蒙脱土负载钴卟啉: 一种在催化醇类氧化制备羰基化合物中可循环使用的高效催化剂

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摘要: 制备了蒙脱土负载的离子型四(1-甲基-4-吡啶基)金属卟啉, 并用于催化醇类氧化制备羰基化合物的反应中。结果表明, 该催化剂表现出优异的活性和产物选择性, 其中在苯甲醇氧化反应中, 苯甲醛收率可达 90%, 且连续重复使用 5 次后, 其活性未见明显下降。

关键词: 金属卟啉; 蒙脱土; 氧化; 醇; 氧气

中图分类号: O643 **文献标识码:** A

收稿日期: 2012-08-20. 接受日期: 2012-09-10.

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基金来源: 国家自然科学基金 (20976203 和 21036009).

本文的英文电子版(国际版)由Elsevier出版社在ScienceDirect上出版(<http://www.sciencedirect.com/science/journal/18722067>).

Cobalt Porphyrin Immobilized on Montmorillonite: A Highly Efficient and Reusable Catalyst for Aerobic Oxidation of Alcohols to Carbonyl Compounds

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Abstract: The highly efficient aerobic oxidation of alcohols to carbonyl compounds was achieved catalyzed by cationic *meso*-tetrakis (1-methyl-4-pyridyl, TM4PyP) metalloporphyrins immobilized in montmorillonite interlayers. Cobalt porphyrin (CoTM4PyP-MT) showed excellent activity and selectivity in the aerobic oxidation of benzyl alcohol, where 90% yield of benzaldehyde was obtained. CoTM4PyP-MT can be five times reused without significant loss of activity.

Key words: metalloporphyrins; montmorillonite; oxidation; alcohol; dioxygen

Received 20 August 2012. Accepted 10 September 2012.

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This work was supported by National Natural Science Foundation of China (20976203 and 21036009).

English edition available online at Elsevier ScienceDirect (<http://www.sciencedirect.com/science/journal/18722067>).

Selective catalytic oxidation of alcohols to corresponding aldehydes is of great importance for both laboratory and synthetic industrial applications [1]. A variety of transition metal-based catalysts has been intensively investigated for the oxidation of alcohols so far [2–6]. As models of cytochrome P450, metalloporphyrins are used as oxygen carrier intermediates and widely as homogeneous catalysts for various biomimetic oxidation reactions as well [7,8]. The homogeneous oxidation of alcohols catalyzed by metal-

loporphyrins has been well investigated with PhIO [9], Cl₂PyNO [10], KHSO₅ [11], and *m*-chloroperbenzoic acid [12] as oxidants. However, metalloporphyrins catalysts decompose easily in the oxidation process and the difficulty of recovery is a major weakness.

Great efforts have been made to immobilize metalloporphyrins onto supports such as organic polymer materials, chemically modified silica surfaces, and mesoporous molecular sieves to promote stability [13–19]. Montmorillonite

is preferable to be used as the support for immobilizing metalloporphyrins due to its large specific surface area, chemical and mechanical stability, layered structure, and high cation exchange capacity [20]. So far, only oxidations of alkanes, cyclohexene, and 2-mercaptoethanol have been reported over by montmorillonite-supported cationic metalloporphyrins [21–24]. To our knowledge, the aerobic oxidation of alcohols catalyzed by montmorillonite-supported metalloporphyrins is still unknown.

In continuation of our ongoing research on the metalloporphyrin-based aerobic oxidation of alcohols [25,26] we demonstrate herein the first successful example of the efficient aerobic oxidation of alcohols catalyzed by montmorillonite-supported metalloporphyrins. This heterogeneous catalyst presents excellent activity and can be five times consecutively reused without significant loss of activity.

1 Experimental

1.1 Materials

Alcohols and carbonyl compounds were of analytical grade and purchased from Alfa Aesar or Aldrich. They were used without further purification unless indicated. Pyrrole and isobutyraldehyde were redistilled before use. All other solvents were analytical grade. The montmorillonite was purchased from Aladdin Reagents.

1.2 Synthesis of *meso*-tetrakis (1-methyl-4-pyridyl) metalloporphyrin [26]

Pyrrole (20 ml) and 4-pyridinecarbaldehyde (20 ml) were refluxed in propionic acid (200 ml) for 1 h to produce *meso*-tetrakis(4-pyridyl) porphyrin (T4PyP) with a yield of 24%. Next, T4PyP (0.25 g) and cobalt acetate (1 g) were refluxed in dimethylformamide (35 ml) for 6 h under nitrogen atmosphere to form *meso*-tetrakis (4-pyridyl) cobalt porphyrin (CoT4PyP) with a yield of 88%.

In the following step, CoT4PyP (0.2 g) and methyl *p*-toluenesulfonate (12 g) were added to 100 ml dimethylformamide solution. The mixture was stirred for 12 h at 90 °C, and the solution was cooled to room temperature. Ethyl ether (20 ml) was added to the mixture and it was kept overnight. After filtration, the filter cake was washed thoroughly with ethyl ether and purified by recrystallization in water/acetone (1:2) to obtain *meso*-tetrakis (1-methyl-4-pyridyl) cobalt porphyrin (CoTM4PyP) with 80% yield. The other metalloporphyrins could be synthesized in similar procedures by replacing Co with both metal ions. The spectral and analysis data of metalloporphyrins catalysts were listed as following. [CoTM4PyP]⁴⁺: EI-MS: *m/z* 735. UV-Vis (H₂O): $\lambda_{\max}$, nm (log ϵ) 418 (2.47),

539 (0.93). IR (KBr, cm⁻¹): 1640, 1005. Anal. calcd. for C₄₄H₂₈N₈Co: C, 71.83; H, 4.93; N, 15.23. Found: C, 71.43; H, 4.72; N, 14.96. [MnTM4PyP]⁴⁺: EI-MS: *m/z* 731. UV-Vis (H₂O): $\lambda_{\max}$, nm (log ϵ) 464 (2.48), 559 (1.25). IR (KBr, cm⁻¹): 1640, 1009. Anal. calcd. for C₄₄H₂₈N₈Mn: C, 72.22; H, 4.96; N, 15.31. Found: C, 71.79; H, 4.92; N, 15.16. [FeTM4PyP]⁴⁺: EI-MS: *m/z* 732. UV-Vis (H₂O): $\lambda_{\max}$, nm (log ϵ) 415 (2.84), 543 (1.23). IR (KBr, cm⁻¹) 1638, 1002. Anal. calcd. for C₄₄H₂₈N₈Fe: C, 72.13; H, 4.95; N, 15.29. Found: C, 72.32; H, 4.95; N, 15.31.

1.3 Preparation of montmorillonite interlayer-fixed metalloporphyrins

A mixture of *meso*-tetrakis (1-methyl-4-pyridyl) metalloporphyrin (Mn, Co, Fe) (100 mg) and montmorillonite (1 g) in 0.1 mol/L nitric acid (100 ml) was submitted to reflux and stirred for 5 h. Then, the mixture was slowly cooled to room temperature. The solid was filtered and washed with water and ethanol for several times. The solid was dried in vacuum at 80 °C. The amount of metalloporphyrin adsorbed into clay was quantified by measuring the amount of MTM4PyP (M = Mn, Co, and Fe) in the nitric acid and filtrate on an Atomic Absorption Spectrometer (Shimadzu AA2580).

1.4 Characterization

The UV-visible spectra of metalloporphyrins were recorded on a Shimadzu UV-2450 UV-Vis spectrophotometer in the range of 200 to 700 nm, using water as solvent. Fourier transform infrared (FT-IR) spectra of the samples were recorded in the range of 4000–400 cm⁻¹ on an FT-IR spectrometer (Bruker, VERTEX 70) using the KBr pellet technique. X-ray diffraction measurements were performed on a D-MAX diffractometer with a Cu *K α* source operated at 40 kV and 30 mA. The specific surface area and pore volume of the montmorillonite was determined from nitrogen adsorption-desorption isotherms (Micromeritics ASAP-2010) before and after immobilization of metalloporphyrins.

1.5 Catalytic oxidation of alcohols

A 20 ml Schlenk tube was charged with benzyl alcohol (1 mmol), catalyst (0.015 g), acetonitrile (4 ml), isobutyraldehyde (3 mmol), and naphthalene (0.2 mmol, inert internal standard) and then the mixture was stirred at 70 °C. Dioxygen was bubbled through the solution. The consumption of the starting benzyl alcohol and formation of products was monitored by GC (Shimadzu GC-2010 plus) or GC-MS (Shimadzu GCMS-QP2010).

For the recycling experiments, the catalyst was recovered

by centrifugation and first washed with water (5 ml) for five times, and then with acetonitrile (10 ml) to remove the occluded reactants and products. After washing, the acetonitrile solution was checked for the presence of reactants/products using gas chromatography. The recycled catalysts were then dried in vacuum at 80 °C for 6 h. The recycled catalyst was reused under the same reaction conditions by compensating the lost amount of catalyst.

2 Results and discussion

2.1 Supported catalyst characterization

In this work, montmorillonite is used for the immobilization of cationic metalloporphyrins because it is an easily commercially available clay with interlayer surface. It is also easily exchanged with solute ions by varying the cationic composition of the solution. In the adsorption process, pyridyl ions of metalloporphyrins are bound to the clay surface by sharing one or several ligands with adsorbent cations as isolated complexes. Consequently, *meso*-tetrakis (1-methyl-4-pyridyl) metalloporphyrins can be firmly anchored onto its surface. In all immobilization procedures nearly all metalloporphyrins were transferred to the solids and low quantities were spectrometrically detected in solution by atomic absorption analyses. Thus, the loaded amounts of the MnTM4PyP, CoTM4PyP, and FeTM4PyP was 4.7×10^{-5} mol/g, 3.8×10^{-5} mol/g, and 3.5×10^{-5} mol/g, respectively.

The immobilization process could also be characterized by the color change of the clays. For MnTM4PyP a change was observed from light green to brown, with a final color of dark brown in the case of the dry solid. The presence of metalloporphyrins in the solid clay was determined by the diffuse reflectance ultraviolet-visible spectra (DRS-UV-Vis) and the all results are summarized in Table 1.

Table 1 UV-Vis data of metalloporphyrins and metalloporphyrins-MT

Compound	Solvent	$\lambda_{\max}/\text{nm}$	
		Soret band	Q band
MnTM4PyP	water	463	561
MnTM4PyP-MT	—	494	588
CoTM4PyP	water	428	540
CoTM4PyP-MT	—	446	571
FeTM4PyP	water	404	512
FeTM4PyP-MT	—	427	534

The Soret peak and Q peak of CoTM4PyP-MT appeared at 446 and 571 nm in the region of 400–700 nm. A red-shift of 18 and 31 nm was observed, respectively, compared with those peaks of CoTM4PyP. The red-shifted Soret peak indi-

cates that there was a coordination bond between CoTM4PyP and montmorillonite. A similar red shift was observed for MnTM4PyP and FeTM4PyP immobilized on montmorillonite.

IR spectra of these metalloporphyrins-MT clays further provide some information about the presence of metalloporphyrins in the clays. The results of the FT-IR spectroscopic measurements for cationic metalloporphyrins, montmorillonite, and metalloporphyrins immobilized in the clay are shown in Fig. 1 for CoTM4PyP as an example.

A broad band at 3400 cm^{-1} is the primary O–H stretching vibration of hydroxyl functional groups for montmorillonite. Another broad band between 1032 and 1300 cm^{-1} can be attributed to the stretching vibration of Si–O bonds. The strong absorption at 1609 cm^{-1} is ascribed to the bending vibration of O–H bonds. After CoTM4PyP was immobilized within the clay, the basic characteristic peaks for montmorillonite hardly changed. A characteristic peak of CoTM4PyP at 1009 cm^{-1} disappeared. Some new bands between 1300 – 1600 cm^{-1} were clearly observed, which are attributed to the pyrrolic C=N stretching modes of the metalloporphyrin skeleton. In addition, the broad peak at 1609 cm^{-1} is sharpened, coupled with a blue shift of 34 cm^{-1} . These changes indicated the presence of metalloporphyrins immobilized in montmorillonite.

Fig. 1. FT-IR spectra of CoTM4PyP, MT, and CoTM4PyP/MT.

XRD was used to determine the influence of metalloporphyrins on the structure of the clay. The diffraction patterns were recorded in the 2θ range of 1° – 80° with a scanning rate of $8^\circ/\text{min}$. The XRD patterns of MT and CoTM4PyP-MT are presented in Fig. 2. It can be seen that the structure of cobalt porphyrin-immobilized clay is similar to that observed for the montmorillonite, indicating that they possess the same morphology and crystalline structure. The solid support is structurally unchanged and the cationic metalloporphyrins should be dispersed within the interlayers.

Moreover, a slight shift of the basal spacing d_{001} (the

Fig. 2. XRD patterns of CoTM4PyP-MT (1) and MT (2).

characteristic reflection) to lower angles with a corresponding increase in the d spacing was observed after the incorporation of CoTM4PyP into the clay. According to the Scherrer formula, the basal spacing of CoTM4PyP-MT was 1.373 nm, which agrees well with the results reported by Kameyama et al. [24]. Similarly, the basal spacings of MnTM4PyP-MT and FeTM4PyP-MT were 1.396 and 1.389 nm, respectively. The metalloporphyrin plane in montmorillonite was estimated to be oriented parallel to the lamella in this clay. Because the thickness of a montmorillonite crystal layer is about 0.96 nm, the thickness of the intercalated CoTM4PyP is estimated at 0.413 nm, and the size of CoTM4PyP is estimated about 0.67 nm. The size of these cationic metalloporphyrins in the axial direction changes depending on the angle of the pyridyl groups located at the *meso*-position. Therefore, the CoTM4PyP intercalation space of 0.413 nm indicates that the pyridine rings are inclined at an angle of about 30° against the porphyrin plane. A schematic model for the intercalation of CoTM4PyP in montmorillonite is shown in Fig. 3.

Fig. 3. Model for the intercalation of CoTM4PyP in montmorillonite.

The specific surface area and pore volume are presented in Table 2. The specific surface area of montmorillonite is

Table 2 Specific surface area and pore volume of MT and metalloporphyrins-MT

Sample	Specific surface area (m^2/g)	Pore volume (cm^3/g)
MT	34	0.043
MnTM4PyP-MT	83	0.085
CoTM4PyP-MT	67	0.059
FeTM4PyP-MT	66	0.056

$34 \text{ m}^2/\text{g}$, which is much lower than that of montmorillonite with immobilized metalloporphyrins. Metalloporphyrin complexes intercalated between the montmorillonite layers could give rise to the formation of new pores and surface area.

2.2 Catalytic performance in aerobic oxidation of alcohols

With benzyl alcohol as model compound, the effects of reaction conditions on the oxidation in the presence of montmorillonite-supported metalloporphyrins have been investigated with molecular oxygen as oxidant and isobutyraldehyde as co-reductant. Benzaldehyde is the main product of the oxidation coupled with a little amount of benzoic acid.

2.2.1 Catalysis of various supported metalloporphyrins

Iron, manganese, and cobalt are the most frequently used metals in oxidation reactions and those metals were chosen to synthesize the cationic metalloporphyrins. The catalytic activity and yield of different metalloporphyrins for benzyl alcohol oxidation by molecular oxygen were investigated. The loaded amount of the different metalloporphyrins immobilized in the montmorillonite interlayer is different as described above. Hence, the used mass of MnTM4PyP-MT, CoTM4PyP-MT, and FeTM4PyP-MT was 12, 15, and 16 mg corresponding to the same molar quantity of each catalyst, i.e. $0.57 \times 10^{-3} \text{ mmol}$. The results are shown in Fig. 4.

As shown in Fig. 4, the catalytic activity of the metalloporphyrins appears to be dependent on the nature of their central ions. The present results clearly show that cobalt porphyrin is considerably more selective than the manganese and iron porphyrin catalysts in the aerobic oxidation of benzyl alcohol. The over-oxidized product benzoic acid was obtained when manganese and iron porphyrin were used as catalyst. The catalytic performance for these heterogeneous catalysts is not closely related with surface area, because MnTM4PyP-MT has the highest specific surface area as shown in Table 2. The activity difference of the various metalloporphyrins is probably related with their electric potential and the stability of metal atom valences.

Fig. 4. Aerobic oxidation of benzyl alcohol catalyzed by various montmorillonite-supported metalloporphyrins. Reaction conditions: benzyl alcohol (1 mmol), acetonitrile (4 ml), isobutyraldehyde (3 mmol), catalyst (0.57×10^{-3} mmol), O_2 bubbling, 2.0 h, 70 °C.

2.2.2 Effect of catalyst amount in aerobic oxidation of benzyl alcohol

Table 3 shows the influence of CoTM4PyP-MT catalyst amount on the aerobic oxidation of benzyl alcohol in the presence of molecular oxygen and isobutyraldehyde.

Table 3 Effect of catalyst amount in the aerobic oxidation of benzyl alcohol

Entry	Amount of catalyst (g)	Conversion (%)	Yield (%)
1	0	11	7
2	0.005	32	32
3	0.01	76	76
4	0.015	90	90
5	0.02	95	82 (13)
6	0.025	98	60 (38)
7 ^a	0.015	15	12

Reaction condition: benzyl alcohol (1 mmol), isobutyraldehyde (3 mmol), CoTM4PyP-MT (0.015 g), acetonitrile (4 ml), O_2 bubbling, 2 h, 70 °C, the numbers in parentheses indicate the yield of benzoic acid.

^aMT as catalyst.

As shown in Table 3, only 11% benzyl alcohol was converted in a blank experiment without catalyst as the reaction was conducted for 2 h (entry 1). Although natural clay usually includes metal ions, only 15% conversion was obtained in the oxidation catalyzed by montmorillonite itself (entry 7). The conversion of benzyl alcohol is considerably enhanced when the heterogeneous catalyst was used (entries 2–6). The CoTM4PyP-MT catalyst is crucial for the reaction which is demonstrated by the fact that the conversion of benzyl alcohol reaches 32% even if the amount of catalyst is only 0.005 g (entry 2). As depicted clearly in Table 3, the reaction rate increases with the increasing catalyst content. Benzyl alcohol was transformed to benzaldehyde with 90%

yield when the amount of catalyst was 0.015 g (0.57×10^{-3} mmol, CoTM4PyP) while benzoic acid was not detected (entry 4). When the amount of catalyst was increased further, the selectivity toward benzaldehyde declined apparently though the conversion exceeded 95% (entries 5 and 6). This indicates that the excess catalyst promotes the over-oxidation of benzyl alcohol. Therefore, the optimal amount of CoTM4PyP-MT for the aerobic oxidation of benzyl alcohol is 0.015 g.

2.2.3 Optimized reaction conditions for aerobic oxidation of benzyl alcohol

It is well-known that the solvent plays an important and sometimes decisive role in the catalytic behavior of a catalyst. As shown in Table 4, a moderate conversion of benzyl alcohol (74%) but excellent selectivity toward benzaldehyde was obtained in cyclohexane (entry 1). Although the oxidation of benzyl alcohol was promoted when the reaction was conducted in benzonitrile, about 23% yield of benzoic acid was obtained (entry 2). Among the used solvents, acetonitrile was most favorable for the benzyl alcohol oxidation by this catalytic system (entry 3). The activity was enhanced with increasing reaction temperature, but the selectivity of benzaldehyde declined apparently when the reaction was conducted at 80 °C. In the absence of isobutyraldehyde, 12% yield of benzaldehyde was obtained after conducting the reaction for 4 h (entry 7). Thus the oxidation was examined with varying molar ratio of substrate to isobutyraldehyde. When the substrate/isobutyraldehyde molar ratio was increased to 1:2, 68% benzyl alcohol was converted (entry 8). However, no significant difference was observed when the substrate/isobutyraldehyde molar ratio reached 1:3 for the present system (entry 9).

Table 4 Oxidation of benzyl alcohol catalyzed by CoTM4PyP-MT under various conditions

Entry	Solvent	T/°C	Conversion (%)	Yield (%)
1	cyclohexane	70	74	74
2	benzonitrile	70	95	72 (23)
3	acetonitrile	70	90	90
4	acetonitrile	50	31	31
5	acetonitrile	60	68	68
6	acetonitrile	80	93	76 (17)
7 ^a	acetonitrile	70	12	12
8 ^b	acetonitrile	70	68	68
9 ^c	acetonitrile	70	91	90

Reaction conditions: Benzyl alcohol (1 mmol), isobutyraldehyde (3 mmol), CoTM4PyP-MT (0.015 g), solvent (4 ml), O_2 bubbling, 2 h, the numbers in parentheses indicate the yield of benzoic acid.

^aIn the absence of isobutyraldehyde, 4 h. ^bIsobutyraldehyde (2 mmol).

^cIsobutyraldehyde (4 mmol).

2.2.4 Aerobic oxidation of various alcohols catalyzed by CoTM4PyP-MT

To evaluate the application range of the catalytic system, various alcohols were used as substrate for the reaction system using only 0.015 g of the montmorillonite-supported cobalt porphyrin (Table 5). As shown in Table 5, most substrates could be smoothly converted to corresponding carbonyl compounds with high conversion rate and excellent selectivity.

It seems that the efficiency of this catalytic system is closely related with the electronic properties of the substrates. Electron-donating groups are more favorable to the formation of carbonyl compounds than electron-withdrawing groups at the *p*-position (entries 1–5).

Table 5 Aerobic oxidation of various alcohols catalyzed by CoTM4PyP-MT

Entry	Substrate	Product	<i>t</i> /h	Conversion (%)	Yield (%)
1			2	90	90
2			1.5	93	93
3			1.5	94	94
4			2	76	75
5			2	53	50
6			3	23	23
7 ^a			2	86	40(46)
8			1.5	81	81
9			2	73	73
10			2	92	89
11			2	86	84
12			2.5	78	64
13			2.5	73	55

Reaction conditions: Substrate (1 mmol), isobutyraldehyde (3 mmol), CoTE4PyP-MT (0.015 g), acetonitrile (4 ml), O₂ bubbling, 70 °C, the numbers in parentheses indicate the yield of benzaldehyde.

This phenomenon is demonstrated further by the aerobic oxidation of 4-pyridinemethanol (entry 6), which indicates that the electron-withdrawing effect retards the combination of substrate with oxidant. The oxidative cleavage of C–C bonds was observed when cinnamyl alcohol was subjected to the reaction system, in which 86% cinnamyl alcohol was converted and benzaldehyde was the main product (entry 7). Secondary alcohols could also be converted to the corresponding ketones in high yield (entries 8–11). For example, 1-phenylethanol was converted efficiently to corresponding carbonyl compound with 89% yield. Carboxylic acids were the main products under the same reaction conditions in the case of saturated primary aliphatic alcohols, for example, 1-hexanol and 1-octanol (entries 12 and 13). This is consistent with our previously reported results where a homogeneous ruthenium porphyrin was used as catalyst [25].

2.2.5 Catalyst reusability and stability

The stability of the CoTM4PyP-MT catalyst was monitored by multiple sequential aerobic oxidation of benzyl alcohol in the presence of isobutyraldehyde. The catalyst was recovered by centrifugation, filtration, washed with acetonitrile, and dried before using it in the subsequent run. The results are presented in Fig. 5.

Fig. 5. Stability and reusability of CoTM4PyP-MT catalyst in the aerobic oxidation of benzyl alcohol.

From Fig. 5, the catalyst was consecutively reused five times without a significant loss of its activity. And no decrease of the selectivity toward benzaldehyde was observed after five cycles. The leaching of metalloporphyrins from the support to the reaction medium was checked by taking UV-Vis spectra of the solution at the end of the reaction. No cobalt porphyrins catalyst was detectable, indicating the metalloporphyrins were tightly bound to the support during the oxidation. The results clearly showed that the supported catalyst was active in the oxidation and could be reused without significant decrease in activity and selectivity.

2.2.6 A Plausible mechanism for aerobic oxidation of alcohols

As reported previously, the mechanism of the homogeneous oxidation catalyzed by metalloporphyrin complexes with aldehydes present is considered to involve a radical and a high-valent metal intermediate. The feature of radical involvement could be inferred from the fact that the oxidation was quenched in the presence of a free radical inhibitor.

A high-valent porphyrin intermediate is generally accepted as the active species in the oxidations catalyzed by metalloporphyrins [8]. The oxidation of alcohols was assumed to occur *via* reactive high-valent metal oxo intermediates, which are generated from a series of radical species in the presence of dioxygen and aldehyde [27]. Therefore, a high-valent Co porphyrin intermediate is generated first in the aerobic oxidation of benzyl alcohol catalyzed by the montmorillonite-supported cobalt porphyrin system. Then the formation of benzylaldehyde is attributed to the reaction of benzyl alcohol with the Co-oxo species, followed by a β -hydride elimination (Scheme 1).

Scheme 1. Plausible mechanism for the aerobic oxidation of benzyl alcohol catalyzed by CoTM4PyP-MT catalyst.

3 Conclusions

In conclusion, the highly efficient oxidation of olefins by molecular oxygen in the presence of montmorillonite-supported metalloporphyrins has been reported. The immobilization of cationic *meso*-tetrakis (1-methyl-4-pyridyl) (TM4PyP) porphyrins (Co, Mn, and Fe) in montmorillonite was confirmed by diffuse reflectance UV spectra, infrared spectra, X-ray diffraction, and nitrogen adsorption isotherms. CoTM4PyP-MT is considerably more efficient than manganese and iron porphyrin catalysts in the aerobic oxidation of alcohols. Electron-donating groups are more favorable to the formation of carbonyl compounds than electron-withdrawing groups at the *p*-position. The catalyst can be five times consecutively reused without sig-

nificant loss of activity and selectivity.

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