

Original Article: The Study of the Modified Silica by Different Metal Ions in Diastereoselectivity of Diels-Alder Reaction



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ABSTRACT

A mild procedure for the diastereoselective Diels-Alder reaction of methyl acrylate and cyclopentadiene was performed using modified silica with different concentrations of metal ions as Lewis acid support. According to the results, among the tested metal ions, cadmium ion supported on the silica was the best diastereoselective catalyst in this reaction.

Introduction

The 1,4-cycloaddition of a double and/or a triple bond to a conjugated diene leads to the formation of C-C bonds which is known as the Diels-Alder reaction [1-3]. Diels-Alder reaction is a valuable procedure for

the preparation of different chemical substances [4], especially natural compounds [5,6]. Diels-Alder adducts are often applied to create synthons, sometimes, uniquely privileged for other synthetic efforts and endeavors [7-9]. To the importance of the Diels-Alder reaction in

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chemical synthesis, different catalysts and conditions have been used to optimize it [10].

Unsymmetrical starting materials imply two different possible products which are called endo and exo compounds. Recently, the stereoselective Diels-Alder reaction promoted by catalysts attracted the attention of scientists. In this regards, different catalysts have been used to gain endo and/or exo selective product including chiral organoaluminum reagent [11], anthracenebisresorcinol derivative [12], chiral Yb(OTf)₃ [13], bis(oxazoline)copper (II) complexes [14], chiral diaquo titanocene complex [15], Cu(OTf)₂ [16], pyridil-bis(oxazoline) Zn (II) [17] and so on. Furthermore, Otto and coworkers investigated the effect of Co²⁺, Ni²⁺, Cu²⁺, and Zn²⁺ ions as catalysts on the rate and endo-exo selectivity of the Diels-Alder reaction in water [18].

Previously, our research group studied the role of incorporated cerium ions on the silica surface in diastereoselectivity of Diels-Alder reaction [19]. In this article, we want to investigate the effect of different metal ions loaded onto the silica pores in endo-exo selectivity of the Diels-Alder reaction.

Experimental

Materials and apparatus

It was explained in supporting information.

General procedure for the preparation of supports

Silica gel (20 g) was added to ammonium solution (100 mL, 1 M) and stirred for 5 min. Then, a given amount of distilled water and a soluble metal salt (0.1 M) (Table 1) were added to the obtained NH₄⁺-SiO₂, the mixture was

stirred for 30 min at room temperature. After this time, the mixture was filtered and washed with acetone and then dried in the oven for 30 min. The solid was stored in a polypropylene bottle as support.

General procedure for Diels-Alder reaction under solvent-free conditions (in a phase of gel)

Methyl acrylate (0.9 mL, 10 mmol) was added to the dried metal ion-SiO₂ (5.5 g) as support in dichloromethane (20 mL) and the mixture was well stirred at ambient temperature for 45 min. Then, the solvent was completely evaporated to obtain a dry powder. The mixture was placed in a cold bath with a temperature of -20 °C, then freshly distilled cyclopentadiene (2.5 mL, 26 mmol) was added to it with vigorous stirring for 45 min. When the addition of cyclopentadiene was completed, the reaction was continued for 2 h at -20 °C. Finally, the crude product was extracted with acetone in a Soxhlet apparatus for about 24 h. The yield and diastereoselectivity of the product were determined by GC with a standard solution of methyl acrylate in dichloromethane.

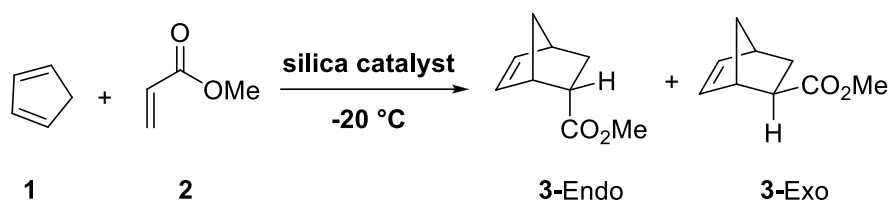
Results and Discussion

In this research, the effect of different metal ions is investigated in the diastereoselectivity of the Diels-Alder reaction. As shown in Table 1, different metal ions including NiCl₂, CoCl₂, CdCl₂, MnCl₂, (NH₄)₂Fe(SO₄)₂, CuCl, and CuCl₂ were used in different volumes to obtain various incorporated samples. Then, each metal ion loaded onto the pores of silica gel was used as catalysts in the Diels-Alder reaction of cyclopentadiene and methacrylate to investigate their diastereoselectivity (Scheme 1).

Table 1. Various quantities used for the preparation of silica supports with different concentrations of metal ions

Sample	Metal ion	The volume of 0.1 M metal ion (mL)	The volume of distilled H ₂ O (mL)	Incorporated metal ion onto the silica pores (%)
SiO ₂	-	-	-	-
Ni ²⁺ @SiO ₂ (50)	-	50	50	50
Ni ²⁺ @SiO ₂ (60)	NiCl ₂	60	40	60
Ni ²⁺ @SiO ₂ (80)	-	80	20	80
Co ²⁺ @SiO ₂ (50)	CoCl ₂	50	50	50

$\text{Co}^{2+}@SiO_2(60)$		60	40	60
$\text{Co}^{2+}@SiO_2(80)$		80	20	80
$\text{Cu}^{2+}@SiO_2(50)$		50	50	50
$\text{Cu}^{2+}@SiO_2(60)$	CuCl_2	60	40	60
$\text{Cu}^{2+}@SiO_2(80)$		80	20	80
$\text{Cu}^{1+}@SiO_2(50)$		50	50	50
$\text{Cu}^{1+}@SiO_2(60)$	CuCl	60	40	60
$\text{Cu}^{1+}@SiO_2(80)$		80	20	80
$\text{Fe}^{2+}@SiO_2(50)$		50	50	50
$\text{Fe}^{2+}@SiO_2(60)$	$(\text{NH}_4)_2\text{Fe}(\text{SO}_4)_2$	60	40	60
$\text{Fe}^{2+}@SiO_2(80)$		80	20	80
$\text{Mn}^{2+}@SiO_2(50)$		50	50	50
$\text{Mn}^{2+}@SiO_2(60)$	MnCl_2	60	40	60
$\text{Mn}^{2+}@SiO_2(80)$		80	20	80
$\text{Cd}^{2+}@SiO_2(1)$		1	99	1
$\text{Cd}^{2+}@SiO_2(5)$		5	95	5
$\text{Cd}^{2+}@SiO_2(10)$		10	90	10
$\text{Cd}^{2+}@SiO_2(25)$	CdCl_2	25	75	25
$\text{Cd}^{2+}@SiO_2(50)$		50	50	50
$\text{Cd}^{2+}@SiO_2(80)$		80	20	80



Scheme 1. Diels-Alder reaction in the presence of the prepared silica catalysts

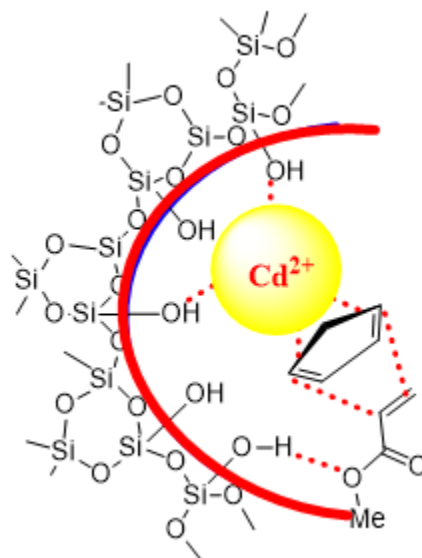
Diastereoselectivity (de) of the prepared silica catalyst in Diels-Alder reactions of cyclopentadiene and methyl acrylate are summarized in Table 2. The reaction was also performed in the presence of pure silica, to investigate the effect of the metal ions on reaction rate. Pure silica conducted the reaction to gain a high yield of product but de was poor (Table 2, Entry 1). It was observed that increasing the incorporated metal ion, leads to an increase of the reaction yield as well as de.

However, there was no significant change of yield and de as the incorporated Cu^{2+} was increased. Additionally, small amounts of incorporated Cd^{2+} onto the silica pores were also studied, in which the results showed high yield with low de (Entries 17-19). Among the tested catalysts, the best results were achieved in the presence of $\text{Cd}^{2+}@SiO_2(80)$ (Entry 25). This could be due to the concentrating methyl acrylates on the surface of silica through coordination with Cd^{2+} (Scheme 2).

Table 2. Catalytic effect of different silica catalysts in diastereoselectivity of Diels-Alder reaction.

Entry	Catalyst	Yield (%)	Diastereoselectivity (%)	Endo/Exo
1	SiO_2	95	66	83/17
2	$\text{Ni}^{2+}@SiO_2(50)$	96	70	85/15
3	$\text{Ni}^{2+}@SiO_2(60)$	98	82	91/9
4	$\text{Ni}^{2+}@SiO_2(80)$	99	92	96/4
5	$\text{Co}^{2+}@SiO_2(50)$	92	82	91/9
6	$\text{Co}^{2+}@SiO_2(60)$	98	84	92/8
7	$\text{Co}^{2+}@SiO_2(80)$	99	86	93/7

8	Cu ²⁺ @SiO ₂ (50)	90	78	89/11
9	Cu ²⁺ @SiO ₂ (60)	86	78	89/11
10	Cu ²⁺ @SiO ₂ (80)	90	78	89/11
11	Cu ¹⁺ @SiO ₂ (50)	87	76	88/12
12	Cu ¹⁺ @SiO ₂ (60)	87	78	89/11
13	Cu ¹⁺ @SiO ₂ (80)	91	78	89/11
14	Fe ²⁺ @SiO ₂ (50)	100	86	93/7
15	Fe ²⁺ @SiO ₂ (60)	100	88	94/6
16	Fe ²⁺ @SiO ₂ (80)	100	90	95/5
17	Mn ²⁺ @SiO ₂ (50)	99.5	80	90/10
18	Mn ²⁺ @SiO ₂ (60)	100	84	92/8
19	Mn ²⁺ @SiO ₂ (80)	100	88	94/6
20	Cd ²⁺ @SiO ₂ (1)	96	70	85/15
21	Cd ²⁺ @SiO ₂ (5)	95	72	86/14
22	Cd ²⁺ @SiO ₂ (10)	96	74	87/13
23	Cd ²⁺ @SiO ₂ (25)	96	78	89/11
24	Cd ²⁺ @SiO ₂ (50)	98	86	93/7
25	Cd ²⁺ @SiO ₂ (80)	100	94	97/3



Scheme 2. The effect of Cd²⁺@SiO₂(80) on the diastereoselectivity of Diels-Alder reaction

Conclusion

As a conclusion, we applied a mild procedure for the diastereoselective Diels-Alder reaction of methyl acrylate and cyclopentadiene using a modified silica surface with various metal ions concentrations of efficient Lewis acid. According to the results, cadmium ion supported on the silica was the best diastereoselective catalyst in this reaction due to the concentrating methyl acrylates on the surface of silica through coordination with Cd²⁺.

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References

1. O. Diels, K. Alder, *Justus Liebigs Ann. Chem.*, **1928**, 460(1), 98-122. [[Crossref](#)], [[Google Scholar](#)], [[Publisher](#)]
2. O. Diels, K. Alder, *Ber. Dtsch Chem. Ges.*, **1929**, 62(8), 2081-2087. [[Crossref](#)], [[Google Scholar](#)], [[Publisher](#)]

3. O. Diels, K. Alder, *Ber. Dtsch Chem. Ges.*, **1929**, 62(8), 2087-2090. [[Crossref](#)], [[Google Scholar](#)], [[Publisher](#)]
4. J. Sauer, *Angew Chem. Int. Ed. Engl.*, **1966**, 5(2), 211-230. [[Crossref](#)], [[Google Scholar](#)], [[Publisher](#)]
5. R.R. Schmidt, *Acc. Chem. Res.*, **1986**, 19(8), 250-259. [[Crossref](#)], [[Google Scholar](#)], [[Publisher](#)]
6. E.J. Corey, T.P. Loh, *Tetrahedron Lett.*, **1993**, 34(25), 3979-3982. [[Crossref](#)], [[Google Scholar](#)], [[Publisher](#)]
7. J.R. McElhanon, E.M. Russick, D.R. Wheeler, D.A. Loy, J.H. Aubert, *J. Appl. Polym. Sci.*, **2002**, 85(7), 1496-1502. [[Crossref](#)], [[Google Scholar](#)], [[Publisher](#)]
8. R.C. Cookson, E. Crundwell, R.R. Hill, J. Hudec, *J. Chem. Soc.*, **1964**, 3062-3075. [[Crossref](#)], [[Google Scholar](#)], [[Publisher](#)]
9. K. Hayakawa, K. Ueyama, K. Kanematsu, *J. Org. Chem.*, **1985**, 50(11), 1963-1969. [[Crossref](#)], [[Google Scholar](#)], [[Publisher](#)]
10. U. Pindur, G. Lutz, C. Otto., *Chem. Rev.*, **1993**, 93(2), 741-761. [[Crossref](#)], [[Google Scholar](#)], [[Publisher](#)]
11. D.M. Birney, K.N. Houk, *J. Am. Chem. Soc.*, **1990**, 112(11), 4127-4133. [[Crossref](#)], [[Google Scholar](#)], [[Publisher](#)]
12. K. Endo, T. Koike, T. Sawaki, O. Hayashida, H. Masuda, Y. Aoyama, *J. Am. Chem. Soc.*, **1997**, 119(18), 4117-4122. [[Crossref](#)], [[Google Scholar](#)], [[Publisher](#)]
13. S. Kobayashi, H. Ishitani, *J. Am. Chem. Soc.*, **1994**, 116(9), 4083-4084. [[Crossref](#)], [[Google Scholar](#)], [[Publisher](#)]
14. D.A. Evans, S.J. Miller, T. Lectka, *J. Am. Chem. Soc.*, **1993**, 115(14), 6460-6461. [[Crossref](#)], [[Google Scholar](#)], [[Publisher](#)]
15. W. Odenkirk, B. Bosnich, *J. Chem. Soc., Chem Commun.*, **1995**, 11, 1181-1182. [[Crossref](#)], [[Google Scholar](#)], [[Publisher](#)]
16. S. Kobayashi, M. Araki, I. Hachiya, *J. Org. Chem.*, **1994**, 59(14), 3758-3759. [[Crossref](#)], [[Google Scholar](#)], [[Publisher](#)]
17. D.A. Evans, M.C. Kozłowski, J.S. Tedrow, *Tetrahedron Lett.*, **1996**, 37(42), 7481-7484. [[Crossref](#)], [[Google Scholar](#)], [[Publisher](#)]
18. S. Otto, F. Bertocin, J.B.F.N. Engberts, *J Am Chem Soc.*, **1996**, 118(33), 7702-7707. [[Crossref](#)], [[Google Scholar](#)], [[Publisher](#)]
19. G. Mohammadi Ziarani, A. Badiei, A Miralami, *Bull Korean Chem. Soc.*, **2008**, 29(1), 47-50. [[Crossref](#)], [[Google Scholar](#)], [[Publisher](#)]
20. R. Keller, H. Wrcoff, L.E. Marchi, *Inorganic Syntheses*, **1946**, 2, 1-4. [[Crossref](#)], [[Google Scholar](#)], [[Publisher](#)]