate of Diels-Alder reaction, [4] and the use of Lewis acids, [5] heterogeneous acids, [6, 7] high pressures, [8, 9] and ultrasound irradiation [10].

Furthermore, the reaction not only occurs in solution but also on solid surfaces such as

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alumina, [11] K10 montmorillonites,[12] and zeolites [13]. Silica gel due to its widespread availability, high surface area, high thermal stability, and many reactive sites for functionalization is accessible support. Silica gel has been used as the catalyst for Diels–Alder reactions [14–17]. For example, ZnCl<sub>2</sub> supported on silica gel was studied in the treatment of furan with acrylonitrile, 2-chloroacrylonitrile, and methyl acrylate [18].

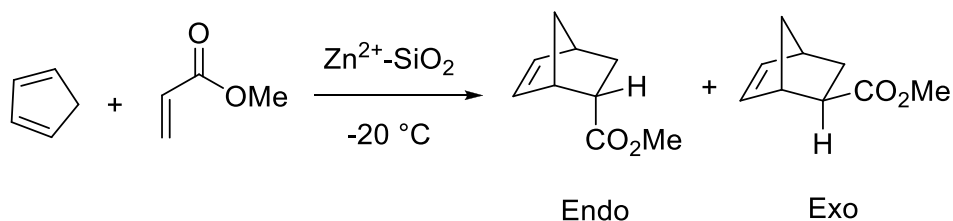
In an earlier study, the diastereoselective Diels–Alder reaction was reported on the silica as support with various concentrations of cerium as Lewis acid catalysts solvent-free conditions [19]. therefore, the Diels–Alder reactions of methyl acrylates with cyclopentadiene, promoted by Zn<sup>2+</sup> on the silica surface as support was reported in this paper. In this regard, many concentrations of Lewis acid ZnCl<sub>2</sub> on silica gel surface were obtained by various zinc ions in alkali conditions.

## Experimental

### Apparatus and analysis

*It was added in Supporting information.*

### Preparation of Silica@Zn<sup>2+</sup>



**Scheme 1.** The Diels–Alder reaction of methyl acrylates and cyclopentadiene.

Then, the diastereoselectivity of Diels–Alder reactions of cyclopentadiene and methyl acrylate with the resulting solid acids was studied (Table 2). The reaction was performed with pure silica, to see the effect of the Zn<sup>2+</sup> concentration on reaction rate. It was observed that the reaction pictures a good yield, with less diastereoselectivity (Table 2, entry 1). The results indicated that an increase in the amount

Silica gel (20 g) was added to ammonium (1 M) for 5 min to gain NH<sub>4</sub><sup>+</sup>-SiO<sub>2</sub>, different volumes of distilled water with different concentrations of zinc chloride were added and mixed for 30 min at room temperature (Table 1.). It was filtered and washed with acetone (30 mL) and dried to get solids as support.

### Diels–Alder reaction under solvent-free conditions (in a phase of gel)

Methyl acrylate (0.9 mL, 10 mmol) was added to Zn<sup>2+</sup>-SiO<sub>2</sub> (5.5 g) as support in a flask. The reaction mixture was stirred for 45 min and cooled at -20 °C, then distilled cyclopentadiene (2.5 mL, 26 mmol) was added to by stirring for 2 h at -20 °C. Finally, the product was extracted by Soxhlet for about 24 h. The yield of the reaction was calculated by GC.

## Results and discussion

The catalytic performance of ZnCl<sub>2</sub> on the silica surface in the cycloaddition reaction of methyl acrylates and cyclopentadiene (Scheme 1). Table 1 shows the experiments using A mL distilled water and B mL zinc chloride (0.1 M) for gaining supports with different concentrations of Zn<sup>2+</sup>.

of ZnCl<sub>2</sub> concentration has a positive effect on the yield and diastereoselectivity. This could be due to the concentrating methyl acrylates on the silica surface by the coordination of methyl acrylate with zinc ions.

The best result was achieved with 80% ZnCl<sub>2</sub> concentration.

**Table 1.** Various quantities used for the preparation of silica supports with different concentrations of Zn<sup>2+</sup>

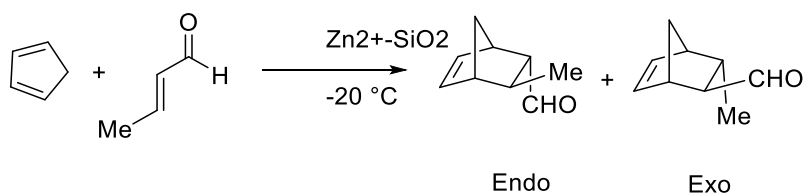
Incorporated metal ion onto the silica pores (%)	Distilled water (A mL)	The volume of 0.1 M ZnCl <sub>2</sub> (B mL)
0	100	-
1	99	1
5	95	5
10	90	10
25	75	25
50	50	50
60	40	60
70	30	70
80	20	80

**Table 2.** The catalytic effect of silica surface supported with different concentrations of Zn<sup>2+</sup> ion on the cycloaddition reactions of methyl acrylates and cyclopentadiene.

ZnCl <sub>2</sub> Concentration (%)	Yield (%)	de (%)
0	95	67
1	96	69
5	96	70
10	97	70
25	97	80
50	97	86
60	99	87
70	99	90
80	100	92

To further explore the potential of this protocol, we investigated the Diels-Alder reaction involving crotonaldehyde and cyclopentadiene by Silica@Zn<sup>2+</sup> as support (50%

ZnCl<sub>2</sub> concentration) (Scheme 2). To our delight, the reaction was accomplished smoothly and the desired cycloadduct was gained in 79% yield with 77% diastereoselectivity.

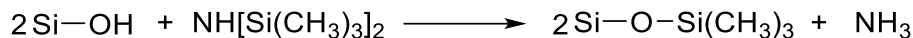
**Scheme 2.** The Diels-Alder reaction of crotonaldehyde and cyclopentadiene.

The catalytic activity was done by the adsorption and coordination of Lewis acid as zinc ion with methyl acrylate and hydrogen bonding of the dienophile by acidic Si-OH on the silica surface.

The silica surface has two functional groups including siloxane (Si-O-Si) and silanol group

(Si-OH) which silanol groups act like weak acids (pK<sub>a</sub> = 9.4).

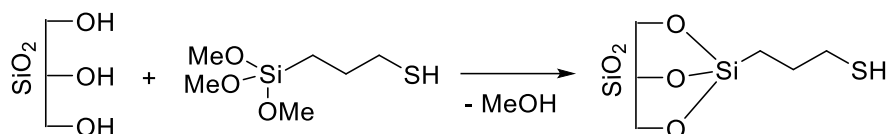
The role of hydrogen bonding on the reaction, treatment of silanols with hexamethyldisilazane (HMDS) was done to protect the remaining free silanol groups according to equation 1.



### Equation 1

The resulting  $\text{Zn}^{2+}$ - $\text{SiO}_2$  (50%  $\text{ZnCl}_2$  concentration) with protected silanol groups was then examined in Diels–Alder reaction of cyclopentadiene and methyl acrylate giving a yield of 97% with 57% diastereoselectivity. The decrease of the selectivity of cycloadducts (from 86% to 57%) is supposed to be the result of a decrease in the formation of silanol groups hydrogen bonds to the methyl acrylate. This means that methyl acrylate molecules can change their positions more freely within the cavities, resulting in poor stereoselectivity of the reaction.

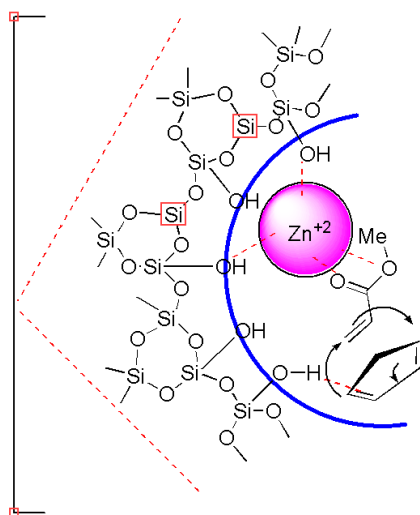
In another experiment, to verify the specific effect of silanol groups, the silica surface was grafted with (3-mercaptopropyl)trimethoxysilane (MPTS) to prepare the thiol functionalities on the surface (Scheme 3). By previous results, it was observed that diastereoselectivity of cycloadducts in the presence of  $\text{Zn}^{+2}$  on the silica surface as support (50%  $\text{ZnCl}_2$  concentration) was decreased from 86% to 65%. Also, in comparison with the result obtained from the silica surface with no  $\text{Zn}^{2+}$  on it (Table 2, entry 1), almost the same diastereoselectivity was observed.



### Scheme 3. Thiol functionalization of the silica surface.

The impregnation of silica surface with  $\text{ZnCl}_2$  was studied, which reduced silanol groups to the minimum level. The Diels–Alder reaction was carried out and 76% diastereoselectivity was obtained.

It could be concluded that silica gel could be a promoter in the Diels–Alder reaction since it involves the formation of hydrogen bonding with  $\text{Zn}^{2+}$ , followed by attracting and fixing dienophile to react with Diene in diastereoselective manner (Scheme 4).



### Scheme 4. hydrogen bonding of dienophile to the hydrogen of the hydroxyl group of silica gel.

## Conclusion

In conclusion, we have reported a very effective heterogeneous catalyst for the Diels-Alder reactions of cyclopentadiene and methyl acrylate. Silica gel could be modified by ZnCl<sub>2</sub> to prepare suitable Lewis acid sites on the surface of the support. The diastereoselectivity of the reaction depends on the zinc concentration on the silica surface. The effective role of silanol groups in increasing stereoselectivities was also studied.

## Acknowledgments

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