Catalytic oxidation of cyclohexene with molecular oxygen by polyoxometalate-intercalated hydrotalcites

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Cyclohexene was oxidized with molecular oxygen over transition-metal-substituted polyoxometalate-intercalated hydrotalcites to produce 2-cyclohexene-1-one and 2-cyclohexene-1-ol with high selectivity under mild reaction conditions.

Keywords: oxidation; cyclohexene; polyoxometalate-intercalated hydrotalcite

Polyoxometalate-pillared layered double hydroxides (or briefly called POM-LDHs) are a new class of catalytic materials developed in recent years [1–5]. However, their use as catalysts has not been well developed. Recently, Drezdzon reported that the $V_{10}O_{28}^{6-}$ and $Mo_7O_{24}^{6-}$ anions intercalated Zn_2Al are effective catalysts for the conversion of 2-propanol and dehydrogenation of *t*-butylethylbenzene [6]. Pinnavaia has noted that the $BVW_{11}O_{40}^{7-}$, $SiV_3W_9O_{40}^{7-}$ and $H_2W_{12}O_{40}^{6-}$ anions pillared Zn_2Al are highly active catalysts for photocatalytic oxidation of isopropanol to acetone [7]. Tatsumi and co-workers have demonstrated that some polyoxometalate-intercalated hydrotalcites show good catalytic activities for the shape selective epoxidation of alkenes with H_2O_2 as oxidant [8]. More recently, Xu et al. have found that some LDHs and their POM intercalates are highly active catalysts for the alkylation of butene with isobutane [9].

The oxidation of cyclohexene on various polyoxometalate catalysts has been investigated [10–12]. With different oxidants, the product distributions are quite variable. Hill and Brown reported the homogeneous oxidation of cyclohexene with PhIO using $(n\text{-}Bu_4N)_4H(M)PW_{11}O_{39}$ (M = Mn, Co, Fe), and showed that epoxide is the main product but no reaction was observed with M = Fe [10]. Mansuy et al. used MP_2W_{17} (M = Mn, Fe)/PhIO systems and found that the main product is epoxide with minor products of allylic alcohol and allylic ketone. Their results also showed that P_2W_{18} and PW_{12} did not catalyse the oxidation of cyclohexene with PhIO [11]. Qin et al. demonstrated that $[(n\text{-}C_4H_9)_4N]_6PZMo(Br)O_{39}$ (Z = Mn^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+} and Cu^{2+}) are highly active catalysts for oxidation of cyclohexene with molecular oxygen [12]. In the present work, we first describe the oxidation of cyclohexene with molecular oxygen using transition-metal-substituted polyoxometalate-intercalated hydrotalcites.

The K^+ salts of the $XW_{11}Z(H_2O)O_{39}^{n-}$ (where X = P, Si, and Z = Mn^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+} and Cu^{2+}) were prepared by previously reported literature procedures [13]. Mg_3Al hydrotalcite (HT) with formulas of $Mg_3Al(OH)_8NO_3{\cdot}xH_2O$ was synthesized by a reported coprecipitation method [14]. Catalysts with compositions of $Mg_3Al(OH)_8{-}XW_{11}Z(H_2O)O_{39}$ (hereinafter called ZPOM-HT), $Mg_3Al(OH)_8{-}PW_{12}O_{40}$ and $Mg_3Al(OH)_8{-}SiW_{12}$ (or WPOM-HT) were prepared by ion-exchange reaction of $Mg_3Al(OH)_8NO_3{\cdot}xH_2O$ in aqueous suspension with aqueous solutions of the POMs. In a typical synthetic experiment, a slurry of 5.0 g (ca. 10.0 mmol) of wet, freshly prepared HT in 50.0 ml of deionized water was stirred for 5 h to ensure complete wetness of the HT. Then, the dilute HNO_3 solution was added to adjust the pH to 5.5–6.0. This acidified slurry was added dropwise to a solution containing 8.5 g (ca. 4.0 mmol) of $K_5PW_{11}Ni(H_2O)O_{39}$ in 50 ml of water at 75°C. The reaction mixture was stirred for 3 h and the green precipitate was recovered by filtration, washed

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with three 100 ml portions of deionized water, and dried at 75°C for 24 h. For the obtained product, chemical analysis indicated the absence of nitrate and the presence of ca. 0.2 mol $PW_{11}Ni(H_2O)O_{39}^{5-}$ per equivalent, as expected for complete exchange. The XRD patterns of the HT precursor and the NiPOM-HT are shown in fig. 1. The presence of reflections at 14.67, 7.29, 4.84, 3.63, 2.90 and 2.41 Å in the pillared product indicates the layered structure [15]. Other pillaring reactions were carried out under the same conditions.

A typical catalytic reaction was performed using the following procedure: In a reaction bottle equipped with a magnetic stirrer and a pipe supplying oxygen, 0.4 g (ca. 0.5 mmol) of catalyst (all catalysts were calcined at 180°C for 5 h to remove water from the interlayer space before they were used) and 10.0 ml of cyclohexene were added. No solvent was employed. The reaction mixture was heated to 70°C under vigorous stirring and O_2 as oxidant was bubbled at a rate of 10.0 ml/min. After a reaction period of 10.0 h, the products were identified by GC/MS and quantitatively determined by GC.

The results of oxidation of cyclohexene over various catalysts are presented in table 1. As table 1 shows, two main products, 2-cyclohexene-1-one and 2-cyclohexene-1-ol, and two minor products, cyclohexene oxide and 1,2-cyclohexane-diol were observed for all catalysts. The ZPOM-HT (Z = Mn, Co, Cu) systems show high activities for the oxidation of cyclohexene with cyclohexene conversions of > 80%. With the FePOM-HT and NiPOM-HT systems, however, the conversions reach only ca. 10%. Obviously, Z ions in the POMs have a significant effect on the oxidation of cyclohexene. With different Z ions, the catalytic activity of the ZPOM-HT systems in the described reaction is in the order:

$$\mathrm{Co} \approx \mathrm{Cu} \approx \mathrm{Mn} \gg \mathrm{Fe} \approx \mathrm{Ni} \approx \mathrm{W}$$

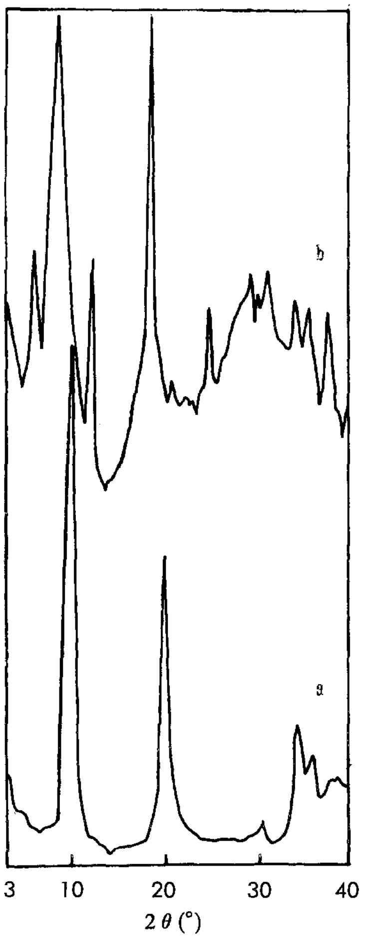

Fig. 1. XRD patterns (Cu Kα) of $Mg_3Al(OH)_8NO_3$ (a) and $Mg_3Al(OH)_8$–$PW_{11}Ni(H_2O)O_{39}$ (b).

We have demonstrated that layered double hydroxides with hydrotalcite structure also show good catalytic activities for the oxidation of cyclohexene with molecular oxygen as oxidant [16][#1]. According to our experiments, with $Mg_3Al(OH)_8NO_3$ as catalyst under the same reaction conditions, the cyclohexene conversion only reaches 7.5%. When the POMs alone were used, the cyclohexene conversions increased and were much higher than that of the HT, but slightly lower than that of the corresponding POM-HTs (see the values in the parentheses in table 1). The experimental results indicate that the oxidation of cyclohexene on POM-HTs is due to both POM and HT. That is, Z ions in the POM pillars and M^{2+} and M^{3+} ions in the hydrotalcite layers are possible active centers for the oxygen transfer in the oxidation of cyclohexene. The catalytic properties of these catalysts may be modified by adjusting the kinds and numbers of metal ions in the pillars and layers. Comparing the results using catalysts with different central atoms in the POMs, it can be seen that the activity increases when P is used instead of Si. But the selectivity of the Si materials is similar while there is a large variation for the P materials. We ascribe these results to the differences of the oxidation potentials of the corresponding heteropolyanions [17].

The product distributions of our results are similar to those reported earlier but we report higher cyclohexene conversions. The production of diol in our systems may be due to the ring-opening of epoxide in these acid–base systems. Recently, Tatsumi et al. reported the shape-selective epoxidation of alkenes catalyzed by $Mo_7O_{24}^{6-}$ and $W_{12}O_{41}^{10-}$ anions pillared hydrotalcites using H_2O_2 as oxidant [8]. In those experiments, diol and epoxide are the main products and no allylic alcohol and allylic ketone are produced. We have used H_2O_2 as oxidant for the present system and found that H_2O_2 was completely decomposed during the initial several minutes of the reaction and much lower cyclohexene conversion was observed. So, the differences in the product

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[#1] In this paper, we describe the oxidation of cyclohexene with O_2 using $M_2^{2+}M^{3+}(OH)_6NO_3$ (M^{2+} = Mn, Co, Ni, Mg, Zn, M^{3+} = Al, Cr, Fe), and found that these catalysts show high activity for the oxidation of cyclohexene and the natures of the M^{2+} and M^{3+} ions have significant effects on the catalytic properties.

Table 1
The oxidation of cyclohexene by $Mg_3Al(OH)_8$–$XW_{11}Z(H_2O)O_{39}$ and O_2 [a]

Catalyst		Conversion (%)	Selectivity (%)			
			epoxide	allylic ketone	allylic alcohol	diol
X = Si,	Z in cat.					
	Mn	79.3	4.4	36.2	58.2	1.2
		(55.8)	(3.1)	(32.8)	(62.1)	(2.1)
	Fe	11.8	2.6	38.9	56.2	2.2
		(11.7)	(2.6)	(43.1)	(52.8)	(1.6)
	Co	87.5	3.4	31.9	62.3	2.5
		(68.1)	(3.5)	(34.7)	(59.1)	(2.6)
	Ni	8.3	2.0	33.4	63.0	0.9
		(8.4)	(2.3)	(38.1)	(51.3)	(1.2)
	Cu	82.4	4.1	36.6	57.5	1.9
		(65.7)	(3.8)	(33.1)	(60.5)	(2.5)
	W	7.8	5.4	37.7	56.4	4.8
X = P,	Z in cat.					
	Mn	86.0	4.1	33.8	59.4	2.7
	Fe	13.0	3.0	47.7	45.4	3.2
	Co	91.7	3.9	29.3	63.5	3.3
	Ni	9.8	3.0	34.9	60.5	1.5
	Cu	89.0	3.6	35.1	57.5	3.7
	W	8.5	4.6	40.1	51.8	3.4

[a] Reaction conditions: reaction temperature, 70°C; reaction time, 10.0 h; catalyst calcined at 180°C for 5 h, 0.5 mmol; cyclohexene, 10.0 ml; flowing rate of O_2, 10.0 ml/min. Values in parentheses are those of the corresponding K^+ salts of the POMs.

distributions may come from a different reaction mechanism. According to our experiments, the oxidation of cyclohexene over POM-HTs is a complicated process, which may consist of direct molecular oxygen transfer on the active centers of Z ions in the POMs (like the mechanism reported in ref. [12]) and crystal lattice oxygen transfer catalyzed by the active centers in the hydrotalcite layers. The details of the reaction mechanism of oxidation of cyclohexene on POM-HT catalysts need to be studied in depth.

In conclusion, we have demonstrated that the transition-metal-substituted polyoxometalate-intercalated hydrotalcites are effective catalysts for oxidation of cyclohexene with molecular oxygen as the oxidant. These catalysts are found to be more active than those of the corresponding HT precursor and salts of POMs. The oxidation abilities can be modified by adjusting the kinds and numbers of M ions in the pillars and layers.

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