Cobalt-substituted polyoxometalate pillared hydrotalcite: Synthesis and catalysis in liquid-phase oxidation of cyclohexanol with molecular oxygen

Suman K. Jana [a,b,*], Yoshihiro Kubota [c], Takashi Tatsumi [a,d,*]

[a] *Chemical Resources Laboratory, Tokyo Institute of Technology, 4259 Nagatsuta, Midori-Ku, Yokohama 226-0583, Japan*
[b] *SABIC Research and Technology Pvt. Ltd., Plot No. 5 & 6, Savli GIDC Estate, Manjusar, Gujarat 391775, India*
[c] *Division of Materials Science and Chemical Engineering, Graduate School of Engineering, Yokohama National University, 79-5 Tokiwadai, Hodogaya-ku, Yokohama 240-8501, Japan*
[d] *Japan Science and Technology Corporation, Saitama 332-0012, Japan*

Abstract

Cobalt-substituted polyoxometalate (POM), α-[SiW$_9$O$_{37}${Co(H$_2$O)}$_3$]$^{10-}$, was heterogenized for its effective use as a solid catalyst in the liquid-phase reaction by inserting it in between the layers of basic Mg$_3$Al-hydrotalcite. It was characterized by FT-IR, UV–vis, X-ray diffraction, N$_2$ adsorption–desorption and elemental analysis. A POM cluster was intercalated into the interlayer of layered double hydroxide (LDH), and the integrity of the cluster [SiW$_9$Co$_3$] was maintained when the hydrotalcite precursor, Mg$_3$Al-LDH-carbonate, was transformed into a mixed-oxide solid solution, followed by the formation of Mg$_3$Al-LDH-hydroxide through hydrolytic reconstruction and Mg$_3$Al-LDH-adipate via anion exchange by organoacid precursor before its use in the pillaring reaction under a stringent N$_2$ atmosphere. The intercalated cobalt-substituted POM cluster showed high catalytic activity and reusability in the liquid-phase selective oxidation of cyclohexanol to cyclohexanone using 1 atmosphere of molecular oxygen under mild reaction conditions.

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1. Introduction

Polyoxometalates (POMs) constitute a diverse class of inorganic oxo-metal clusters composed of early transition metals in their highest oxidation state [1]. They have tunable acidic and redox properties that can be controlled by changing the constituent elements. The use of POMs as oxidation catalysts has attracted attention because unlike organic porphyrins, which tend to oxidize and degrade after a few catalytic cycles, POMs resist oxidation due to the presence of W or Mo atoms in their highest oxidation state [1,2]. It is well known that heteropoly compounds can catalyze oxidation processes and that catalytic performance is greatly enhanced by the incorporation of transition metals [3]. The transition metal-substituted POMs are more attractive and interesting catalytic materials, particularly when the metals occupy the lacunary or defect position of the POM structure. Such compounds can be viewed as transition metal complexes with an inorganic POM ligand that acts as a potential multielectron acceptor. To date, lacunary POMs have been the most widely investigated oxidation catalyst because, besides having available open coordination sites on the transition metals (expected to be beneficial for oxidative catalytic reactions), they have high thermal stability and can be readily synthesized.

Although a number of catalytic applications of transition metal-substituted POM in the liquid-phase oxidation have been reported, those applications have been mostly in homogeneous catalytic reactions [4–10]. Thus, those catalytic routes were not environmentally benign. Because of the difficulty associated

* Corresponding authors. Address for correspondence of S.K. Jana is SABIC Research and Technology Pvt. Ltd., Plot No. 5 & 6, Savli GIDC Estate, Manjusar, Gujarat 391775, India and of T. Tatsumi is Chemical Resources Laboratory, Tokyo Institute of Technology, 4259 Nagatsuta, Midori-Ku, Yokohama 226-0583, Japan. Faxes: +91 2667 264245 (S.K. Jana), +81 45 924 5282 (T. Tatsumi).

E-mail addresses: suman@sabicind.com (S.K. Jana), ttatsumi@cat.res.titech.ac.jp (T. Tatsumi).

with the heterogenization of homogeneous POMs, exploitation of their truly heterogeneous catalytic applications in the liquid-phase oxidation process has been seriously impaired. Therefore, it is important to heterogenize catalytically active POM clusters for their effective use in the liquid-phase reactions. Layered anionic clays are a class of layered materials of current interest because of their potential for shape recognition of guest materials in addition to their widespread catalytic applications [11]. Among the various classes of anionic lamellar solids, layered double hydroxide (LDH) seems to be the attractive host for accommodating POM anions as pillars in between their interlayer spaces. Because LDH is the only known family of layered material with a permanent positive charge on its layers, this property seems to be essential and beneficial for successful and strong pillaring [12,13]. However, because of the strong basicity of LDH, which causes decomposition of the starting precursors due to a strong acid–base reaction, a strategy to control the pillaring reactions is necessary to successfully intercalate the POM between hydrotalcite layers [14,15].

The present work was undertaken to heterogenize catalytically active POM clusters to obtain materials that have the properties of both the POM (i.e., oxidation catalysis) and the layered structure of the hydrotalcite (i.e., basic sites and high surface area) without substantial decomposition of the starting precursors. Differences in pillaring methods and the use of preswelling agents were considered to be factors affecting the intercalation of POM. The resulting tri-cobalt-substituted POM pillared hydrotalcite was tested for its catalytic performance in the selective oxidation of cyclohexanol to cyclohexanone using the atmospheric pressure of molecular oxygen as an oxidant and 1,4-dioxane as a solvent under mild reaction conditions. The product formed in the selective cyclohexanol oxidation, cyclohexanone, is a very important chemical intermediate used mainly as a starting material for the synthesis of two important nylons—nylon-6,6 and nylon-6.

2. Experimental

2.1. Preparation of precursors

2.1.1. Mg₃Al-LDH-carbonate

Mg_3Al-LDH-carbonate was prepared through a slightly modified conventional co-precipitation method as follows [16]. A mixed Mg^{2+} and Al^{3+} metal nitrate aqueous solution ($Mg^{2+}/Al^{3+} = 3.0$ mol mol^{-1}) was added dropwise to an aqueous Na_2CO_3 solution at 70 °C under vigorous stirring. The solution pH was adjusted to 10.5 ± 0.1 by aqueous NaOH. The resulting gel-like material was then aged at 90 °C for 12 h. The slurry thus obtained was cooled to room temperature and separated by filtration, then washed with distilled water several times and dried at 100 °C for 20 h.

2.1.2. Mg₃Al-LDH-hydroxide

An aqueous suspension of Mg_3Al-LDH-hydroxide (1.0 wt%) was prepared by thermal decomposition of Mg_3Al-LDH-carbonate, followed by its subsequent hydrolytic reconstruction. In a typical procedure, 1.0 g of Mg_3Al-LDH-carbonate

was calcined in a quartz tube at 450 °C for 15 h under flowing N_2 to obtain a mixed-oxide solid solution. The resulting oxide mass was then allowed to make contact with 100 ml of degassed H_2O by stirring under nitrogen atmosphere, resulting in Mg_3Al-LDH-hydroxide after the reaction period of 5 days.

2.1.3. Mg₃Al-LDH-adipate

Mg_3Al-LDH-adipate was prepared by adding an aqueous suspension of synthetic Mg_3Al-LDH-hydroxide to an excess of 4 wt% aqueous adipic acid solution in the presence of N_2 atmosphere at 50 °C under stirring, followed by aging for 10 h. The resulting Mg_3Al-LDH-adipate was then separated by decantation and stored under suspension in degassed water.

2.1.4. Na₁₀[α-SiW₉O₃₄]

Sodium α-9-tungstosilicate, $Na_{10}[\alpha\text{-}SiW_9O_{34}]$, was prepared as described previously [17].

2.1.5. H₁₀[SiW₉O₃₇{Co(H₂O)}₃]

The H^+-form of cobalt-substituted POM, $H_{10}[SiW_9O_{37}\{Co(H_2O)\}_3]$, was synthesized as described previously [18]. Typically, sodium α-9-tungstosilicate (44.65 g, 0.016 mol) was added in small portions to a solution of $Co(CH_3COO)_2 \cdot 4H_2O$ (12.0 g, 0.048 mol) in water (600 ml) under vigorous stirring. Because the former salt was almost insoluble at room temperature, the solution temperature was slowly raised during the addition to solubilize it. At 80 °C, the solution changed in color from red to brown, and the dissolution of sodium α-9-tungstosilicate became apparent. Then 400 ml of water was added to ensure complete dissolution. Further stirring of the solution at 80 °C for another 1 h resulted in the cobalt-substituted polyoxometalate. The H^+ form of POM was separated from the unreacted cobalt precursor by passing the aforementioned mixture through a cation-exchange resin. The resulting solution was then used directly for the preparation of cobalt-substituted POM pillared Mg_3Al-hydrotalcite.
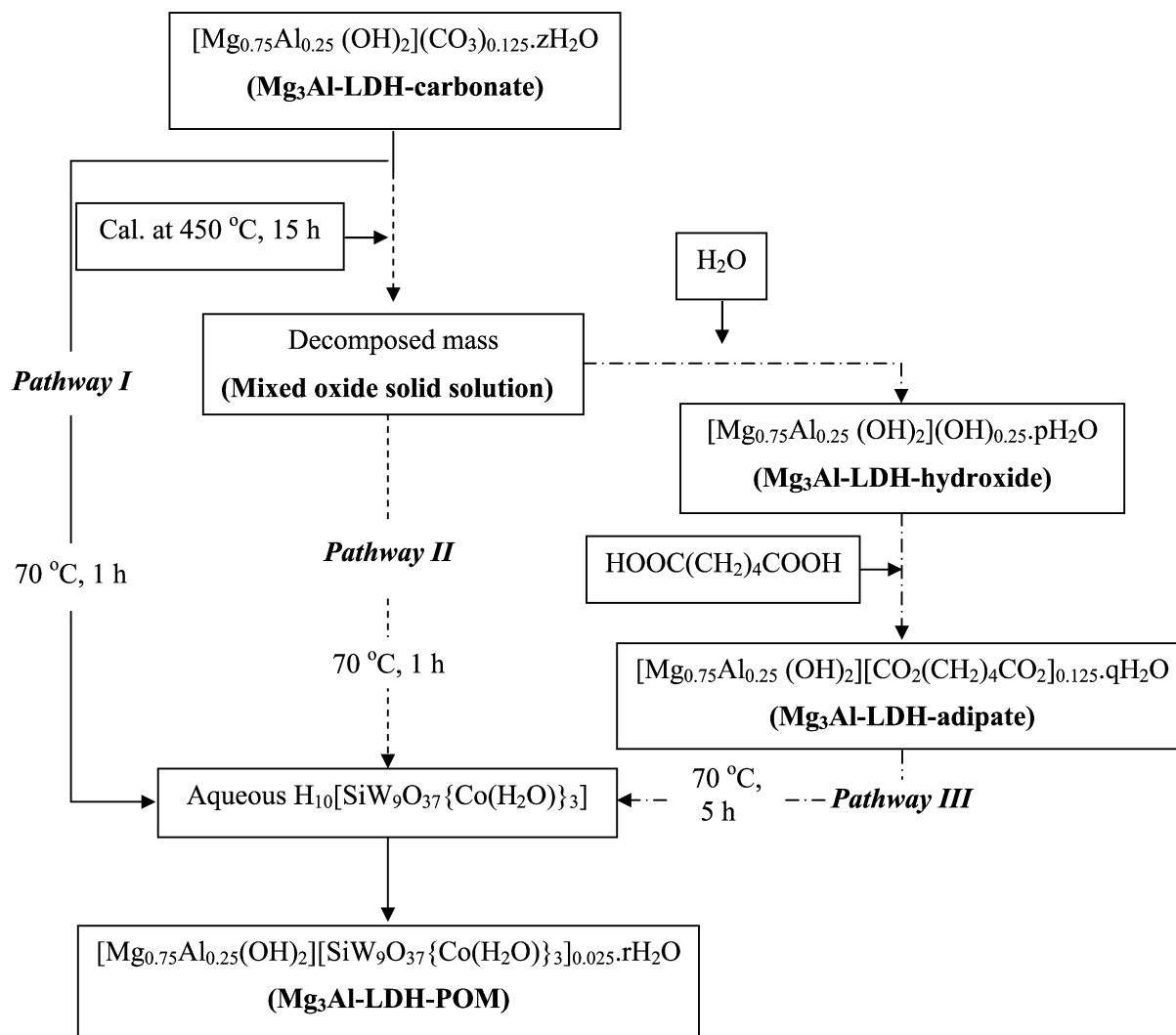
2.1.6. K₁₀[SiW₉O₃₇{Co(H₂O)}₃]

The potassium salt of cobalt-substituted POM, $K_{10}[SiW_9O_{37}\{Co(H_2O)\}_3]$, used as a reference solid, was prepared by adding dropwise aqueous KCl into the aqueous solution of cobalt-substituted POM, $H_{10}[SiW_9O_{37}\{Co(H_2O)\}_3]$, followed by stirring at room temperature for 12 h.

2.2. Pillaring techniques

2.2.1. Pillaring of Mg₃Al-LDH by cobalt-substituted POM for synthesizing cobalt-substituted POM pillared hydrotalcite (Mg₃Al-LDH-POM)

Pillaring reactions were carried out under a stringent N_2 atmosphere to avoid the contact with atmospheric CO_2. Distilled water was used for the preparation of all aqueous solutions. The H^+ form of POM solutions (0.01 M), in threefold excess of the anion exchange capacity of LDH, was used for the pillaring reactions. The three different pillaring techniques used in the present work are outlined in Scheme 1. In a typical intercalation procedure, an aqueous suspension of hydrotalcite

Scheme 1. Synthetic routes for Mg$_3$Al-LDH pillared by cobalt substituted polyoxometalate, α-[SiW$_9$O$_{37}${Co(H$_2$O)}$_3$]$^{10-}$.

or hydrotalcite-derived precursor was added dropwise to an aqueous POM solution (obtained by passing through a cation-exchange resin) at room temperature. After complete addition of the hydrotalcite or hydrotalcite-derived mass, the resulting mixture was stirred at 70 °C for up to 5 h longer. The solid product was then washed with water and dried at 100 °C for 12 h under vacuum.

2.3. Physical measurements

Cobalt-substituted POM with or without heterogenization by pillaring was characterized by FT-IR, UV–vis, N$_2$ adsorption–desorption, elemental analysis, and X-ray diffraction (XRD) measurements. FT-IR spectra were collected using a Perkin Elmer 1600 FT-IR spectrometer; samples were prepared as KBr pellets. Diffuse reflectance UV–vis absorption spectra were measured using a Jasco V-550 UV–vis spectrometer. N$_2$ adsorption–desorption experiments were performed using a Bell Japan Belsorp 28SA sorptometer at −196 °C. Powder XRD patterns were obtained using a Mac Science M3X Model 1030 instrument equipped with a Cu$K\alpha$ radiation. Elemental

analysis was performed using a Perkin–Elmer 240C elemental analyzer.

2.4. Catalysis

Aerial oxidation of cyclohexanol over various metal containing POM catalyst was carried out in a magnetically stirred glass reactor (50 cm^3 capacity) equipped with a reflux condenser and a temperature controller by continuously bubbling oxygen (flow rate, 5.0 ml min^{-1}) through a vigorously stirred liquid reaction mixture containing 10 mmol of cyclohexanol, 100 mmol of solvent, and 0.06 mmol of catalyst based on cobalt, in the form of fine powder, at 100 °C for up to 12 h. The reaction products, identified by comparison with the authentic samples, and unconverted cyclohexanol in the reaction mixture were analyzed by gas chromatography with a flame ionization detector using the internal standard method. The product stream also was analyzed by HPLC (SHIMADZU LC-VP) to further confirm the amount of carboxylic acid byproducts formed (if any) due to overoxidation of the primary ketone product.
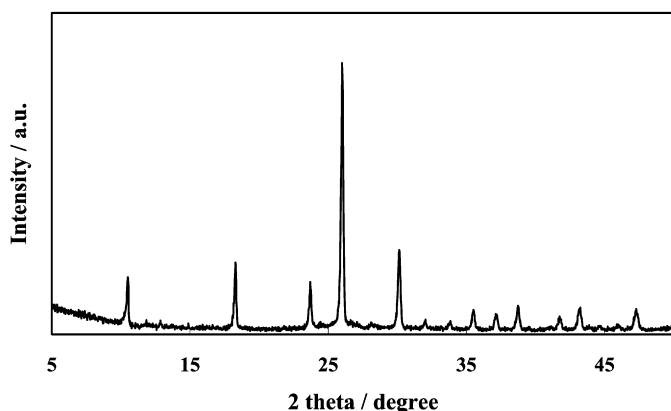
Fig. 1. X-ray diffraction pattern of K-salt of cobalt substituted polyoxometalate, α-[SiW$_9$O$_{37}$\{Co(H$_2$O)\}$_3$]$^{10-}$.

3. Results and discussion

3.1. Synthesis and characterization of cobalt-substituted POM cluster

Formation of the cobalt POM cluster by the reaction of sodium α-9 silicotungstate with the cobalt acetate in an aqueous medium was confirmed by XRD, FT-IR, and UV–vis studies. The XRD pattern in Fig. 1 demonstrates the crystalline nature of potassium salt of cobalt-substituted POM. The FT-IR spectra in the range of 1100–550 cm^{-1} assigned to the characteristic fingerprint region of the POM cluster and the UV–vis absorptions at 492, 513, and 538 nm corresponding to octahedral Co of cobalt-substituted POM are quite similar to those reported earlier [19]. The amounts of Si, W, and Co in cobalt-substituted POM were confirmed by elemental analysis. It is important here to note that the synthesis of cobalt-substituted POM by the reaction between sodium α-9 silicotungstate and cobalt acetate in nonaqueous media was not successful under similar experimental conditions.

3.2. Pillaring cobalt-substituted POM cluster in between the layers of Mg$_3$Al-hydrotalcite

As shown in Scheme 1, three different approaches (pathways I–III) were used to intercalate cobalt-substituted POM anions between the layers of basic Mg$_3$Al-hydrotalcite. In all three approaches, Mg$_3$Al-LDH-carbonate was used as the starting material. Pathway I examined the possibility of the direct conversion of Mg$_3$Al-LDH-carbonate to Mg$_3$Al-LDH-POM by the anion-exchange method. In both pathways II and III, the starting precursor material, Mg$_3$Al-LDH-carbonate, was first transformed to a mixed-oxide solid solution. The resulting mixed oxide was then allowed to undergo a reconstruction reaction through the "memory effect" of hydrotalcite in the presence of aqueous POM for its transformation into Mg$_3$Al-LDH-POM in pathway II. Alternatively, the solid solution was converted into the synthetic Mg$_3$Al-LDH-hydroxide intermediate by hydrolytic reconstruction process (interlayer anion hydroxide), followed by its transformation into organoacid precursor (interlayer anion adipate) by the reaction with aqueous
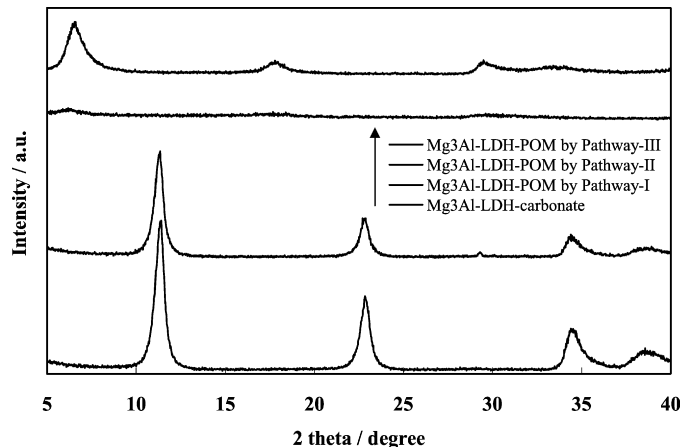

Fig. 2. X-ray diffraction pattern of the samples obtained by three different pathways used for the preparation of cobalt substituted polyoxometalate pillared Mg$_3$Al-LDH.

adipic acid solution by the anion-exchange method. Then the organoacid precursor was finally transformed into the desired pillared Mg$_3$Al-LDH-POM (interlayer anion POM) product by an ion-exchange reaction between Mg$_3$Al-LDH-adipate and cobalt POM in aqueous medium in pathway III.

XRD patterns of the solid samples obtained by three different pillaring techniques are presented in Fig. 2. The direct anion exchange of carbonate of the interlayer of the Mg$_3$Al-LDH-carbonate precursor by the POM anion produced no desired pillared Mg$_3$Al-LDH-POM product. This is likely due to the fact that the carbonate anion has a strong affinity to retain its position in the interlayer of basic hydrotalcite material; thus, in its presence, intercalating POM between the layers of Mg$_3$Al-LDH material by simple ion exchange proved quite difficult. However, the observed decrease in the XRD peak intensities of the solid sample obtained from the direct anion-exchange method compared with that of the parent hydrotalcite suggests that an acid–base reaction between hydrotalcite and the H$^+$ form of POM occurred to some extent even though intercalation was unsuccessful. The synthesis of Mg$_3$Al-LDH-POM by adopting the "memory effect" of hydrotalcite also was almost unsuccessful under the conditions in pathway II. The resulting material after the reconstruction time of 5 h showed an XRD pattern due mostly to the starting precursor, the mixed-oxide solid solution, along with a very small amount of pillared product; the shift in XRD peaks characteristic of hydrotalcite material toward the lower angle indicates the formation of cobalt-substituted POM pillared Mg$_3$Al-hydrotalcite. The formation of a very small amount of pillared product in pathway II seems to be due to the slow rate of the pillaring reaction between the mixed-oxide solid solution and the H$^+$ form of the POM precursor compared with the competitive acid–base reaction. However, the XRD pattern of the material obtained by pathway III indicates successful pillaring of cobalt-substituted POM into the interlayer of Mg$_3$Al-LDH. Incorporating adipate anions into the interlayer of Mg$_3$Al-LDH precursor before introduction of POM clusters makes it possible not only to speed up the anion-exchange reaction between the relatively easily labile adipate anion and the POM cluster,

Table 1
Physicochemical properties of Mg_3Al-LDH with or without incorporation of cobalt substituted polyoxometalate

Sample	Inorganic anion	Precursor material	Composition (Mg:Al:Co)	S_{BET} ($m^2\,g^{-1}$)	$S_{microporous}$ ($m^2\,g^{-1}$)
Mg_3Al-LDH-carbonate	CO_3^{2-}	–	3.02:1.0:0	103	0
Mg_3Al-LDH-hydroxide	OH^-	LDH-CO_3^{2-}	2.98:1.0:0	–	–
Mg_3Al-LDH-POM by pathway I	α-[$SiW_9O_{37}\{Co(H_2O)\}_3$]$^{10-}$	LDH-CO_3^{2-}	2.01:1.0:$\ll$0.01	92	0
Mg_3Al-LDH-POM by pathway II	α-[$SiW_9O_{37}\{Co(H_2O)\}_3$]$^{10-}$	Calcined LDH-CO_3^{2-}	2.39:1.0:0.01	185	2
Mg_3Al-LDH-POM by pathway III	α-[$SiW_9O_{37}\{Co(H_2O)\}_3$]$^{10-}$	LDH-adipate	2.57:1.0:0.35	107	29
K_{10}[$SiW_9O_{37}\{Co(H_2O)\}_3$]	α-[$SiW_9O_{37}\{Co(H_2O)\}_3$]$^{10-}$	–	–	4.7	0

but also to reduce the risk of a severe acid–base reaction between the two precursors, because the highly acidic H^+ form of POM has a strong tendency to hydrolyze in the presence of highly basic hydrotalcite material. These findings suggest that pathway III is a more efficient approach for synthesizing the intercalated product compared with the other methods.

The physicochemical properties of the Mg_3Al-LDH-carbonate, Mg_3Al-LDH-hydroxide, and the materials obtained by three different pathways are presented in Table 1. Results of elemental analysis indicate that no significant change in the Mg/Al ratio occurred after the hydrolytic reconstruction of Mg_3Al-LDH-carbonate; however, a decreased concentration of Mg^{2+} ions was found in the resulting material obtained through all three pathways. These findings suggest that during all three processes, simple acid–base reactions occurred between the precursor materials, resulting in partial dissolution of Mg^{2+} ions from the basic Mg_3Al-LDH precursor material. The acid–base reaction was relatively severe in pathway I compared with the other two pathways, particularly pathway III. This was expected, because pathway I followed a direct anion-exchange reaction between the highly acidic H^+ form of POM and highly basic hydrotalcite precursors. In contrast, by exchanging an hydroxyl anion with an adipate anion before the incorporation of heteropolyoxometalate, the basicity of hydrotalcite precursor decreased and the mobility of the interlayer anion increased, and thus the severity of the acid–base reaction was decreased considerably in pathway III. It is important here to note that a small amount of cobalt was observed in the materials obtained by pathways I and II even though intercalation was unsuccessful; this was due mainly to the adsorption of cationic and/or anionic cobalt species on the basic hydrotalcite or hydrotalcite-derived supports. As shown in Table 1, the BET surface area (measured by N_2 adsorption–desorption) of the Mg_3Al-LDH-carbonate hydrotalcite was decreased significantly after the hydrolytic reconstruction process; however, it was increased slightly after the successful intercalation of cobalt-substituted POM cluster into the interlayer of Mg_3Al-LDH (pathway III). More importantly, the structure of the Mg_3Al-LDH-POM intercalate obtained by pathway III contained some micropores not found in the parent Mg_3Al-LDH-carbonate precursor. Table 2 suggests that about 25% of the surface area of the Mg_3Al-LDH-POM intercalates prepared by pathway III arose from the gallery micropores, whereas no microporous surface area was observed for the starting Mg_3Al-LDH-carbonate precursor.

Table 2
Cyclohexanol oxidation over Mg_3Al-hydrotalcite pillared by various transition metal substituted polyoxometalate catalysts (cyclohexanol = 10 mmol, 1,4-dioxane = 100 mmol, catalyst = 0.06 mmol based on Co, Cu, Fe, Ni or Cr, oxygen flow = 5 ml min^{-1}, temperature = 100 °C and reaction time = 12 h)

Transition metal containing polyoxometalate	Conversion (%)	Selectivity (%)
α-[$SiW_9O_{37}\{Co(H_2O)\}_3$]$^{10-}$	67	100
α-[$SiW_9O_{37}\{Cu(H_2O)\}_3$]$^{10-}$	14	99.7
α-[$SiW_9O_{37}\{Fe(H_2O)\}_3$]$^{7-}$	13	99.3
α-[$SiW_9O_{37}\{Ni(H_2O)\}_3$]$^{10-}$	5	99.5
α-[$SiW_9O_{37}\{Cr(H_2O)\}_3$]$^{7-}$	4	99.4
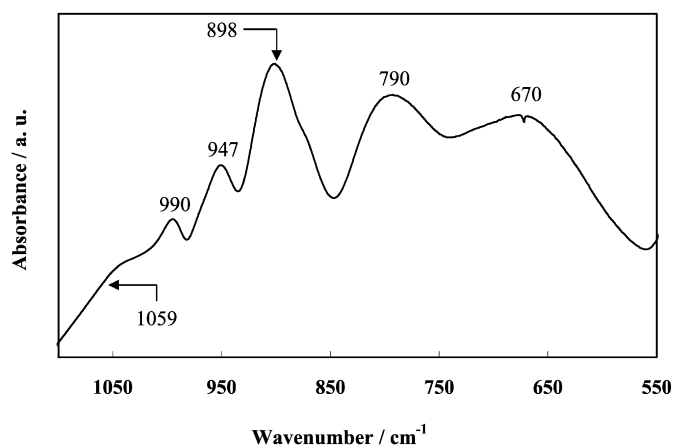
Fig. 3. FT-IR spectra of cobalt substituted polyoxometalate, α-[SiW_9O_{37}-$\{Co(H_2O)\}_3$]$^{10-}$, pillared Mg_3Al-LDH obtained by pathway III.

The retention of cobalt-substituted POM clusters in the Mg_3Al-LDH-POM intercalates obtained by pathway III was further confirmed by FT-IR and UV–vis measurements. No significant change/shift was observed in the Si–O and W–O–W stretching frequencies of the cobalt-substituted POM after its intercalation into the layers of Mg_3Al-LDH (Fig. 3). After intercalation, the Si–O and W–O–W stretching frequencies appeared at 1059 and 898 cm^{-1}, compared with 1056 and 896 cm^{-1} for the nonintercalated cobalt-substituted POM sample. However, cobalt-substituted POM with or without intercalation exhibited similar absorption bands in the UV–vis spectra (not shown). It is important here to note that no significant decrease in the W/Co ratio of cobalt-substituted POM was observed after its intercalation into the layers of Mg_3Al-LDH, as confirmed by elemental analysis (not shown). This finding confirms that only a negligibly small amount of cluster degradation

occurred due to the acid–base reaction between the precursor materials during the synthesis of cobalt-substituted POM pillared Mg_3Al-LDH by pathway III.

The foregoing characterization results indicate that among the three pathways that we used to prepare Mg_3Al-LDH-POM, pathway III produced the most effective material for successful pillaring of cobalt-substituted POM clusters in between the layers of Mg_3Al-hydrotalcite material with little degradation of the starting precursors.

3.3. Catalytic results

We tested the catalytic activity of the cobalt-substituted POM pillared Mg_3Al-LDH (Mg_3Al-LDH-POM) prepared by pathway III in the selective oxidation of cyclohexanol to cyclohexanone using 1 atmosphere of molecular oxygen as an oxidant and 1,4-dioxane as a solvent. The time course in Fig. 4 demonstrates that Mg_3Al-LDH-POM effectively catalyzed aerial oxidation of cyclohexanol. The cyclohexanol conversion increased almost linearly with time, forming cyclohexanone selectively in the presence of cobalt-substituted POM pillared Mg_3Al-LDH. After 12 h, the conversion of cyclohexanol reached 67% with a cyclohexanone selectivity of 100%. No other products (including carboxylic acid, which was expected due to the overoxidation of cyclohexanone) were detected. However, a small amount ($\sim$1%) of byproducts (mostly containing keto-1,4-dioxane) arose from the oxidation of solvent.
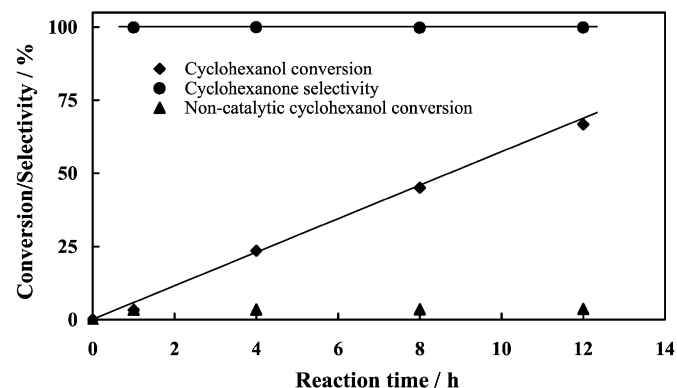

Fig. 4. Time course of cyclohexanol oxidation over cobalt substituted polyoxometalate pillared Mg_3Al-LDH prepared by pathway III (cyclohexanol = 10 mmol, 1,4-dioxane = 100 mmol, catalyst = 0.06 mmol based on cobalt, oxygen flow = 5 ml min^{-1} and temperature = 100 °C).

Similar byproducts also were observed even in the absence of cyclohexanol in the reaction mixture. It is important to note that cyclohexanol oxidation hardly occurred in the absence of cobalt-substituted POM pillared Mg_3Al-LDH or in the presence of Mg_3Al-LDH alone ($<$1% cyclohexanol conversion after 12 h). The activity of cobalt-substituted POM without intercalation was slightly lower (62% conversion in 12 h) compared with that of the cobalt-substituted POM pillared Mg_3Al-LDH; however, both catalysts demonstrated similar cyclohexanone selectivity, close to 100%.

A number of POMs of similar structure but containing different transition metals (e.g., Cu, Fe, Ni, Cr) were prepared following methods described in the literature and intercalated between the layers of Mg_3Al-LDH according to pathway III. The catalytic activity of the resulting transition metal-substituted POM pillared samples also was tested in cyclohexanol oxidation by molecular oxygen. Among the various transition metal-substituted POM pillared Mg_3Al-LDHs, the cobalt-containing pillared Mg_3Al-LDH exhibited significantly greater cyclohexanol oxidation activity than the other transition metal-containing pillared Mg_3Al-LDH catalysts. The selectivity for cyclohexanone over all of the pillared catalysts was 100%.

Table 3 compares the cyclohexanol oxidation activity (expressed in terms of turnover frequency [TOF]) of cobalt-substituted POM pillared Mg_3Al-LDH and previously reported solid catalysts [20–24]. The table shows that the cobalt-containing catalyst (TOF = 9.3 h^{-1}) was more active than Pt (10%)/MgO (TOF = 7 h^{-1}), RuO_2 (10%)/FAU zeolite (TOF = 1.4 h^{-1}), $Ru_{0.35}MnFe_{1.5}Cu_{0.15}O_x$ (TOF = 0.3 h^{-1}), and $Ru_{0.3}Co_2CeO_x$ (TOF = 1 h^{-1}) and less active than Ru-silicotungstate (TOF = 23 h^{-1}). The cobalt-substituted POM pillared Mg_3Al-LDH exhibited much lower activity but much higher cyclohexanone selectivity than Ru-silicotungstate, and thus appears to be a more efficient catalyst for the selective oxidation of cyclohexanol to cyclohexanone using 1 atm of molecular O_2 as an oxidant.

After the oxidation run, the cobalt-substituted POM pillared Mg_3Al-LDH can be separated from the reaction mixture by simple filtration. The pillared catalyst exhibited similar XRD and FT-IR patterns before and after use in the oxidation reaction; moreover, the surface area of the catalyst did not change significantly during the reaction. These findings suggest that the cobalt-substituted POM pillared Mg_3Al-LDH catalyst was quite stable under the oxidative atmosphere and in the

Table 3

Comparison of the earlier reported solid catalysts with the present ones for their activities in the selective oxidation of cyclohexanol to cyclohexanone in the presence of molecular oxygen as an oxidant

Catalyst	Temperature (°C)	Solvent	TOF (h^{-1})	Yield (%)	Selectivity (%)	Reference
Pt (10%)/MgO	100	Water (pH 9)	7	70	100	[20]
RuO_2 (10%)/FAU zeolite	80	Toluene	1.4	43	> 99	[21]
$Ru_{0.35}MnFe_{1.5}Cu_{0.15}O_x$	25	Toluene	0.3	71	100	[22]
$Ru_{0.3}Co_2CeO_x$	60	Trifluorotoluene	1	81	98	[23]
Ru-silicotungstate	100	Isobutylacetate	23	54	81	[24]
Co substituted POM pillared Mg_3Al-LDH	100	1,4-Dioxane	9.3	67	100	Present work

present liquid-phase reaction conditions. To confirm the heterogeneous nature of cobalt-substituted POM pillared Mg_3Al-LDH in the liquid-phase oxidation reaction, the solid catalyst was filtered off from the reaction mixture while hot after 4 h, and the reaction was conducted using the resulting filtrate for another 8 h. No significant change in cyclohexanol conversion was observed, indicating that the oxidation reaction catalyzed solid cobalt-substituted POM pillared Mg_3Al-LDH was mostly heterogeneous. Elemental analysis by the inductively coupled plasma (ICP) method also confirmed the presence of only trace amounts (at the ppb level) of leached cobalt ions in the resulting filtrate.

To further confirm the heterogeneous nature of the cobalt-substituted POM pillared Mg_3Al-LDH in the cyclohexanol oxidation reaction, the catalyst was reused several times after the solid was separated from the liquid reaction mixture by centrifugation, followed by several washings with reactant cyclohexanol while avoiding the loss of fine catalyst particles. After the fourth reuse of the catalyst, the selectivity for cyclohexanone was close to 100% in all the cases and cyclohexanol conversion hardly changed. These findings suggest that cyclohexanol oxidation over the cobalt-substituted POM pillared Mg_3Al-LDH is truly heterogeneous in nature.

In a separate control experiment, oxidation of benzyl alcohol by atmospheric pressure of molecular oxygen was performed over cobalt-substituted POM with or without intercalation under the following reaction conditions: 10 mmol of benzyl alcohol, 100 mmol of 1,4-dioxane, and 0.02 mmol catalyst based on Co at 100 °C. The homogeneous cobalt-substituted POM demonstrated inferior performance to the cobalt-substituted POM intercalated Mg_3Al-LDH. After 5 h of reaction, 79% conversion of benzyl alcohol with 98.4% selectivity for benzaldehyde were obtained over pillared catalyst, compared with 68% conversion of benzyl alcohol with 85.9% selectivity for benzaldehyde over the nonintercalated catalyst. This finding suggests that basic sites of the pillared catalyst assist the POM to produce benzaldehyde selectively from benzyl alcohol compared with the nonintercalated sample. The precise reason for the highly selective formation of benzaldehyde over cobalt-substituted pillared Mg_3Al-LDH remains unclear; however, it is important to note that basic NiAl-hydrotalcite have been reported for the selective oxidation of benzylic alcohols to their corresponding aldehydes by molecular oxygen [25].

Because cobalt-substituted POM pillared Mg_3Al-LDH exhibited very high activity in the cyclohexanol oxidation reaction, in an another control experiment, oxidation of cyclohexane by atmospheric pressure of molecular oxygen was attempted over the same catalyst under the following reaction conditions: 10 mmol of cyclohexane, 100 mmol of 1,4-dioxane, and 0.06 mmol catalyst based on Co at 80 °C. The cyclohexane conversion was only ∼1%, with 100% selectivity for the products (cyclohexanol and cyclohexanone) after the reaction period of 12 h. The extremely poor catalytic performance of cobalt-substituted POM pillared Mg_3Al-LDH for the oxidation of cyclohexane compared with that for the oxidation of cyclohexanol seems to be due to the lower reactivity of cyclohexane and the

differences in the cyclohexane oxidation process. This is likely due to the participation of two different types of functional groups in the two foregoing oxidation reactions—that is, the C–H bond (in cyclohexane oxidation) versus the C–OH bond (in cyclohexanol oxidation).

4. Conclusion

Cobalt-substituted silicotungstate, α-$[SiW_9Co_3O_{37}]^{10-}$, was successfully intercalated between the layers of MgAl-hydrotalcite material. Evidence of the intercalation of cobalt-substituted POM clusters into the hydrotalcite sample was provided by spectroscopic techniques. The intercalated tri-cobalt-substituted POM cluster was catalytically active for the selective oxidation of cyclohexanol to cyclohexanone using atmospheric pressure of molecular oxygen as an oxidant. In addition, the major advantages of the pillared cobalt-substituted POM cluster over the nonintercalated ones were the ease in separation and recovery of the pillared solid from the liquid-phase reaction mixture, allowing recycling for repeated reactions without significant loss of activity.

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