Silica and Alumina Modified by Lewis Acids as Catalysts in Diels-Alder Reactions of Carbonyl-Containing Dienophiles

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Abstract: Several aluminium and titanium derivatives are supported on silica and alumina. Some of the solids obtained contain strong Lewis acids sites and are efficient catalysts in Diels-Alder reactions of carbonyl-containing dienophiles. In cyclopentadiene reactions, high conversions and endo/exo selectivities are obtained in short reaction times, without excess of diene and with a small amount of catalyst at room temperature. With less reactive dienes, temperature, diene proportion and reaction times must be increased. However, high regio and endo/exo selectivities are obtained. The catalyst obtained by treatment of silica with diethyl aluminium chloride retains a great deal of its catalytic activity when recovered or stored in the open air for one month.

INTRODUCTION

The Diels-Alder reaction is a very useful synthetic tool because it is one of the most effective methods for obtaining six-membered rings with high stereochemical control. It has been reported that several inorganic solids, such as silica gel,^{1,2} magnesium silicate,² alumina,^{2,3} zeolites,⁴ and clays⁵ are efficient catalysts in Diels-Alder reactions. Recently, we have studied several factors influencing the K10 montmorillonite-catalyzed Diels-Alder reaction between methyl acrylate and cyclopentadiene⁶ and we have shown that the solvent plays a decisive role.⁷ Furthermore, we have shown that clay calcination improves the activity of the catalyst, which can be recovered without a loss of its catalytic activity.⁸ However, in reactions of carbonyl-containing dienophiles, the activity is far less than that of traditional Lewis acids in homogeneous reactions. Given the interest of Diels-Alder reactions, it is important to search for solids with better catalytic properties for reactions of carbonylcontaining dienophiles. In view of the higher activity of tetrahedral compared to octahedral aluminium Lewis acids, Drago and Getty⁹ have prepared strong Lewis acids, containing tetrahedral aluminium sites, by reaction of an inorganic oxide with aluminium chloride:



A similar strategy has been used to obtain a chiral Lewis acid by the reaction of alumina with BBr_3 and (-)-menthol:¹⁰



New Lewis acids are usually obtained by the reaction of monoalcohols and diols with several aluminium and titanium derivatives (chlorides, ethyl and diethyl aluminium chlorides, titanium diisopropoxide dichloride, titanium tetraisopropoxide).¹¹ It is interesting to test whether a similar strategy can be used to support aluminium and titanium on inorganic oxides and whether the solids obtained are effective catalysts in Lewis acid-catalyzed organic reactions.

In this paper we use the above-mentioned strategy to support aluminium and titanium on silica and alumina, and the solids obtained are used as catalysts in Diels-Alder reactions.

RESULTS AND DISCUSSION

Silica gel (Merck, silicagel 60, 63-200 nm) and alumina (Merck, aluminium oxide 60, 63-200 nm) were activated by several methods and refluxed with $AlClEt_2$ and $TiCl_4$ in toluene. The excess of homogeneous catalyst was eliminated and the solids obtained were used as catalysts in the model Diels-Alder reaction between methyl acrylate (1) and cyclopentadiene (2) (Scheme 1).

Table 1 gathers the results obtained and compares them with the non-catalyzed reaction and with the best results obtained with heterogeneous catalysts. Although silica and alumina catalyze the reaction, the catalytic activity is greatly increased by treatment with Lewis acids. In fact, some of these catalysts are among the most active described to date for heterogeneous catalysis of Diels-Alder reactions of carbonyl-containing dienophiles. High chemical yields are obtained in short reaction times without an excess of diene and with a small amount of catalyst. If the new aluminium or titanium sites are the active ones, dienophile-catalyst ratios range from 5.2 to 10, then these solids display truly catalytic behavior. Table 1. Results Obtained from the Reaction between Methyl Acrylate (1) and Cyclopentadiene (2) in toluene at 20°C

Solid	Pre-activation	Lewis acid (meq/g of solid)	Al or Ti incorporated (mmol/g) ^a	2:1 ratio	catalyst:1 ratio (g/meq)	% conversio 30 min	mb 2 h	endo/exob
ľ	•			3:1	ł	1	6	73:27
Zn(II)-K10 ^c	none		ı	3:1	0.17	I	22	94:6
Zn-Y zeolite ^d	none	•	•	1:1	0.10	·	95	96:4
SiO ₂	Ae	•	·	1:1	0.13	2	26	86:14
siO ₂	none	AlEt ₂ CI (2.5)	1.26	1:1	0.13	27	59	95:5
siO ₂	A ^e	AlEt ₂ CI (2.5)	1.43	1:1	0.13	96	<u> 8</u> 6	95:5
SiO ₂	Bf	AlEt ₂ Cl (2.5)	1.40	1:1	0.13	53	57	94:6
siO ₂	A ^e	TiCl ₄ (2.5)	1.21	1:1	0.13	72	85	93:7
SiO ₂	Bf	TiCl4 (2.5)	1.38	1:1	0.13	57	3	93:7
Al ₂ O ₃	ප	ı	ſ	1:1	0.13	~	17	92:8
Al ₂ O ₃	none	TiCI4 (1.0)	0.70	1:1	0.13	55	80	92:8
Al ₂ O ₃	පී	AlEt ₂ CI (1.0)		1:1	0.13	29	65	93:7
Al ₂ O ₃	å	AlEt ₂ C1 (1.0)		1:1	0.13	30	65	93:7
Al ₂ O ₃	ዄ	A1Et ₂ C1 (2.5)	•	1:1	0.13	80	93	92:8
Al ₂ O ₃	ඊ	TiCl ₄ (1.0)	0.87	1:1	0.13	60	75	93:7
Al ₂ O ₃	å	TiCl4 (1.0)	0.75	1:1	0.13	40	74	93:7
Al ₂ O ₃	ዄ	TiCl ₄ (2.5)	0.89	1:1	0.13	59	75	93:7
	ı	AJEtCl ₂	•	1:1	0.13	100	ī	94:6
^a Determined by l treatment with HC	Plasma Emission S	ipectroscopy ^b Determin teating at 400°C under v	hed by GC ^c Ref. 8 ^d 3h at 0 ^o actum	°C , ref. 4b ^e	Activated by heating	at 140° under va	cuum ^f	Activated by

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Scheme 1

If the percentage of conversion after 30 min. is considered a measurement of the reaction rate, the fastest reactions are obtained when the inorganic solid is treated with an excess of $AlClEt_2$. The pre-activation of the support also plays an important role, the best results being obtained when this treatment is carried out by heating under vacuum. In general, silica catalysts are more efficient than alumina catalysts, which may be due to the greater amount of metal incorporated and to the greater surface area of the silica used (silica: 476 m² g⁻¹, alumina: 76.3 m² g⁻¹).

Higher overall conversions are obtained with aluminium-modified catalysts, which may be accounted for by a more extensive oligomerization of the diene with titanium-modified catalysts.

The best results, including *endo/exo* selectivity, are obtained when SiO_2 · AlClEt₂ is used as a catalyst. The infrared spectra of pyridine adsorbed on the catalysts used in this work revealed the presence of both Lewis and Brønsted sites. However, the noticeable catalytic activity of the SiO_2 · AlClEt₂ catalyst can be explained by the presence of strong Lewis acid sites, as shown by the large frequency shifts of the Lewis acid band (Table 2).

Solid	Pre-activation	Lewis acid	Shift of Lewis band (cm ⁻¹) ^a
SiO ₂	A		7.7
SiO ₂	Α	AlEt ₂ Cl	14.8
SiO2	Α	TiCl ₄	7.7
Al_2O_3	С	-	6.4
Al_2O_3	С	TiCl ₄	7.7
Al_2O_3	D	TiCl ₄	8.5

Table 2. Infrared Frequency Shifts for Pyridine Adsorbed onto the Catalysts

^a The shift is measured after evacuation at 120°C under 10^{-6} torr of the sample exposed to pyridine. The frequency for the free pyridine band is 1438.5 cm⁻¹.

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Solid	Pre-activation	Lewis acid (meq/g of solid)	Al or Ti (mmol/g) ^b	number of recovering ^c	2:1 ratio	%con 30 min	wersio 2 h	л ^d 24 h	endo/exo ^d
SiO,	A	AlEt,Cl (2.5)	1.43	1 0	1:1	8	86		95:5
4		ł	1.35	· –1	1:1	30	65	8	95:5
				7	1:1	15	47	85	94:6
				£	1:3	46	1	8	94:6
sio,	Ae	AlEt,CI (2.5)	1.43	0	1:1	35	2	16	95:5
•				t.	1:1	32	67	91	95:5
				6	1:1	18	48	22	94:6
sio,	A	TiCl ₄ (2.5)	1.21	0	1:1	7	85	16	93:7
ł				1	1:1	Ŧ	16	69	81:19
SiO,	A ^e	TiCl ₄ (2.5)	1.00	0	1:1	80	19	64	90:10
A, O,	D	AlEt ₂ Cl (1.0)	•	0	1:1	8	65	ı	93:7
4		ł		4	1:1	ı	15	ı	88:12
Al ₂ O ₃	ď	AlEt ₂ CI (1.0)	•	0	1:1	,	ł	18	78:22
AJ,O,	D	TICI4 (1.0)	0.75	0	1:1	40	74	ı	93:7
1		1	0.75	7	ы	•	•	18	75:25
Al ₂ O ₃	å	TiCl4 (1.0)	0.75	0	1:1	9	1	50	82:18

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It has been described⁹ that $AlCl_3$ is easily released from the surface of inorganic oxides in time, and hence only short term activity results. It is interesting to test whether the catalysts used in this work can be recovered and/or stored without loss of catalytic activity. As can be seen in Table 3 most of the catalysts lose their activity after recovery or storage, which results in slow reactions with *endo/exo* selectivities which approach those obtained in the noncatalyzed reactions. Plasma emission spectroscopy analyses show that this behavior cannot be accounted for by a loss of aluminium or titanium, and we suggest that it may be due to the hydrolysis of metal-chlorine bonds by atmospheric moisture and to the formation of cyclopentadiene polymers on the surface of the catalyst. Fortunately, the SiO₂· AlClEt₂ catalyst can be recovered, even after storage for one month, which gives rise to high conversions without loss of catalytic activity. Given that aluminium is not easily released from the surface of the silica, we propose for this catalyst a structure different from that described by Drago and Getty.⁹



Given that the best results are obtained with silica gel activated by method A (see Experimental section), we tested the modification of this solid with several other aluminium or titanium derivatives. The results obtained (Table 4) show that only AlCl₂Et leads to an active catalyst, but it cannot be recovered without a loss of its catalytic activity.

Table 4.	Results Obtained from the Reaction between Methyl Acrylate (1) and Cyclopentadiene
	(2) in Toluene at 20°C catalyzed by Silica Gel Modified with Several Aluminium and
	Titanium Derivatives. ^a

Lewis acid	Al or Ti	number of	%сс	onversi	ion	endo/exo ^d
(mmol/g of solid)	(mmol/g) ^b	recovering ^c	30 min	2 h	24 h	
AlEtCl ₂ (2.5)	1.07	0	41	70	95	95:5
-	0.95	1	8	17	57	90:10
Al(CH ₃) ₃ (2.5)	2.10	0	5	18	64	91:9
TiCl ₂ (OiPr) ₂ (2.5)	1.23	0	8	25	84	90:10
Ti(O ⁱ Pr) ₄ (2.5)	0.96	0	2	7	36	82:18

^a With 0.13 g of catalyst per mmol of dienophile and a 1:1 diene:dienophile molar relationship ^b Determined by Plasma Emission Spectroscopy ^c The catalyst was recovered by filtration and reactivation by method A ^d Determined by GC

The comparison between the aluminium catalysts suggests that both the amount of aluminium incorporated, which increases with an increase in the number of alkylaluminium functions, and the presence of chlorine are important. Therefore, in the case of AlClEt₂ a compromise between both factors, leading to the more active catalyst, is reached.

In the case of the titanium derivatives the situation seems to be more complex. The comparison between $TiCl_4$ and $Ti(O^iPr)_4$ reveals the great importance of chlorine atoms, as expected from their influence on Lewis acidity. The lack of catalytic activity of the $Ti(O^iPr)_4$ catalyst supports the idea of catalyst deactivation by hydrolysis of titanium-chlorine bonds. In solution $TiCl_2(O^iPr)_2$ catalyst loses isopropanol by reaction with diols to form $TiCl_2-diol$ catalysts. A similar structure should be expected for silicas treated with $TiCl_4$ and $TiCl_2(O^iPr)_2$. However, the catalytic activity of the latter solid is halfway between those of silicas treated with $TiCl_4$ and $Ti(O^iPr)_4$. We propose that a partial alcoholysis of titanium-chlorine bonds, by the isopropanol released from titanium, takes place, so several titanium species are present in the silica treated with $TiCl_2(O^iPr)_2$:



The best catalyst was tested in three additional Diels-Alder reactions (Table 5). The heterogeneous catalyst has a noticeable catalytic effect, especially if the small amount of catalyst used is taken into account. However, this activity is noticeably reduced, in comparison with homogeneous catalysts, when less reactive dienes (6, 8) are used (Scheme 2). Nevertheless, high regio or *endo/exo* selectivities are obtained even at 60° C.

In conclusion, the treatment of silica gel and alumina with several Lewis acids leads to heterogeneous catalysts which are efficient for Diels-Alder reactions of carbonyl-containing dienophiles. The SiO_2 AlClEt₂ catalyst is the most efficient and can be recovered and stored without a great loss of its catalytic activity.

Table 5. Results Obtained from the Reactions between Methacrolein (4) and Cyclopentadiene (2) in Toluene, Methyl Acrylate (1) and Isoprene (6) in 1,2-Dichloroethane, and Methyl Acrylate and Cyclohexadiene (8) in Toluene.	
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Diene	Dienophile	Catalyst (amount/mmol of dienophile)	T (°C)	diene:dienophile	%conve 30 min	rsion ^a 24 h	exo/endo ^a	para/meta ^a
7	4	AlEt ₂ Cl (0.25 mmol)	-25	3:2	6 6	,	88:12	1
2	4	•	20	1:1	•	80	80:20	,
7	4	SiO ₂ . AlEt ₂ Cl (0.09 g)	20	1:1	92	·	85:15	
9	1	AlEtCl ₂ (0.10 mmol)	20	3:2	ı	100 ^c	ı	95:5
9	1	•	20	6:1	·	0		·
9	1	SiO ₂ ' AlEt ₂ Cl (0.80 g)	20	6:1	ł	42	ı	94:6
9	1	•	60	3:1	·	7	1	70:30
9	1	SiO2 [.] Alet ₂ Cl (0.80 g)	60	3:1	ŀ	85	ı	92:8
80	1	•	80	3:1	ł	<1 ^c	13:87	
80	1	SiO2. AlEt ₂ CI (0.13 g)	60	3:1	ı	50	2:98	•

^a Determined by GC ^b % conversion after 15 min ^c % conversion after 3 h



Scheme 2

EXPERIMENTAL

Silica gel and alumina were purchased from Merck and used as received or after activation by one of the following methods, after drying at 140°C for one night:

- SiO₂, method A: 24°C ; 2°C/min ;140°C (5 h) ; -1°C/min ; 80°C (1h)
- SiO₂, method B: silica gel (1g) was refluxed with 35% HCl (9ml) for 8 h, filtered-off, washed with hydrogen chloride-free water and dried at 140°C under vacuum for one night.

- Al₂O₃, method C: 24°C ; 3°C/min ;400°C (4 h) ; -2.5°C/min ; 80°C (1h)

- Al₂O₃, method D: 24°C ; 2°C/min ;140°C (5 h) ; -1°C/min ; 80°C (1h)

Surface areas were calculated from BET nitrogen isotherms determined at 77 K. Silica gel has a surface area of 476 m² g⁻¹, which decreases to 340 m² g⁻¹ when treated with AlClEt₂ or TiCl₄. Alumina has a surface area of 78 m² g⁻¹, which increases to 107 m² g⁻¹ after activation with Lewis acids. The micropore volume (pore sizes \leq 1nm) are within 0.15-0.22 ml g⁻¹ for silicas and within 0.03-0.05 ml g⁻¹ for aluminas. Acidic properties were determined by

adsorption of pyridine as probe molecule on self-supported wafers. The wafers were compressed under 5 tons cm⁻² pressure to obtain disks 18 mm in diameter with a weight of ~10 mg cm⁻². The resulting wafers were placed in cells (equipped with KBr windows and connected *via* stopcocks to a vacuum line) where the treatment of the catalysts was performed. Infrared spectra were recorded using a Nicolet 320 FT-IR spectrometer after desorption of pyridine at 120°C.

Preparation of the catalysts:

To a mixture of alumina or silica gel (1g), activated by one of the above-mentioned methods, and dry toluene (10 ml), 1 ml or 2.5 ml of a 1M solution of the corresponding aluminium or titanium derivative was added. The resulting mixture was refluxed under argon for 48 h, toluene was eliminated *via* syringe, and the solid repeatedly washed with dry toluene (5 x 10 ml).

After Diels-Alder reactions, catalysts were recovered by filtration, washed with dry toluene and heated at 140°C under vacuum for 24 h.

Reaction procedures:

Reaction between methyl acrylate and cyclopentadiene. A mixture of the corresponding catalyst (1g) and methyl acrylate (0.645 g, 7.5 mmol) in dry toluene (15 ml) under argon at 20°C was shaken for 15 min, then freshly distilled cyclopentadiene (0.495 mg, 7.5 mmol) was added, the flask was shaken and the reaction monitored by gas chromatography (FID from Hewlett-Packard 5890 II, cross-linked methyl silicone column 25 mm x 0.2 mm x 0.33 μ m, helium as carrier gas, 17 p.s.i., injector temperature 230°C, detector temperature 250°C, oven temperature program 50°C (3 min) - 25°C/min - 100°C (9 min), retention times: methyl acrylate 1 2.7 min, *exo* cycloadduct 3x 12.7 min, *endo* cycloadduct 3n 12.9 min).

Reaction between methacrolein and cyclopentadiene. A mixture of silica (1g, activated by method A and treated with AlClEt₂) and methacrolein (0.742 g, 10.6 mmol) in dry toluene (15 ml) under argon at 20°C was shaken for 15 min, then freshly distilled cyclopentadiene (0.698 mg, 10.6 mmol) was added, the flask was shaken and the reaction monitored by gas chromatography (FID from Hewlett-Packard 5890 II, cross-linked methyl silicone column 25 mm x 0.2 mm x 0.33 μ m, helium as carrier gas, 17 p.s.i., injector temperature 230°C, detector temperature 250°C, oven temperature program 40°C (3 min) - 25°C/min - 100°C (8 min), retention times: methacrolein 1 2.6 min, *exo* cycloadduct 5x 10.8 min, *endo* cycloadduct 5n 11.4 min).

Reaction between methyl acrylate and isoprene. A mixture of silica (1g, activated by method A and treated with $AlClEt_2$) and methyl acrylate (0.161 g, 1.875 mmol) in dry 1,2-dichloroethane (7.5 ml) under argon at 20°C or 60°C was stirred for 15 min, isoprene (0.764 mg, 10.6 mmol or 0.382 mg, 5.625 mmol) was then added, the mixture stirred and the reaction monitored by gas chromatography (FID from Hewlett-Packard 5890 II, cross-linked methyl silicone column 25

mm x 0.2 mm x 0.33 μ m, helium as carrier gas, 17 p.s.i., injector temperature 230°C, detector temperature 250°C, oven temperature program 50°C (3 min) - 25°C/min - 100°C - 2°C/min - 120°C - 25°C/min - 250°C (5 min), retention times: methyl acrylate 1 2.7 min, *meta* cycloadduct 7m 13.2 min, *para* cycloadduct 7p 13.5 min).

Reaction between methyl acrylate and cyclohexadiene. A mixture of silica (1g, activated by method A and treated with AlClEt₂) and methyl acrylate (0.645 g, 7.5 mmol) in dry toluene (15 ml) under argon at 60°C was stirred for 15 min, then cyclohexadiene (102.5 g, 22.5 mmol) was added, the flask stirred and the reaction monitored by gas chromatography (FID from Hewlett-Packard 5890 II, cross-linked methyl silicone column 25 mm x 0.2 mm x 0.33 μ m, helium as carrier gas, 18 p.s.i., injector temperature 230°C, detector temperature 250°C, oven temperature program 50°C (3 min) - 25°C/min - 125°C - 5°C/min - 150°C - 25°C/min - 200°C (3 min), retention times: methyl acrylate 1 2.7 min, *exo* cycloadduct 9x 11.1 min, *endo* cycloadduct 9n 11.4 min).

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