

Selective synthesis of primary methoxypropanol using clay supported tris(2,4-pentanedionato)zirconium(IV)

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Abstract

2-Methoxy-1-propanol has been selectively synthesized using clay supported tris(2,4-pentanedionato)zirconium(IV), prepared by facile ion-exchange process. The tris(2,4-pentanedionato)zirconium(IV) cation was synthesized by refluxing zirconium chloride with acetylacetonate in chloroform. The heterogenized complex showed an increase in conversion rate and selectivity compared to the homogeneous one. Selectivity of 58% towards primary methoxypropanol was achieved under mild reaction condition. The clays selected as supporting materials were synthetic taeniolite and natural bentonite. It was observed that natural bentonite showed similar activity to synthetic taeniolite as a catalyst support.

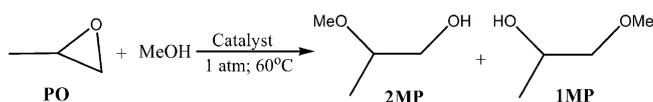
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1. Introduction

Acid catalysis has been of great interest in organic synthesis. One of the challenges is designing acid catalysts to synthesize primary methoxypropanol, which is used as a versatile synthetic intermediate. Clay has drawn much attention as catalyst support due to its layered structure [1–6]. This work deals with the pillarization of synthetic and natural clays with zirconium metal complex, forming organic/inorganic hybrid acid catalyst for synthesizing 2-methoxy-1-propanol (2MP) from propylene oxide (PO) and methanol (Scheme 1). Theoretically, the use of any acid catalyst is supposed to result in primary methoxypropanol. But in practice, the use of conventional acid catalysts (e.g. TiCl_4 , FeCl_3 and ZrCl_4) always results in higher selectivity towards 1-methoxy-2-propanol (1MP) instead of 2MP. The problem of separation also makes those catalysts less favorable in industry.

A previous work was able to achieve 51.1% of 2MP using $\text{Co}_2(\text{CO})_8$ catalyst [7]. Here, selectivity of 58% towards 2MP was achieved under milder condition by immobilized zirconium complex. The catalyst precursor used in this work was tris(2,4-pentanedionato)zirconium(IV) ($[\text{Zr}(\text{acac})_3]^+$, denoted as Zr-acac3) cation. The selected clays were lithium taeniolite ($\text{Li}[(\text{Mg}_2\text{Li})(\text{Si}_4\text{O}_{10})\text{F}_2]$) and natural bentonite taken from East Java, Indonesia ($\text{K}_{0.022}\text{Ca}_{0.180}\text{Na}_{0.008}[(\text{Si}_{3.626}\text{Al}_{0.374}\text{O}_{10})(\text{Al}_{1.589}\text{Fe}_{0.296}\text{Ti}_{0.023}\text{Mg}_{0.284})(\text{OH})_2]$), which is close to beidellite structure [8]. The synthesized zirconium complex was then immobilized into taeniolite (C.E.C. = 268.2 meq./100 g) and natural bentonite (C.E.C. = 82.0 meq./100 g), denoted as Zr-acac3/TN and Zr-acac3/BNT, respectively by simple ion-exchange method.



Scheme 1.

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2. Experimental

2.1. Synthesis of tris(2,4-pentanedionato)zirconium(IV) chloride

A solution of acetylacetone (3.0 ml, 29.1 mmol) in chloroform (30 ml) was added dropwise under inert atmosphere into a solution of zirconium tetrachloride (2 g, 8.58 mmol) in chloroform (30 ml) at 65 °C. The reaction mixture was refluxed for 15 h at 65 °C. After the reflux, the solution was immediately cooled down at 0 °C to let a crystallization process occur and the chloroform was removed under vacuum. Faint yellow powder of the product was recrystallized to release impurities and dried *in vacuo* overnight before analysis. Analysis was conducted by UV–vis, FT-IR, ¹H NMR and CH Analysis.

[Zr(acac)₃]Cl: yield 20%; UV λ_{max} (MeOH), 308.0 (ε 8869) nm; δ_H (400 MHz, DMSO), 2.004 (s, 6H); 5.872 (s, 1H); FT-IR ν_{max}, ν_{C–H} (methyl), 2995–2922 (w); ν_{C=O}, 1572 (s); ν_{C=C} (enol form), 1533 (s) cm⁻¹; Anal. Calc. for [Zr(acac)₃]Cl: C, 42.49; H, 4.99. Found: C, 41.51; H, 5.13.

2.2. Catalyst preparation

Clays (lithium taeniolite from Topy Industry Co., Ltd. and natural bentonite) of 0.1 g respectively were swollen by deionized water (20 ml). The synthesized complex, [Zr(acac)₃]Cl (50% of the C.E.C.), was dissolved in deionized water (20 ml) and added into the swollen clay followed by stirring for 48 h at ambient atmosphere. The catalysts were characterized using XRD, FT-R and UV–vis.

2.3. Synthesis of 2-methoxy-1-propanol

Propylene oxide (0.25 ml, 3.55 mmol) was added into methanol in excess (10 ml, 0.274 mol) containing 1 mol% of the active catalyst. The catalyst was dried under vacuum overnight prior to the catalytic experiment. The reaction mixture was refluxed at 60 °C. Analysis was conducted by GC and GC-MS.

3. Results and discussion

As shown in Table 1 (entries 1–5), conventional acid catalysts (i.e. TiCl₄, FeCl₃, NiCl₂, CoCl₂ and ZrCl₄) demonstrated relatively low catalytic activity for the reaction of propylene oxide with methanol. The low catalytic activity was also observed in the case of the homogeneous zirconium complex (Table 1, entry 6). Interestingly, the immobilization of the zirconium complex into layered structures, such as taeniolite and bentonite, was able to increase the selectivity of catalysts as well as the conversion rate of the reaction as they were employed in the catalytic reactions run for 24 h (Table 1, entries 7 and 8). The selectivity increased to 58% in the reaction using zirconium complex either supported into taeniolite or bentonite, raising up under milder reaction con-

Table 1
Synthesis of primary methoxypropanol from propylene oxide and methanol^a

Entry	Catalyst	Host	Conversion (%PO)	Yield (%2MP)	Selectivity (%2MP)
1	TiCl ₄ ^b	–	17	3	45
2	FeCl ₃	–	64	30	50
3	NiCl ₂	–	21	5	32
4	CoCl ₂	–	23	5	26
5	ZrCl ₄	–	50	8	39
6	Zr-acac ₃	–	41	11	34
7	Zr-acac ₃	TN	>99	57	58
8	Zr-acac ₃	BNT	>99	58	58
9	Zr-acac ₃	Zeolite ^c	74	31	42
10	–	TN	24	5	20
11	–	BNT	29	11	38

^a Reaction condition: catalyst 1 mol%; propylene oxide 3.55 mmol; methanol 0.247 mol; 60 °C; 1 atm; 24 h.

^b Room temperature; catalyst 10 mol%.

^c Natural zeolite containing 18% clinoptilolite.

dition to 19% compared to the homogeneous state or 7% compared to the previous work, of which the reaction was run under the following conditions: 160 °C; 1 h; 40 kg/cm² CO and 80 kg/cm² H₂ using Co₂(CO)₈ catalyst [7]. Actually, unless the heterogeneous and homogeneous catalysts reached the same conversion rate, we could not directly compare the selectivity between them. To ascertain the fact, the time course of catalytic reactions which were run for 90 min using Zr-acac₃/TN and Zr-acac₃/BNT was observed. The length of time was sufficient to observe the change of selectivity towards conversion since the catalytic reaction using Zr-acac₃/TN fully completed in 90 min (Fig. 1).

As we can observe from Fig. 1, both Zr-acac₃/TN and Zr-acac₃/BNT reached selectivity of around 60% towards 2MP when their conversions were about 40% although the selectivity of the homogeneous catalyst, Zr-acac₃, was only 34% at the same conversion (Table 1, entry 6). Therefore we

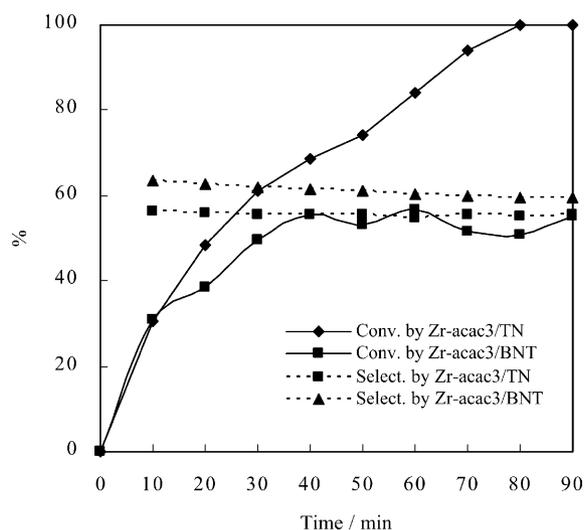


Fig. 1. Time course of the reactions. The selectivity of the reaction using either Zr-acac₃/TN or Zr-acac₃/BNT was approximately 60% at which the conversion rate was about 40%.

conclude that the selectivity of the heterogenized complex into clay was higher than that of the homogeneous one. The enhancement in conversion rate can be explained from a desolvation phenomenon during an ion-exchange reaction of an intercalated metal, most likely due to the ionic interaction between the metal and the negative charge of the layers. Such a phenomenon was previously reported by Suzuki et al. [9,10] in their work on ion-exchange properties on layered materials, such as hectorite, taeniolite and γ -titanium phosphate. Here, the desolvation property explained that during the catalytic reaction, the number of methanol inside the interstitial layer, solvating the zirconium complex, was lower than that in homogeneous state due to weakened solvation ability of methanol. However, it augmented the contact of the catalyst precursor with the substrate, enhancing the conversion rate of the reaction.

The use of natural zeolite as a catalyst support has also been observed to evaluate the performance of selected clays towards other supporting material (Table 1, entry 9). It was found that in this work layered structures such as taeniolite and bentonite were superior to the selected zeolite.

To assure the better performance of the synthesized solid acid catalyst compared to others, an experiment using well-known protic acid catalyst, *p*-toluenesulfonic acid was carried out. The catalyst was able to achieve >99% conversion after 24 h reaction, showing equal activity to the synthesized solid zirconium acid catalyst. However, the selectivity was still lower than that of the clay supported zirconium complex. It only achieved 55% of selectivity towards **2MP**, and also left a separation problem.

The clearance space of interstitial layer expanded to 0.57 nm in taeniolite and 1.0 nm in bentonite (Table 2), indicated by the shift of (001) reflection to lower angle (Fig. 2), due to the catalyst immobilization. In the case of taeniolite pillarization, it was moderately close to the molecular size of Zr-acac3 with the assumption that the complex was arranged as the structure model in Fig. 3. Such a limited interlayer space can enforce the interaction between the active site (zirconium atom) and substrate (**PO**), resulting in an increase in the product selectivity. The catalysts swelled during the catalytic reaction. The swelling expansion depended on the solvent. Experiments of swelling the lithium taeniolite with various solvents showed that expansion was proportional to the dielectric constant of the solvent (Table 3). Lithium taeniolite was used instead of taeniolite supported

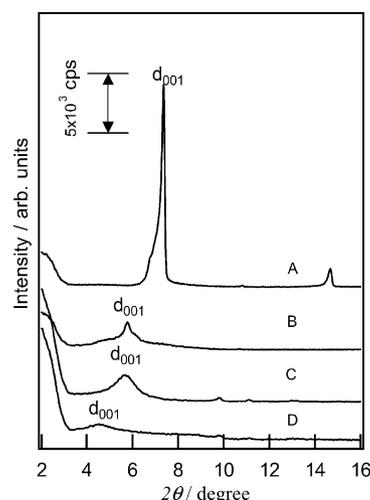


Fig. 2. Powder XRD patterns of zirconium complex intercalated taeniolite and bentonite. (A) taeniolite (TN), (B) Zr-acac3/TN, (C) bentonite (BNT), (D) Zr-acac3/BNT. (A) and (B) were measured at 20 mA, 25 kV; while (C) and (D) at 20 mA, 50 kV.

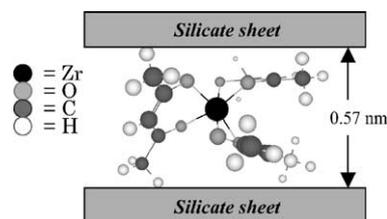


Fig. 3. Proposed arrangement of Zr-acac3 in the interlayer of taeniolite.

zirconium complex due to their expansion proportionality and the ease of observing the change of expansion accurately [4].

Among the solvents used here, methanol resulted in the highest expansion. The expansion of the interlayer clay was important since the molecular length of zirconium complex was longer than the interlayer size of the clay in the dry state (molecular length of Zr-acac3 is 0.98 nm). Several angstrom units of expansion could increase mobility of the zirconium complex slightly, which was important for the complex to get the optimal arrangement in the interlayer. This would then enable the active site to be easily reached by the substrate.

The formation of primary methoxypropanol occurred by an S_N1 mechanism, in which the catalyst first activated the substrate through **PO** cleavage, forming a secondary car-

Table 2
Loading amounts and XRD parameters^a of clay supported Zr-acac3

Sample	L.A. ^b (meq./100 g)	d_{001} (nm)	C.S. ^c (nm)
TN	–	1.21	0.25
Zr-acac3/TN	112	1.53	0.57
BNT	–	1.56	0.60
Zr-acac3/BNT	78	1.96	1.00

^a Cu- K_{α} .

^b Loading amount.

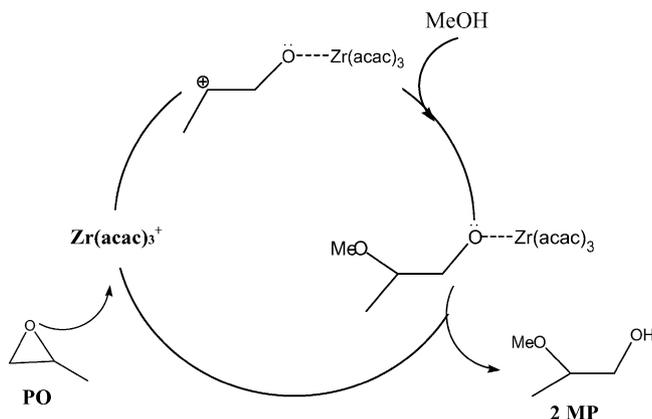
^c Clearance space = d_{001} – 0.96 nm (thickness of layer).

Table 3
XRD parameters^a of lithium taeniolite swollen with various solvents

Solvent	ϵ^b	d_{001} (nm)	C.S. (nm)	Expansion (nm)
None	–	1.21	0.25	–
Methanol	33.0	1.37	0.41	0.16
Ethanol	25.3	1.33	0.37	0.12
Toluene	2.4	1.22	0.26	0.01
<i>n</i> -Hexane	1.9	1.21	0.25	–

^a Cu- K_{α} .

^b Dielectric constant of solvents [11].



Scheme 2. Proposed catalytic cycle.

Table 4

Solvent effect examined on homogeneous and heterogeneous zirconium acid catalyzed reaction^a

Entry	Catalyst	Solvent	Conversion (%PO)	Selectivity (%2MP)
1	Zr-acac3	Methanol	11	49
2		Ethanol	Trace	0
3		Toluene	Trace	0
4		<i>n</i> -Hexane	0	0
5	Zr-acac3/TN	Methanol	>99	56
6		Ethanol	2	0
7		Toluene	4	38
8		<i>n</i> -Hexane	Trace	57
9	Zr-acac3/BNT	Methanol	55	60

^a Reaction condition: 60 °C; 1 atm; 90 min; catalyst 1 mol%; propylene oxide 3.55 mmol; methanol 6.17 mmol (ignored if used as solvent); solvent 10 ml.

bocation (Scheme 2). The other way of PO cleavage led to a primary carbocation, which was less stable than the secondary one. The selection of proper solvent was important since protic and polar solvent would lead to the solvation of methoxy nucleophile. The use of less polar solvent also demonstrated low performance since the clay was hardly swelled (Table 4), resulting in difficult re-arrangement of the catalyst inside the layer to be easily reached by the substrate.

4. Conclusion

New organic/inorganic hybrid acid catalysts have been prepared by immobilization of tris(2,4-pentanedionato) zirconium(IV) cation as the catalyst precursor into layered

structures, such as taeniolite and bentonite. The synthesized catalysts were suitable for selective synthesis of primary methoxypropanol, which was difficult to be synthesized by conventional acid catalysts. The immobilization of the complex into the clays has increased catalytic performance as well as the selectivity. The catalyst showed better performance even under mild reaction condition compared to the previous work. It was also observed that natural bentonite possessed similar activity to taeniolite as a catalyst support when they both were employed in the catalytic reaction run for 24 h, indicating the potential use of natural bentonite from Indonesia as a supporting material.

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