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Research Note

CO_2 fixation using recoverable chromium salen catalysts: use of ionic liquids as cosolvent or high-surface-area silicates as supports

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Abstract

Two series of recoverable and reusable chromium salen catalysts for the CO_2 addition to styrene epoxide to form cyclic carbonate have been tested under supercritical conditions (100 bar and 80 °C). In one of the cases, tetra-*tert*-butylsalen chromium (substrate-to-catalyst ratio 875) was dissolved in an ionic liquid, 1-butyl-3-methylimidazolium hexafluorophosphate ($bmimPF_6$), and after the products were extracted with diethyl ether the ionic liquid containing the complex was reused up to four consecutive runs. However, only modest conversions ($> 50\%$) and product selectivities ($> 79\%$) were achieved under these conditions, although decreasing the substrate-to-catalyst ratio showed some enhancement in the epoxide conversion. In the other system, a chromium salen catalyst was adsorbed on aminopropylsilyl-modified silica and ITQ-2. The solids were tested as heterogeneous catalysts but complete desorption of the complexes was observed after the first use. The best recoverable catalyst of the series was obtained when chromium salen was covalently anchored to silica support through a linker resulting from nucleophilic substitution between aminopropylsilyl-modified silica and chloromethyl-substituted complex. In this case, the solid was still active after the fourth reuse and exhibited 100% carbonate selectivity at about 70% epoxide conversion.

1. Introduction

One of the hot topics in green chemistry is the use of renewable feedstocks and more specifically CO_2 [1–5]. The process of CO_2 fixation is particularly challenging due to its thermodynamic stability and chemical inertness. Recently, it has been reported that chromium and cobalt salen complexes in the presence of bases can catalyze the addition of CO_2 to epoxides to form cyclic carbonates [6–11]. Other metal complexes such as porphyrins and hydroxyquinolinates have also been used [12–14]. However, the main drawback in this process is the separation of the catalysts from the reaction mixture and hence reuse of the catalyst. In order to make the CO_2 fixation greener, a general strategy consists in converting the homogeneous catalyst into a heterogeneous system. With this aim in mind, in the present work, we compare the catalytic activity of a series of recoverable chromium salen catalysts for the CO_2 addition to epoxide to form cyclic carbonates.

2. Experimental

2.1. Compounds and materials

5-Chloromethyl-3-*tert*-butylsalicylaldehyde (**5**) [21], the mixture of asymmetric ligands **8a–c** [22] and complexes **9a–c** [23], and tetra-*tert*-butyl chromium (III) salen complex were prepared according to the literature [23]. ITQ-2 was synthesized as reported earlier [24] by ultrasound delamination of a MCM-22 precursor previously submitted to swelling by ion exchanging the initial hexamethyleneimine template by hexadecyltrimethyl ammonium cations. FTIR spectra of unsupported asymmetric ligand and complex were recorded at room temperature in a Nicolet 710 FT spectrophotometer making KBr pellets. Diffuse reflectance UV–vis spectra of the opaque powders were recorded in a Var-

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ian Cary 5G UV–vis NIR spectrophotometer adapted with a praying mantis attachment and using $BaSO_4$ as the reference.

2.2. Anchoring procedure

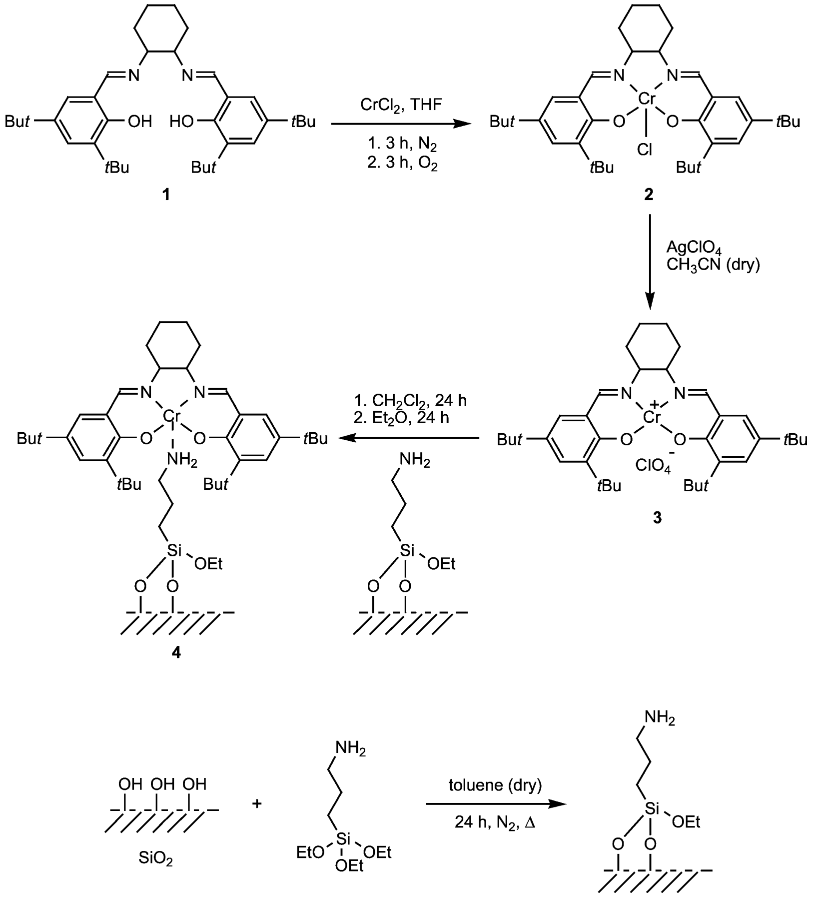
After dehydration of the solids at 200 °C for 2 h (under 10^{-2} Torr), the required amount of 3-aminopropyltriethoxysilane (moles SiO_2/moles amine = 5) in dry toluene was added. The suspension was stirred under nitrogen atmosphere and refluxed for 24 h. The solid was filtered and Soxhlet-extracted with dichloromethane for 24 h.

For preparation of Cr-salen/NH_2SiO_2 and Cr-salen/NH_2ITQ, a mixture of (*R*,*R*)-(−)-*N*,*N*′-bis(3,5-di-*tert*-butylsalicylidene)–1,2-cyclohexanediaminochromium chloride and silver perchlorate in dry acetonitrile was stirred at room temperature for 16 h (Scheme 1). After filtration through Celite and washing with acetonitrile, the filtrate was concentrated and then dichloromethane and solid aminopropyl-anchored support were added. The suspension was stirred at room temperature for 24 h, filtered, resuspend in diethyl ether, and stirred at room temperature for 24 h. After filtration, the solids were dried under 10^{-1} Torr for 2 h at 45 °C.

For the preparation of Cr-salen/SiO_2, (*R*,*R*)-*N*-(3,5-di-*tert*-butylsalicylidene)–*N*′-(3-*tert*-butyl-5-chloromethylsalicylidene)–1,2-cyclohexanediaminato [22] and the corresponding chromium complex [23] were synthesized as reported in the literature. Then, a known amount of the Cr-salen complex was added to a suspension of the modified solids in dry toluene and stirred at reflux temperature for 48 h according to the procedure reported in the literature for the preparation of MCM-41-type silica-bound manganese (III) Schiff-base complexes [25]. The suspension was filtered and Soxhlet-extracted with dichloromethane for 24 h and dried under 10^{-1} Torr for 2 h at 45 °C.

2.3. Reaction procedure

Styrene oxide (3.56 mmol), triethylamine, or *N*-methylimidazole (10 µl) was dissolved in dichloromethane (0.4 ml) or an ionic liquid, 1-butyl-3-methylimidazolium hexafluorophosphate ($bmimPF_6$), and charged into a high-pressure autoclave (Büchi). The corresponding chromium salen catalyst (30 mg) was added and the autoclave was sealed and then charged with liquid CO_2. The reaction mixture was mechanically stirred at 100 bar and 80 °C for 6 h. After this time, CO_2 was slowly released into a chamber open to the atmosphere. The reaction mixture remaining in the autoclave vessel was collected and analyzed by gas chromatography (HP 5890) using a 30-m capillary column of crosslinked 5% phenylmethylsilicone. The identity of the cyclic carbon-



Scheme 1.

ate and phenylglycol was confirmed by comparison with the commercial samples and also by GC-mass analysis (HP 6890).

3. Results and discussion

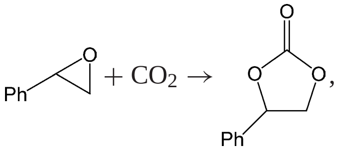
In the first strategy we have modified the process based on the homogeneous phase to allow the recovery of the catalyst by using a room temperature ionic liquid [15,16], namely 1-butyl-3-methylimidazolium hexafluorophosphate ($bmimPF_6$). Most of the salen complex remains dissolved in the ionic liquid during extraction of the reaction products with diethyl ether. The second strategy is based on supporting the chromium salen complex on a high-surface-area solid. In related precedent, aluminum phthalocyanine was covalently bonded to silica and used as heterogeneous catalyst for the CO_2 fixation [13]. For the present work, we have used modified amorphous silica and delaminated zeolite ITQ-2 as solid supports. The main textural properties of these solids are presented in Table 1.

The simplest strategy for anchoring the complex to a support consists in adsorbing the chromium salen complex onto an aminopropylsilyl-modified support (Cr-salen/NH_2SiO_2 and Cr-salen/NH_2ITQ-2). In this case the complex remains bonded to the solid surface (SiO_2 or ITQ-2) through the coordinative apical bond between the terminal amino group of the 3-aminopropylsilyl group attached to the solid surface and the chromium ion of the complex. Scheme 1 shows the preparation procedure followed to obtain the Cr-salen/NH_2SiO_2 and Cr-salen/NH_2ITQ solid catalysts.

Our previous work in related metal salen complex catalysts anchored on solids [17,18] led us to anticipate that despite the simplicity of the preparation method for Cr-salen/NH_2SiO_2 and Cr-salen/NH_2ITQ-2, binding the support through the metal would lead to a considerable degree of complex detachment as compared to a more elaborated synthetic route in which the chromium salen complex is anchored through a terminal substituent on the ligand. Therefore, we have also prepared a catalyst in which the chromium salen is covalently tethered to the silica particle through an amino linker connected to one phenolic ring of the salen ligand. The preparation of Cr-salen/SiO_2 was accomplished as indicated in Scheme 2. The key step in the synthesis is the formation of a statistical mixture of three salen ligands **8a–c** where the predominant symmetric tetra-*tert*-butylsalen **8a** cannot be anchored on the solid. The ratio of the asymmetric *p*-(chloromethyl) salen **8b** to the bis-(*p*-chloromethyl) derivative **8c** was 6 to 1 (see Scheme 2 for reagent stoichiometries and product distribution). Since purification of this mixture by chromatography is difficult due to hydrolysis ligands **8a–c** were converted into the corresponding complexes **9a–c** and finally tethered to 3-aminopropylsilyl-modified silica. Thus, the Cr-salen/SiO_2 catalyst contains a mixture of mostly monopodally anchored **9b** and a lesser amount of **9c**, the latter being anchored either mono-or bipodally.

The chromium content and other analytical data of the series of catalysts are also included in Table 1. In addition to elemental analysis (Cr, C, and N), the presence of intact Cr-salen complexes adsorbed onto the solids can be confirmed by diffuse reflectance UV–vis (ligand-to-metal charge transfer band at 520 nm) and IR (1620 and 1591 cm^{-1} vibration bands attributed to $C{=}N\cdots$Metal interaction and to the phenolic ring) spectroscopies. These spectroscopic features agree with the data reported in the literature [18].

The reaction of styrene oxide with CO_2 to form a cyclic carbonate [Eq. (1)],

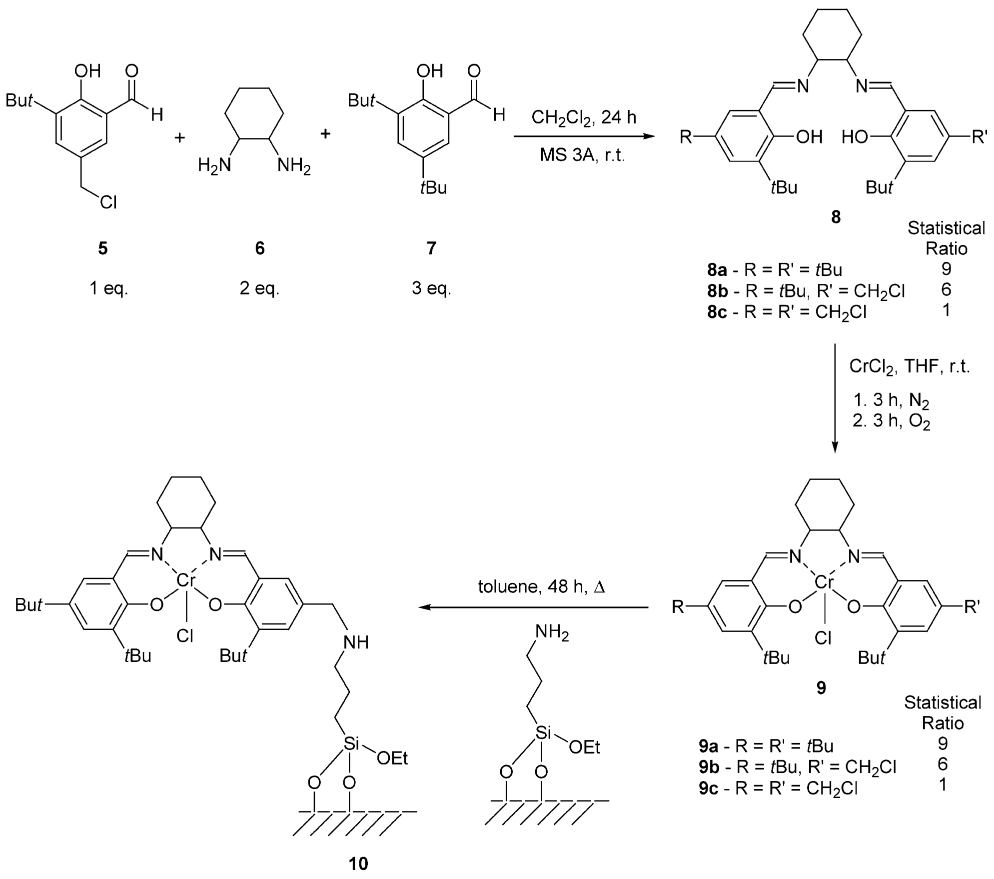


(1)

in the presence of the four Cr-salen catalysts was carried out under supercritical conditions since it is known that supercritical CO_2 and ionic liquid are completely miscible [15,16,19]. In addition, we have previously reported that the gas-like diffusion characteristic of reagents under supercritical conditions plays a favorable role in heterogeneous catalysis using microporous solids, enhancing the activity compared to conventional solvents due to an increase of the diffusion coefficients [20]. Besides *N*-methylimidazole, triethylamine was also used as base (see Table 2). For the reactions carried out in the absence of $bmimPF_6$, a small volume of dichloromethane or dimethyl carbonate (0.4 ml in a 50 ml reactor) was added as cosolvents to increase the solubility in the medium of styrene oxide and the base. Dichloromethane should be avoided in green chemistry, but here it was used as reference to compare with other media, particularly $bmimPF_6$. The results obtained under the conditions studied are summarized in Table 2. For the sake of comparison, we have also included in Table 2 previous results from the literature.

Table 1
Analytical and textural data of the recoverable catalytic systems used in this work

Support	Catalyst	Complex solid binding	Analytical data (%)		
			Cr	C	N
Amorphous silica	Cr-salen/NH_2SiO_2	Through the metal	0.84	11.93	1.86
> 1 μm, 210 $m^2\ g^{-1}$	Cr-salen/SiO_2	Through the ligand	1.01	11.56	1.73
ITQ-2	Cr-salen/NH_2ITQ-2	Through the metal	0.59	12.39	1.49
< 0.5 μm, 730 $m^2\ g^{-1}$					



Scheme 2.

Table 2
Results of the reaction of styrene oxide (3.56 mmol) with CO_2 under supercritical conditions (100 bar, 80 °C) in a 50 ml reactor after 6 h in the presence of Cr-salen catalysts using a base as cocatalyst (10 µl)

Catalyst	Substrate to catalyst molar ratio	Cosolvent[a]	Conversion[b] (%)	Selectivity[c] (%)	Mass balance[d] (%)
Cr-salen/NH_2SiO_2	875	CH_2Cl_2	66	89	100
Cr-salen/NH_2ITQ-2	816	CH_2Cl_2	71	91	69
Cr-salen/SiO_2	583	$(MeO)_2CO$	72	100	48
Cr-salen/SiO_2	583	CH_2Cl_2	74	100	62
Cr-salen/SiO_2 (use 4)	583	CH_2Cl_2	68	100	48
Cr-salen (not recoverable)	875	CH_2Cl_2	75	100	57
Cr-salen (use 1)	875	$bmimPF_6$	25	79	80
Cr-salen (use 2)	875	$bmimPF_6$	35	68	100
Cr-salen (use 3)	875	$bmimPF_6$	37	67	100
Cr-salen (use 4)	875	$bmimPF_6$	48	56	92
Cr-salen	292	$bmimPF_6$	50	100	54
Cr-salen[e] (not recoverable)	875	CH_2Cl_2	81	93	55
Cr(salen)[f]	1000	–	48.4	100	–

[a] The amount of 0.4 ml of an organic solvent was used.
[b] Based on the disappearance of styrene.
[c] Besides cyclic carbonate the only by-product detected was phenylglycol.
[d] The incomplete mass balance is mostly due to reagent and product losses during the discharge of the contents from the reactor.
[e] Triethylamine was used instead of *N*-methylimidazole.
[f] Data taken from the literature [11] for a reaction carried out in neat propylene oxide (35 ml) at 25 °C.

In all cases, the only products observed were the corresponding cyclic carbonate accompanied in some cases with minor amounts of phenylglycol. The latter by-product appears particularly when using ionic liquid as cosolvent and would arise from the Lewis acid-catalyzed hydrolysis of the epoxide. As seen in Table 2, Cr-salen dissolved in $bmimPF_6$ ionic liquid is a recoverable and reusable system for the CO_2 insertion to the epoxide ring. The major shortcoming of the catalytic system based on the chromium salen in ionic liquids is a more time-consuming workup that in addition requires exhaustive liquid–liquid extraction using volatile organic solvents and the lower conversions. Conversion increased when a lower substrate to catalyst ratio was used. The lower activity of Cr-salen in bmimPF$_6$ as compared to dichloromethane could probably reflect differences in viscosity and other physical properties of the solvent as well as lower tolerance of bmimPF$_6$ to basic conditions. Also upon extensive reuse, some leaching of the chromium catalyst to the organic solvent used in the extraction occurs, eventually leading to a decrease in the catalytic activity. This depletion of chromium salen complex in the catalyst derives from a minor solubility of the complex in diethyl ether.

The catalytic activity of Cr-salen/NH$_2$SiO$_2$ and Cr-salen/NH$_2$ITQ-2 is very high, but the solids become largely depleted of chromium in the first run as evidenced by the decrease in the intensity of the characteristic ligand to metal charge transfer UV–vis band of the complex at 520 nm. Visually the color of the fresh catalyst fades considerably after the first use. In contrast, in the case of Cr-salen/SiO$_2$ where the complex is covalently connected to the solid particles through the ligand, the solid can be simply recovered after reaction by filtration, and reused in consecutive runs after washing with organic solvents without any significant decay in the catalytic activity.

In summary, dissolving Cr-salen complex in a room temperature liquid ionic and anchoring the complex on a high-surface-area solid support are viable strategies to transform the catalytic CO$_2$ fixation by reaction with epoxides into a reusable catalytic process. These modified Cr-salen systems exhibited high catalytic and selectivity toward the formation of cyclic carbonates. When dissolved in ionic liquid or covalently anchored on the solid the catalyst can be recovered and reused four runs without any significant decrease in activity.

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