A convenient method for the transformation of epoxide to aldehyde and acetonide mediated by Cr-PLM

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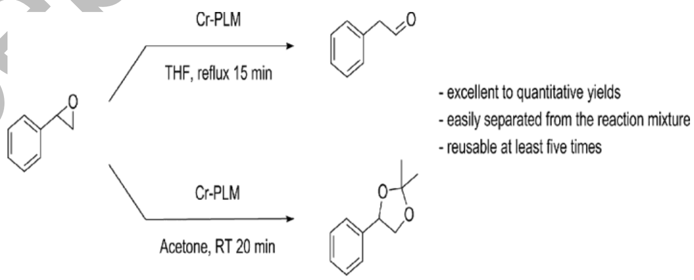
Abstract

Chromium-pillared montmorillonite (Cr-PLM) could be synthesized and efficiently utilized for styrene oxide transformations. The target aldehyde product could be quantitatively achieved from the isomerization of styrene oxide by using 10 wt% of Cr-PLM under reflux temperature for 15 min. The acetonide product could be achieved in excellent yield from the reaction of styrene oxide and acetone by using 10 wt% of Cr-PLM under room temperature for 20 min. The catalyst could be recovered and reused at least five times without loss of activity.

Graphical Abstract



KEYWORDS: clay catalyst; chromium pillared clay; epoxide; isomerization; acetonide

INTRODUCTION

Epoxides are versatile intermediates in synthetic organic chemistry since they can be easily transformed into valuable chemicals with a wide range of functional groups [1,2]. The isomerization of epoxides to carbonyl compounds is one of the most useful synthetic transformation. The products from epoxide isomerization are widely used in pharmaceutical, perfume, agrochemical industries and others. Various Lewis acid reagents have been addressed for epoxide isomerization such as $InCl_3$ [3], $BF_3 \cdot Et_2O$ [4], lithium salts [5], $MgBr_2$ [6] and $Pd(OAc)_2$ in the presence of a phosphine ligand with frequently used in stoichiometric amounts [7]. Since some of these reagents are toxic, corrosive and air- or moisture-sensitive. Heterogeneous catalysts have been developed to overcome these drawbacks due to their easiness in separation and reusability with low toxicity. Solid acid catalysts, such as zeolites [8,9], Nafion-H [10] and heteropoly acids [11] have been applied for this isomerization reaction. However, the aldehyde products could be undergone the competitive aldol condensation or polymerization makes some process suffers from the rapid catalyst deactivation by coke formation [9,12]. The development of catalytic processes for the isomerization of styrene oxide still attracted much attention in the fine chemical industry.

Pillared clays are micro-mesoporous materials synthesized by exchanged cations with polyoxocations into the interlayer of clay. After calcination, the intercalated polyoxocations are transformed into inorganic oxide-pillared between the silicate layers contribute high surface area and acidic property. Pillared clays have been shown to contain both Brønsted and Lewis acid sites. Several modifications of pillared clays produce a wide range of catalytic activities for utilizing in numerous applications such as adsorbents and efficient catalysts [13–17]. The investigation on the catalytic performance of the pillared clay materials has increased considerably, mostly in acid catalysis. Acid catalyzed reactions and selective oxidation can be occurred efficiently by using chromium pillared clay catalysts such as benzylic oxidation [18], oxidation of chlorinated hydrocarbons [19], propene oxidation [20] and synthesis of octahydroxanthenes [21]. Due to the variety of chromium oxidation states made it is an interesting metal for catalytic applications [22].

In this work, we report the utilization of chromium pillared montmorillonite as a solid acid catalyst for the transformation of styrene oxide. The corresponding aldehyde derived from styrene oxide isomerization, phenylacetaldehyde, is an important intermediate for the production of floral fragrances (a narcissus-like smell), pharmaceuticals, pesticides and herbicides [12]. As for the transformation to acetonide products that used in the pharmaceutical and fragrance production were also revealed. To our best knowledge, there is no report on the utilization of chromium pillared clays as a catalyst for these reactions.

RESULTS AND DISCUSSION

Characterization Of Catalysts

The XRD patterns of Cr-pillared clay and parent montmorillonite are shown in Fig. 1. The d_{001} basal spacing of Cr-PLM was found as a broad peak and larger basal spacing, compared with the parent clay. The reflection angle (2θ) of Cr-PLM and parent clay at the 001 plane are determined as 6.30° and 6.90°, corresponding to a basal spacing (d_{001}) value of 14.0 and 12.8 Å which revealed that the Cr_2O_3 clusters were intercalated into the interlayer of montmorillonite [23].

The BET specific surface area and acidity of synthesized clay catalyst and montmorillonite clay are displayed in Table 1.

The nitrogen adsorption–desorption isotherms of Cr-PLM suggested the type IV isotherm according to the IUPAC classification with H4 type of hysteresis loop, indicating that the Cr pillaring precursor converted to mesoporous pillared structure between the clay layer [24]. The higher BET specific surface area of the synthesized Cr-pillared clay was obtained as expected. The pillaring process resulting in the improvement of acidity to 2.039 mmol/g. This total acidity (both weak and strong acid sites) of pillared clay was derived from Brønsted and Lewis acid sites [23–25]. The amount of weak Brønsted acidic sites was detected at the lower temperature NH_3 desorption whereas the strong Lewis acidic sites were detected at the high temperature desorption of NH_3. Brønsted acid site is related to the coordination of water molecule with chromium in pillars, while Lewis acid site is ascribed to the Cr_2O_3 in pillars [23,25].

Catalytic Activity Of Cr-Pillared Clay In Styrene Oxide Transformation

The Isomerization Of Styrene Oxide

The isomerization of styrene oxide was selected for the catalytic activity testing of synthesized clay catalysts. Various factors were carefully investigated to optimize the conditions for the isomerization of styrene oxide to produce phenylacetaldehyde.

Firstly, various solvents were screened for styrene oxide isomerization at room temperature (Table 2).

The use of 1,4-dioxane provided the desired product in 22% yield, whereas using CH_2Cl_2, 1,2-DCE, EtOAc, CH_3CN or toluene, the products were obtained in low yields. Using THF as solvent gave the best yield of phenylacetaldehyde.

The catalytic activity of the acidity improved Cr-pillared montmorillonite for styrene oxide isomerization to selectively furnish corresponding aldehyde was investigated (Table 3).

No isomerization activity was observed when the reactions were performed in the absence of clay catalyst or in the presence of montmorillonite under refluxing THF. The quantitative yield of phenylacetaldehyde was obtained when refluxing styrene oxide in THF with 10 wt% of Cr-PLM for 4 h. It should be mentioned that Cr-PLM was a highly effective catalyst for isomerization. To obtain optimal conditions for this catalytic system, reaction time and temperature were investigated. The reaction could be carried out at room temperature to afford the product of 35% within 15 min and continued for 6 h to complete the reaction. Therefore, the shorten reaction time could be achieved by raising temperature. Under refluxing within 15 min, the quantitative yield could be furnished. The proposed mechanism of styrene oxide isomerization catalyzed by Cr-PLM is presented in Fig. 2. The aldehyde formation proceeds *via* coordination of metal cation of clay catalyst to the epoxide oxygen atom followed by C–O bond cleavage to form a more stable benzylic cation. Then 1,2-shift of a hydrogen atom and regenerated the active catalyst to give phenylacetaldehyde.

The isomerization of *trans*-stilbene oxide was used to demonstrate regioselectivity since the isomerization can take place with either phenyl migration to produce diphenylacetaldehyde or with hydrogen migration to furnish 2-phenylacetophenone. The reaction time and the amount of Cr-PLM for the isomerization of *trans*-stilbene oxide were examined to optimize the reaction conditions (Table 4).

The isomerization of *trans*-stilbene oxide could be carried out utilizing Cr-PLM at reflux temperature. The yield of product was increased when prolonged the reaction time. Nevertheless, a relatively long reaction time as 6 h led to the formation of undesired 2-phenylacetophenone. Increasing amount of Cr-PLM, only desired product was obtained in excellent yield. Prolonged the reaction time to 4 h could not enhance the yield. Under these conditions *trans*-stilbene oxide underwent regioselective isomerization to produce diphenylacetaldehyde as the major product in excellent yield. Interestingly, the catalyst could be reused at least five times without loss of activity.

The Synthesis Of Acetonide

1,3-Dioxolanes are widely used protecting group for the synthetic carbohydrate and steroid chemistry [26–29]. In the pharmaceutical and fragrance industries, acetonides (2,2-dimethyl-1,3-dioxolanes) are used both as intermediates and as final products [30–34]. Epoxides can be transformed to acetonides straightforwardly with carbonyl compounds, generally with ketones, in the presence of Brønsted or Lewis acid catalysts [35–40]. In recent years, the development and application of effective heterogeneous catalysts has increased greatly [41–45]. Pillared clays have been shown to be effective catalysts for the transformation of epoxides to acetonides.

Hence, the catalytic activity of synthesized clay catalysts was examined for the synthesis of acetonide from styrene oxide and acetone (Table 5).

When the reactions were carried out in the absence of clay catalyst or in the presence of montmorillonite, no desired product was obtained. Cr-pillared clay gave 96% yield of acetonide much higher than unmodified montmorillonite with 8% of the isomerized aldehyde according to the high acidity and the suitable interlayer spacing of Cr-PLM. Shortened the reaction time to 20 min, the catalytic efficiency was still great. Furthermore, the high yield of acetonide product was obtained, when 2 mL of acetone was used. Thus, it was revealed that Cr-PLM could be used as an efficient catalyst for the synthesis of acetonide from styrene oxide.

The proposed mechanism of the synthesis of acetonide from styrene oxide and acetone catalyzed by Cr-PLM is presented in Fig. 3. The acetonide formation proceeds *via* the coordination of a metal cation of the catalyst with the epoxide oxygen atom. Followed by nucleophilic epoxide ring-opening through the carbonyl oxygen and then regenerated the active catalyst led to dioxolane ring formation.

The Synthesis Of Acetonides From Other Epoxides With Acetone

Various epoxides were reacted with acetone using a catalytic amount of Cr-PLM. The excellent yields of the corresponding acetonides were obtained in all cases with different reaction conditions (Table 6).

The transformation of styrene oxide to the corresponding acetonide was much faster than the reaction of terminal aliphatic epoxide such as 1-dodecene oxide. Because of the stable benzylic cation was formed while epoxide has undergone ring-opening. Epoxides with ethereal linkage need more strongly reaction condition to obtain their corresponding acetonides in high yields. Owing to the steric effect of bulky phenyloxy, butyloxy, and *t*-butyloxy groups on the epoxide ring decreased the rate of reaction. The catalyst could be reused at least five times without loss of catalytic activity.

CONCLUSION

A convenient catalytic method for styrene oxide transformation have been developed by utilizing Cr-PLM. Excellent yields of the corresponding products from both of the styrene oxide isomerization and the acetonide synthesis were obtained. Cr-PLM was found to be highly effective, easily separable and could be reused at least five times without loss of catalytic activity.

EXPERIMENTAL

Materials

Bentonite clay (Cernic International Co. Ltd.) with the typical chemical analysis of (wt%): SiO_2 63.60, Al_2O_3 17.60, Fe_2O_3 3.10, CaO 3.00, Na_2O 3.40, K_2O 0.50, was used as raw material for catalyst preparation. Raw clay material was firstly purified by fractionated centrifugation to remove quartz and other impurities.

The synthesized clay catalyst was characterized by XRD, surface area analyzer and NH_3-TPD. The XRD patterns of parent clay and synthesized Cr-pillared clay were obtained by a Rigaku, D/MAX-2200 Utima-plus X-ray powder diffractometer with a monochromator for Cu K_α radiation (40 kV, 30 mA). The 2θ was ranged from 2-30º at a scanning rate of 3º/min and a step size of 0.02º. The BET specific surface areas of parent clay and synthesized Cr-pillared clay were obtained from surface area analysis using the Microtrac BELSORP mini-II adsorption instrument. Acidity of all clay materials was measured by temperature-programmed desorption (TPD) method. The TPD spectra of ammonia were recorded by the BELCAT equipped with thermal conductivity detector.

For the catalytic study, products from epoxide transformation were determined by Varian CP-3800 GC (FID, BP1 column, 30 m). The ^1H NMR spectra were obtained in $CDCl_3$ and determined by Varian Mercury plus 400 NMR spectrometer which operated at 399.84 MHz.

Preparation And Characterization Of Cr-Pillared Clay Catalyst

Bentonite was purified by fractionated sedimentation. Raw bentonite was suspended in deionized water under vigorous stirring at room temperature. The colloid clay was centrifuged, after that quartz sediments and other impurities could be separated. The colloid bentonite was collected and dried at 100 ºC. The purified bentonite as montmorillonite was characterized by XRD, BET and TPD method.

Cr-pillared montmorillonite was synthesized according to the method reported by Yurdakoç et al. with some modifications [25]. $CrCl_3·6H_2O$ (2.67 g) was dissolved in 100 mL of deionized water. Na_2CO_3 (0.02 g) was added to the $CrCl_3$ solution at room temperature. This solution mixture was then aged at 95 ºC for 40 h. At the same time, 2 g of montmorillonite was suspended in 100 mL of deionized water under stirring at room temperature. Afterwards, the warm hydrolyzed chromium solution was slowly added to the montmorillonite suspension and stirred for 24 h. The Cr-pillared montmorillonite suspension was collected by centrifugation, washed with deionized water until chloride ions were eliminated, dried at 100 ºC and calcined at 300 ºC for 5 h. The calcinated products were designated as Cr-PLM. The obtained Cr-PLM was characterized using XRD, BET and TPD method.

GENERAL CATALYTIC PROCEDURE

For The Isomerization Of Styrene Oxide

Cr-PLM (10 wt%) was added to the mixture of styrene oxide (1 mmol) and THF (5 mL) and the reaction was then continuously stirred for desired time and temperature (monitored by TLC). After the appropriate time or the reaction was completed, the catalyst was easily filtered out, and thoroughly washed with Et_2O. The solvent was partly evaporated under reduced pressure. The obtained mixture was taken and analyzed by GC with the addition of an exact amount of an appropriate internal standard.

For The Synthesis Of Acetonide

Cr-PLM (10 wt%) was added to the mixture of styrene oxide (1 mmol) and acetone (3 mL) and the reaction was then continuously stirred for desired time and temperature (monitored by TLC). After the appropriate time or the reaction was completed, the catalyst was easily filtered out, and thoroughly washed with acetone. The solvent was partly evaporated under reduced pressure. The obtained mixture was taken and analyzed by GC with the addition of an exact amount of an appropriate internal standard.

Recovery And Reuse Of Cr-Pillared Clay

Cr-PLM could be easily recovered from the reaction mixture by filtration or centrifugation. After washing with Et_2O, dried at 120 ºC in oven for 2 h, the regenerated Cr-PLM was used in the next run.

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Table 1 The amount of acidity and surface area of catalysts

Entry	Catalyst	Surface area (m^2/g)	Acidity (m mol/g		Total acidity (mmol/g)
			Weak acid sites	Strong acid sites	
1	Cr-PLM	91.2	0.126	1.913	2.039
2	Montmorillonite	58.4	0.000	1.188	1.188

Table 2 The solvent effect on isomerization of styrene oxide catalyzed by Cr-PLM

Entry	Solvent	Recovery (%)[a]	Yield (%)[a]
1	CH_2Cl_2	88	6
2	1,2-DCE	81	12
3	1,4-dioxane	72	22
4	EtOAc	84	14
5	THF	70	35
6	CH_3CN	95	3
7	toluene	100	10

Reaction conditions: styrene oxide (1 mmol), Cr-PLM (10 wt%), solvent (5 mL) at room temperature (30°C) for 15 min.

[a] determined by GC using an internal standard technique

Table 3 Catalytic activity of clay catalysts in the isomerization of styrene oxide

Entry	Catalyst	Temp.	Time (h)	Recovery (%)[a]	Yield (%)[a]
1	-	reflux	4	quant.	0
2	Montmorillonite	reflux	4	quant.	0
3	Cr-PLM	reflux	4	0	quant.
4	Cr-PLM	RT (30 ^{o}C)	0.25	70	35
5	Cr-PLM	RT (30 ^{o}C)	6	0	quant.
6	Cr-PLM	reflux	0.08	14	89
7	Cr-PLM	reflux	0.25	0	quant.

Reaction conditions: styrene oxide (1 mmol), clay catalyst (10 wt%), THF (5 mL)

[a] Determined by GC using an internal standard technique

Table 4 The isomerization of *trans*-stilbene oxide catalyzed by Cr-PLM

Entry	Catalyst amount (wt%)	Time (h)	Recovery (%)[a]	Yield (%)[a,b]
1	10	0.25	60	35
2	10	1	44	51
3	10	6	11	73 (12)[c]
4	30	1	5	91
5	30	4	6	92

Reaction conditions: trans-stilbene oxide (1 mmol), Cr-PLM (vary), THF (5 mL) at reflux temperature

[a] determined by GC using an internal standard technique

[b] diphenylacetaldehyde

[c] The yield of 2-phenylacetophenone is shown in the parenthesis

Table 5 Catalytic activity of clay catalysts in the synthesis of acetonide

Entry	Catalyst	Time (h)	Recovery (%)[a]	Yield (%)[a,b]	
1	-	2	96	0	2
2	Montmorillonite	2	93	0	3
3	Cr=PLM	2	0	96	8
4	Cr=PLM	0.33	0	93	11
5	Cr=PLM	0.33	0	98	9

Reaction conditions: styrene oxide (1 mmol), acetone (3 mL), clay catalyst (10 wt%) at room temperature (30°C)

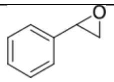
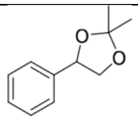
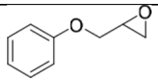
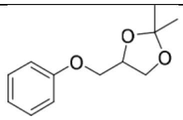
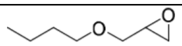
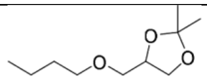
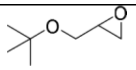
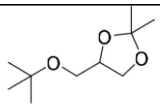
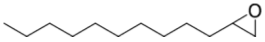
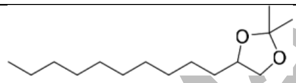
[a] determined by GC using an internal standard technique

[b] 2,2-dimethlyl-4-phenyl-1,3-dioxolane

[c] phenylacetaldehyde

[d] acetone (2 mL)

Table 6 The synthesis of acetonides catalyzed by Cr-PLM

Entry	Epoxides	Acetonides	Yield (%)[a]
1[b]			98
2[c]			97
3			102
4[d]			97
5			99

Reaction conditions: epoxide (1 mmol), acetone (2 mL and Cr-PLM (10 wt%) at reflux temperature for 2 h

[a] determined by GC using an internal standard technique

[b] Cr-PLM (10 wt%) at room temperature (30 °C) for 20 min

[c] Cr-PLM (20 wt%) at reflux temperature for 4 h

[d] Cr-PLM (10 wt%) at reflux temperature for 4 h

Fig. 1. X-ray diffraction patterns of (a) montmorillonite and (b) Cr-pillared montmorillonite.

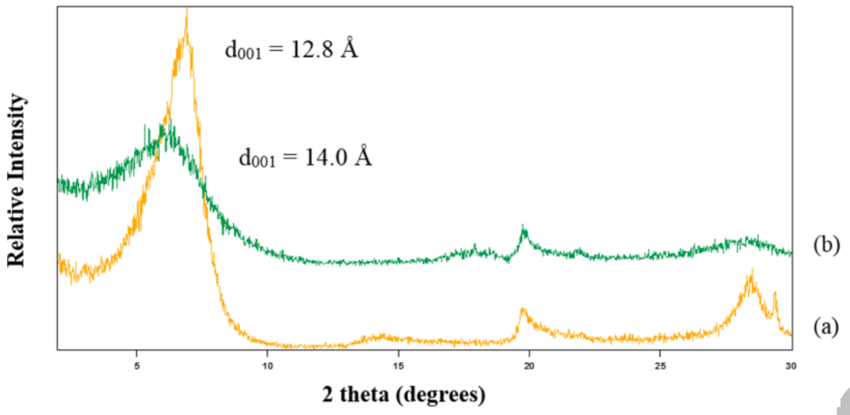


Fig. 2. Proposed mechanism for styrene oxide isomerization catalyzed by Cr-PLM.

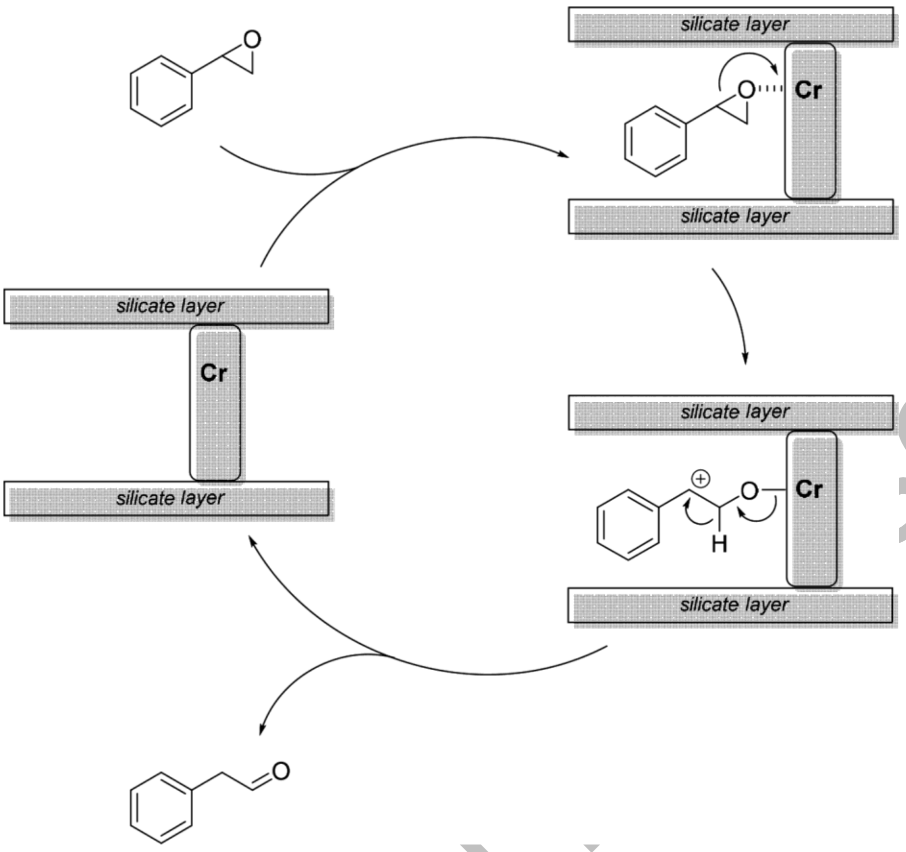


Fig. 3. Proposed mechanism for the synthesis of acetonide catalyzed by Cr-PLM.