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# Mn(III) active site in hydrotalcite efficiently catalyzes the oxidation of alkylarenes with molecular oxygen

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<i>Keywords:</i> Alkylarenes oxidation NiMn Hydrotalcite Kinetic study Aerobic oxidation Mn(III) cation	Developing efficient heterogeneous catalytic systems based on easily available materials and molecular oxygen for the selective oxidation of alkylarenes is highly desirable. In the present research, NiMn hydrotalcite (Ni <sub>2</sub> Mn- LDH) has been found as an efficient catalyst in the oxidation of alkylarenes using molecular oxygen as the sole oxidant without any additive. Impressive catalytic performance, excellent stability and recyclability, broad applicable scope and practical potential for the catalytic system have been observed. Mn <sup>3+</sup> species was proposed to be the efficient active site, and Ni <sup>2+</sup> played an important role in stabilizing the Mn <sup>3+</sup> species in the hydro- talcite structure. The kinetic study showed that the aerobic oxidation of diphenylmethane is a first-order reaction over Ni <sub>2</sub> Mn-LDH with the activation energy ( $E_a$ ) and pre-exponential factor ( $A_0$ ) being 85.7 kJ mol <sup>-1</sup> and 1.8 × 10 <sup>9</sup> min <sup>-1</sup> , respectively. The Gibbs free energy ( $\Delta G^{\neq}$ ) was determined to be -10.4 kJ mol <sup>-1</sup> K <sup>-1</sup> for the oxidation based on Eyring-Polanyi equation, indicating the reaction is exergonic. The mechanism study indicated that the reaction proceeded through both radical and carbocation intermediates. The two species were then trapped by molecular oxygen and H <sub>2</sub> O or hydroxyl species, respectively, to yield the corresponding products. The present research might provide information for constructing highly efficient and stable active site for the catalytic aerobic oxidation based on available and economic material.

#### 1. Introduction

Efficient and selective activation of  $\alpha$ -C–H bonds of alkylarenes is one of the most important and challenging research topic, and has attracted much attentions from chemists. Development of efficient and practical catalytic systems for the reaction is of both academic and practical interests. Much effort has been devoted to the oxidative activation of alkylarenes, and many catalytic systems have been developed using peroxides, such as TBHP (*tert*-butyl hydroperoxide) [1–6], H<sub>2</sub>O<sub>2</sub> [7–10], ozone [11,12], NaIO<sub>4</sub> [13,14] and *m*CPBA (*m*-chloroperoxybenzoic acid) [15], and so on. Compared with peroxides, molecular oxygen obviously has the advantages of being less costly, environmentally friendly, practically safe and easily controllable.

A variety of aerobic systems have been developed, but radical initiators were usually required [16–18]. Supported gold nanoparticles (Au NPs@3D-(N)GFs) synthesized by Kazerooni et al. [19] exhibited excellent performance in the oxidation of alkylarenes. However, the stability of the catalyst was not satisfactory enough, and the use of a noble metal

would limit its wide application. Palladium NCN and CNC pincer complexes [20], Pd(OAc)<sub>2</sub>/bis-triazole system [21] and an enzyme-like system based on 1,2,4-triazole-type ligands and nickel(II) bromide [22] have been described by Urgoitia's group, but NaOAc was required as additive in all catalytic systems. Moreover, these noble metal-based catalysts are not cost effective. Monjezi, et al. [23] have developed a nano-sized Co-Mn catalyst and investigated its performance in the aerobic oxidation of diphenylmethane. Under high pressure, the conversion and the selectivity reached 87 % and 90 %, respectively. The catalytic system also suffered the drawbacks of laborious preparation and poor stability. A MnO<sub>2</sub>@wool complex has been found to be able to catalyze the selective aerobic oxidation of alkylarenes [24]. In the aerobic oxidation of diphenylmethane, qualitative yield of the corresponding ketone could be obtained in 9 h. However, the catalyst was produced through the oxidation of wool with KMnO<sub>4</sub>, which is an environmentally unfriendly process. In addition, the catalytic efficiency still needs to be improved. Ji and coworkers [25] have developed a catalytic system including metalloporphyrins as the catalysts and cumene as a

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Fig. 1. XRD pattern (A) and SEM image (B) of Ni<sub>2</sub>Mn-LDH.

co-substrate. The yield of benzophenone reached 96 % in the aerobic oxidation of diphenylmethane under the selected conditions, but the process consumed a large amount of cumene, leading to the difficulty of purification and high costs. The vapor phase oxidation of diphenylmethane in air over CeAlPO-5 catalysts under high temperature 325 °C has also been reported [26].  $MN(SiMe_3)_2$  [M = K, Na or Li] has been found effective in the aerobic oxidation of diarylmethanes [27], but excess base was required as the reactant, and the yields of the corresponding products were not attractive. Mn- or Cr-containing mesoporous molecular sieves have also been found effective in the catalytic oxidation of alkylarenes to ketones using  $O_2$  as the sole oxidant [28,29], but the conversion of substrate was quite low. Heterogeneous catalysts based on Mn complexes or metal-organic framework have been prepared by Kuwahara and the coworkers, and moderate yields of the carbonylation products could be obtained [30,31]. Recently, Yamaguchi's group developed a series of transition-metal-containing manganese oxides (M–MnO<sub>x</sub>) through a low-temperature reduction method [32], and good catalytic performance for the Ni–MnO<sub>x</sub> has been observed in the aerobic oxidation of alkylarenes. To sum up, the present catalytic systems for the aerobic oxidation of alkylarenes suffer some drawbacks, including using expensive noble metal or ligands, low efficiency, requirement of additives, higher reaction temperature or high pressure of oxygen. In addition, some of these are homogeneous, which would result in difficulty in recycling of catalysts and purification of product. From the viewpoint of sustainable chemistry, it is highly desirable to search for efficient heterogeneous catalytic systems originated from easily available materials and molecular oxygen for the selective oxidation of alkylarenes.

LDHs (layered double hydroxides) has a hydrotalcite-like structure and are represented by the general formula of  $[M(II)_{(1-x)}M$  $(III)_x(OH)_2]^{x+}[A^{n-}]_{x/n}\cdot mH_2O$  [33,34]. It has been an important catalyst due to its adjustability of the compositions [35,36], and further their physic-chemical properties. Actually, LDHs has been widely employed in various organic transformations based on its characteristic properties of basicity and the redox functionality. Jana, et al. have employed Ni<sub>5</sub>Al hydrotalcite in the aerobic oxidation of diphenylmethane, but only a 62 % conversion could be obtained even under high reaction temperature [37].  $MnO_4^{-1}$ -exchanged Mg–Al hydrotalcite also was prepared and tested in the transformation [38], but the conversion was quite low.

In our continuous research on the development of efficient catalytic systems for the oxidative activation of C–H bonds, LDHs with different compositions have been tested using the aerobic oxidation of diphenylmethane as the model reaction. We found that Ni<sub>2</sub>Mn-LDH could smoothly accelerate the oxidation and exhibited the highest catalytic activity under the selected conditions (Fig. S1 and Table S1). Based on the findings, the selective aerobic oxidation of  $\alpha$ -C–H bonds of arylenes under the catalysis of Ni<sub>2</sub>Mn-LDH has been studied in detail in the present study. The effects of conditions on the reaction, relationship of structure and activity, reaction kinetics and thermodynamics, and recyclability were systematically investigated. The active catalytic site

for the transformation has been tried to be determined based on the results of series of controlled experiments and characterization of the catalyst. Furthermore, the possible reaction pathways were proposed according to the intermediate analysis and isotope labeled experiments.

#### 2. Experimental

#### 2.1. Preparation of LDHs catalyst

Ni<sub>2</sub>Mn-LDH was obtained according to our previous reported method [39]. Firstly, A solution of NaOH (0.06 mol, 2.4 g) and NH<sub>3</sub>·H<sub>2</sub>O (25–28 wt%, 4.2 g) in 150 mL deionized water was prepared in a 500 mL three-neck round bottom flask. Then, a mixture of Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (0.06 mol, 17.4 g) and MnCl<sub>2</sub> (0.03 mol, 3.8 g) in 150 mL deionized water was slowly added into the flask with mechanical stirring at 30 °C under air atmosphere. After the titration, the resulting suspension was digested at 60 °C for 24 h. Finally, the formed precipitate was separated and washed with water and dried at 120 °C over night. The Ni<sub>2</sub>Mn-LDH sample was obtained in a brown powder. CuMgAl-LDH, Ni<sub>2</sub>Al-LDH, Co<sub>2</sub>Al-LDH and Mn<sub>2</sub>Al-LDH were prepared through similar procedures using the corresponding nitrates as the precursors.

# 2.2. Characterization of LDH samples

The identification of the crystallization of the prepared samples were confirmed through Powder X-ray diffraction (XRD) using a Rigaku D/max 2500 PC X-ray diffractometers with Cu-K $\alpha$  (1.5402 Å) radiation. Surface morphology was analyzed by scanning electron microscopy (SEM) with a JEOL JSM-6360LA scanning electron microscope. The compositions of samples were determined by inductively coupled plasma analysis (ICP) using a Varian Vista-AX device. X-ray photoelectron spectroscopy (XPS) measurement was analyzed on a Thermo Scientific ESCALAB 250Xi instrument. Porosity and surface area data were collected on a micromeritics ASAP2010C apparatus, using nitrogen as the adsorbate at liquid nitrogen temperature. The surface area was calculated using the BET method and the pore size distributions were deduced through the BJH method.

#### 2.3. Catalytic aerobic oxidation of alkylarenes

The oxidation was carried out in a carousel reaction tube to which diphenylmethane (1.0 mmol), Ni<sub>2</sub>Mn-LDH (0.2 g), dodecane (2 mL) and chlorobenzene (0.5 mmol, used as the internal standard reference) were added. The mixture was then magnetically stirred at 120 °C under oxygen atmosphere (1 atm). The reaction was sampled periodically and analyzed through a gas chromatograph (Shimadzu GC-2010AF). After the reaction, the catalyst was separated via filtration, washed with ethyl acetate, dried at 120 °C for 4 h and introduced into a new reaction to recycle the catalyst. The conversion of the diphenylmethane and the



Fig. 2. (A) Full-scan XPS spectrum of the Ni<sub>2</sub>Mn-LDH sample. Fine-scan XPS spectra of (B) O 1s, (C) Ni 2p, and (D) Mn 2p catalysts.

selectivity of benzophenone were calculated using the internal standard method according to the GC analysis with no allowance for the background. The turnover frequency (TOF) value was calculated based on the mol of diphenylmethane converted per hour per mol of Mn on the surfaces of catalysts. The catalytic oxidations of other substrates were conducted with similar procedure, and the conversion and selectivity were calculated using the normalization method. Some of the products were isolated using flash chromatography analyzed through a NMR spectrometer.

# 2.4. <sup>18</sup>O-labeled $H_2^{18}O$ experiments

To a mixture of diphenylmethane (1.0 mmol), Ni<sub>2</sub>Mn-LDH (0.2 g), dodecane (2 mL), chlorobenzene (0.5 mmol, used as the internal standard reference) in a carousel reaction tube,  $H_2^{18}O$  [40 mg (2 mmol), 97 % <sup>18</sup>O enriched, Aladdin Chemical Co.] was added. The reaction mixture was stirred for 120 min at 120 °C under oxygen atmosphere (1 atm) and then directly analyzed by GC–MS. The <sup>16</sup>O and <sup>18</sup>O composition in benzophenone were determined by the relative abundance of mass peaks at m/z = 182 for <sup>16</sup>O and m/z = 184 for <sup>18</sup>O.

#### 3. Results and discussion

#### 3.1. Characterization of Ni<sub>2</sub>Mn-LDH

The XRD pattern of the Ni<sub>2</sub>Mn-LDH depicted in Fig. 1A exhibits intense typical reflections located at the angles of a hydrotalcite-like phase. The sharp and asymmetrical diffraction peaks at 11°, 23° and 35° are related to (003), (006) and (009), respectively; broad and asymmetrical peak for (018) located at about 40° [40,41]. No diffractions for impurities can be found, indicating the good purity of the sample. The distinguished peaks at 60–61° for the (110) and (113) suggest its good crystallization [35,36]. The SEM image of Ni<sub>2</sub>Mn-LDH obviously shows the plate-like agglomerated crystals, also demonstrating the formation of hydrotalcite structure (Fig. 1B). The basal spacing distances of LDHs are actually determined by the size of anions between the layers and the value can be calculated from the reflection (003). A value of 7.89 Å was obtained for the prepared Ni<sub>2</sub>Mn-LDH sample, generally equal to the reported results [42], indicating the anions in the brucite are mainly  $CO_3^2$  and OH–.

The surface chemical properties Ni<sub>2</sub>Mn-LDH were then characterized. The atomic concentrations of the Ni<sub>2</sub>Mn-LDH sample and the chemical environments of the nickel, oxygen and manganese were investigated by XPS, and the spectra can be found in Fig. 2. Fullspectrum XPS (Fig. 2A) indicates the presence of Ni, Mn, O and C in the Ni<sub>2</sub>Mn-LDH. The chemical shifts in the O 1s spectra can be used to identify the species in the sample. Analysis of O 1s spectra (Fig. 2B) for Ni<sub>2</sub>Mn-LDH shows that the sample is composited of metal hydroxides, namely that of Ni and Mn, in consistent with the XRD pattern [43]. For the XPS spectra of the Ni 2p3/2 (Fig. 2C), only one peak can be fitted at a binding energy of ca. 855.5 eV, and a spin-energy separation of about 17.6 eV is observed, which refer to Ni(OH)<sub>2</sub> according to the reported results in literatures [43–45].

Unlike the Ni 2p3/2, the XPS spectra of the Mn 2p3/2 can be fitted by three peaks (Fig. 2D), and binding energies of ca. 637.5 eV, ca. 642.1 eV and ca. 646.5 eV are identified to  $Mn^{2+},\,Mn^{3+}$  and  $Mn^{4+},\,respectively$ [46–48], indicating that the oxidation of  $Mn^{2+}$  to  $Mn^{3+}$  and  $Mn^{4+}$  took place during the synthesis of NiMn hydrotalcite. It is obvious that the content of Mn<sup>3+</sup> was significantly higher than Mn<sup>2+</sup> and Mn<sup>4+</sup>, and about a value of 78 % could be observed. The observation is consistent with the XRD analysis, because the trivalent cation is essential for the formation of hydrotalcite structure [49,50]. In the previous reports about the Mn-contained catalysts for oxidation transformation, Mn<sup>3+</sup> has been proposed as a key catalytic site [32,51]. Therefore,  $Mn^{3+}$  in the Ni<sub>2</sub>Mn-LDH might be responsible for its high catalytic performance. To the best of our knowledge, there has been no report for effectively constructing the stable Mn<sup>3+</sup>. Some materials containing Mn<sup>3+</sup> have been reported, such as hierarchical brush-like a-MnO2 and Co3O4 nanoarrays [52] and magnetic composites of biochar and MnFe<sub>2</sub>O<sub>4</sub>  $(MnFe_2O_4/MX)$  [53], but only 51.2 % and 33 % content of the Mn<sup>3</sup>

Effect of solvents on the diphenylmethane oxidation.

Entry O2 Ni <sub>2</sub> Mn-LDH					
	Solvent	Conv. (%)	Sel. (%)		
1	<i>p</i> -xylene	48	>99		
2	benzyl benzoate	6	54		
3	diphenyl ether	9	>99		
4	polyethylene glycol-200	5	>99		
5	$\gamma$ -valerolactone	5	97		
6	diglycol	4	>99		
7	DMF	22	67		
8	mesitylene	47	>99		
9	dodecane	80	>99		



Fig. 3. Effect of temperature on the diphenylmethane oxidation.

respectively, could be obtained. The low content of the catalytic site should limit its catalytic performance. Therefore, the present study might provide an effective method to construct  $Mn^{3+}$  on the basis of hydrotalcite structure, which will be helpful to prepare efficient catalysts with high catalytic performance.

#### 3.2. Catalytic performance of Ni<sub>2</sub>Mn-LDH

The catalytic performance of  $Ni_2Mn$ -LDH in the aerobic oxidation of alkylarenes using diphenylmethane as the model substrate was then systematically investigated. The effects of reaction conditions on the oxidation were firstly examined and optimized.

Various solvents, including *p*-xylene, benzyl benzoate, diphenyl ether, polyethylene glycol-200 (PEG-200), dimethylformamide (DMF),  $\gamma$ -valerolactone, diglycol, mesitylene and dodecane, have been investigated in the diphenylmethane oxidation. Using Ni<sub>2</sub>Mn-LDH as the catalyst, most of the selected solvents exhibited excellent selectivities of benzophenone. On the whole, solvents with weak polarity were superior to polar solvents, and the dodecane with the lowest polarity exhibited the highest conversion and yield (Table 1, entry 9). Although PEG-200 gave good result in the oxidation over Pd NCN and CNC pincer complexes [20], it provided negligible result in the present catalytic system.

Reaction conditions: diphenylmethane 1 mmol, catalyst 0.2 g, solvent 2 mL, 100  $^{\circ}$ C, 6 h, O<sub>2</sub> (1 atm).

The results of the effect of temperature on the catalytic reaction are displayed in Fig. 3. It is obviously observed that high temperature evidently improved the catalytic reactivity. The reaction finished within 100 min. under a reaction temperature of above 120  $^{\circ}$ C, while only about 32 % conversion could be obtained at 80  $^{\circ}$ C. In spite of this, no significant by-product was observed in the reaction. Under the optimized conditions, quantitative yield of benzophenone could be efficiently obtained in the catalytic aerobic oxidation of diphenylmethane over Ni<sub>2</sub>Mn-LDH.

Reaction conditions: diphenylmethane 1 mmol, Ni<sub>2</sub>Mn-LDH 0.2 g, dodecane 2 mL,  $O_2$  (1 atm).

To compare the present catalytic system with known catalysts, some typical reported results for the aerobic oxidation of diphenylmethane to benzophenone are collected in Table 2. The catalytic systems based on noble metals (entries 1-3) exhibited excellent reactivity in the oxidation. However, the additive NaOAc was required in the cases of Pd pincer complexes. Gold nanoparticles supported on three-dimensional nitrogen-doped graphene-based frameworks (Au NPs@3D-(N)GFs) gave a 94 % conversion of the substrate in 5 h, but the stability was not good enough [20]. In addition, the high costs of the noble metal based catalysts limit their large-scale application. The NiBr<sub>2</sub> complexes have also been investigated by the same research group (entries 4-5), but the catalytic efficiency was obviously low in comparison with Pd. MnTPPCl combined with cumene as the co-substrate could efficiently catalyze the transformation, but a large amount of cumene added in the system should result in difficulty of the separation [25]. The above homogeneous catalytic systems generally suffered by the low efficiency of recyclability of the catalyst. Some heterogeneous catalysts have also

Table 1	2
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Some typical catalytic results for the aerobic oxidation of diphenylmethane.

Entry	Catalyst	Additive	Reaction time (h)	TOF $(h^{-1})$	Conv. (%)	Sel. (%)	Ref.
1	Pd NCN pincer complexes	NaOAc	24	_	98 <sup>a</sup>		[20]
2	Pd CNC pincer complexes	NaOAc	24		94 <sup>a</sup>		[20]
3	Au NPs@3D-(N)GFs	-	5	-	94	>99	[19]
4	NiBr <sub>2</sub> / 1,2,4-triazole	NaOAc	48	-	84 <sup>a</sup>		[22]
5	NiBr <sub>2</sub> / bis-triazolyl ligand	NaOAc	48	-	97 <sup>a</sup>		[22]
6	MnTPPCl	cumene	12	-	96	100	[25]
7	Co/Mn-BSO <sub>0.01</sub> nanocatalyst	-	3		87	90	[23]
8	MnO <sub>4</sub> <sup>-1</sup> -exchanged Mg–Al hydrotalcite	-	5	8.0	27.4	100	[36]
9	Ni <sub>5</sub> Al-LDH hydrotalcite	-	5	-	62	96.9	[35]
10	CrMCM-41	-	24	-	51	98	[29]
11	MnS-1(10 bar)	-	6	12	4	100	[28]
12	MnMCM-41(10 bar)	-	6	16	14	100	[28]
13	MnMCM-48(10 bar)	-	6	17	15	100	[28]
14	PC-MnO <sub>2</sub>	-	6		95 <sup>a</sup>		[49]
15	MnO <sub>2</sub> @wool	-	9	-	100 <sup>a</sup>		[24]
16	Ni-MnO <sub>x</sub>	_	5	-	>99 <sup>a</sup>		[30]
17	Ni <sub>2</sub> Mn-LDH	-	1.7	12.6	>99	>99	This work

<sup>a</sup> Yield of benzophenone.

Catalytic aerobic oxidation of various alkylarenes under Ni<sub>2</sub>Mn-LDH.

Entry	Substrate	Product	Reaction time (h)	Yield <sup>a</sup> (%)
1		°	1.7	>99
2	F		10.5	93
3	C	F O F	1.5	>99
4		CI	1.5	98
5			2.5	92
6			3.5	>99
7		O O O	4	>99 (91)
8			2.5	97
9			3.5	81 (63)
10	Br	Br	12	83 (69)
11	Br	O O O	12	79 (66)
		o o		
12			<b>40</b> <sup>5</sup>	2
13		NO	20	3 19
				5
14			20	2
15			1	>99

Reaction conditions: substrate 1 mmol, Ni\_2Mn-LDH 0.2 g, dodecane 2 mL, 120  $^\circ \! C,$  O\_2 (1 atm).

 $^a$  Calculated via the normalization method based on the GC–MS analysis, and isolated yield in brackets.  $^b$  80 °C.

Catalytic aerobic oxidation of some other substrates with -CH2- in different environments.

Entry	Substrate	Product	Reaction time (h)	Yield <sup>a</sup> (%)
1			6.5	95
2 <sup>b,c</sup>	Č C	ОН	4	83 <sup>b,c</sup>
3			16	78
4 <sup>b</sup>			48	trace
5 <sup>d,e</sup>			8	84
6 <sup>d,e</sup>			10	66
<b>7</b> <sup>d,e</sup>	→ F N N		4	57
8 <sup>d,e</sup>			10	43
9 <sup>d</sup>	N I		4	18
		Г		53
10 <sup>d</sup>		N	24	8

Reaction conditions: substrate 1 mmol, Ni<sub>2</sub>Mn-LDH 0.2 g, dodecane 2 mL, 120 °C, O<sub>2</sub> (1 atm).

<sup>a</sup> Calculated via the normalization method based on the GC–MS analysis, and isolated yield in brackets.

- <sup>b</sup> DMSO was used as the solvent.
- <sup>c</sup> 80 °C.
- $^{\rm d}\,$  Mesitylene was used as the solvent, 160 °C.

<sup>e</sup> It was difficult to isolate the product even using flash chromatography, therefore, these products were analyzed by GC–MS.

been developed. Supported Co-Mn catalyst (Co/Mn-BSO0.01 nanocatalyst) could give good result for the reaction, but high reaction temperature and pressure of oxygen were required (entry 6). Under the mild conditions, most of the heterogeneous catalytic systems based on non-noble metals could not give satisfied catalytic reactivity in the oxidation, although the selectivity was high enough (entries 7–12). Porous chitosan and wool supported MnO<sub>2</sub> catalysts [24,54] and Ni-MnO<sub>x</sub> [32] exhibited excellent catalytic activities in the aerobic oxidation of diphenylmethane, however, the preparing processes were quite complicated. In comparison with these results, the present Ni<sub>2</sub>Mn-LDH catalyst can be conveniently prepared by simple coprecipitation method. And the catalytic system can provide excellent catalytic performance and almost qualitative yield in the oxidation of diphenylmethane under relatively milder conditions. The TOF has also been calculated for the Ni<sub>2</sub>Mn-LDH catalytic system based on the mol number of Mn on the surface of catalyst, which was estimated based on the BET and XPS data (the details for the calculation can be found in Supporting Information). And a TOF value of 12.6 h<sup>-1</sup> was obtained for the present catalytic system. Although it is on the same level as reported results (entries 8, 11–13), these catalytic systems can not give satisfied oxidation yields.

# 3.3. Catalytic activity of Ni<sub>2</sub>Mn-LDH for other alkylarenes oxidation

With the interesting finding for the excellent catalytic performance of Ni<sub>2</sub>Mn-LDH in the aerobic oxidation of diphenylmethane, we tried to investigate the scope of catalytic system, and various alkylarenes were employed as substrates under the optimized reaction conditions (Table 3). The --CH<sub>2</sub> --group of all the alkylbenzene substrates was oxidized to carbonyl with excellent selectivity (>99 %), showing high chemoselectivity in the transformation. Diphenylmethane and its analogs could be well tolerated in the catalytic system, and excellent yield of the corresponding oxidative products could be obtained (entries 1-3). Electronic effect can be obviously observed in the reaction, and the substrates with electro-donating group located in the aryl rings have the higher activity than the ones with electron-withdrawing substituents. When xanthene was used as the substrate, the reaction could finish in 1.5 h, shorter than that for diphenylmethane (entry 4); in contrast, a prolonged time was required for bis(4-fluorophenyl)methane (entry 2–3), which should be due to the deactivation of the F- groups. Similar results were also found in the cases of 2-benzylpyridine and 4-benzylpyridine (entries 5-7). Fluorene and its derivatives could also be well tolerated over the catalytic system (entries 8-11), and good to excellent yields for the carbonylation products were obtained. Substrates with electron-withdrawing substituents dramatically decrease the reactivity, which can be deduced from the reaction time, in consistent with the above observations. Ethylbenzene and its derivatives could not give the corresponding carbonylation products even under high temperature and prolonging time, which should be ascribed to the low activation of methyl group (entries 12-14). When 9,10-dihydroanthracene was introduced as the substrate, dehydrogenative aromatization product with excellent selectivity was obtained (entry 15). No oxygenation product, namely anthracene-9,10-dione, could be detected, quite different from that under the catalysis of Pd NCN or CNC pincer complexes [20] and metalloporphyrins [55].

Furthermore, some other substrates with -CH2 -in different environments have also been tested in the catalytic system (Table 4). The aerobic oxidation of 1,2-diphenylethan-1-one could proceed smoothly in the Ni<sub>2</sub>Mn-LDH catalytic system, and excellent yield of the 1,2-dicarbonyl compound could be obtained (entry 1). Interestingly, when 3,4dihydronaphthalen-2(1H)-one was used as the substrate, 2-naphthol was formed in an excellent 83 % yield (entry 2), suggesting that dehydrogenative aromatization took place in the case. Although some methods have been reported for the dehydrogenative aromatization of cyclohexenones [56,57], the present catalytic system will provide a simple process to synthesize naphthol from naphthalenone based on heterogeneous catalyst and using molecular oxygen as the sole oxidant. Benzylic ethers were also introduced as substrate to synthesis the corresponding benzoate esters. Under the catalysis of Ni<sub>2</sub>Mn-LDH, benzyl methyl ether could transform to methyl benzoate in good yield (entry 3), significantly higher than the reported result [58]. However, the oxidation of isochroman could not happened (entry 4). Isoquinolones, which are important synthetic intermediates for biologically active molecules [59-61], could be obtained in moderate to good yield when isoquinolines were used as the substrates using mesitylene as the solvent (entries 5–8). We speculated that tandem reaction sequence of dehydrogenation-oxidation happened in the catalytic system. Electronic effect could also be observed in these cases. The substrate with electron-withdrawing substituent in the phenyl reduced the reactivity, while electron-donating group improved the reaction rate. Although some methods have been reported for the synthesis of isoquinolones with various starting materials [62-64], the present protocol has the advantages of simple starting material, heterogeneous catalysis and mild reaction conditions. However, for the N,N-dimethylbenzylamine, only a 18 % yield of the oxygenation product could be obtained (entry 9), and benzaldehyde was found as the main by-product. When N-benzyl-N-ethylaniline was introduced into the reaction, only the imine could be observed by GC-MS in about 8% yield, probably resulted from de-ethylation and dehydrogenation. No oxygenation product for the substrate could be observed, which might be due to the steric-hindrance.

Based on the aforementioned pieces of results, the  $Ni_2Mn$ -LDH catalytic system has exhibited excellent activities in the oxidation of alkylarenes, and high yields were obtained for most of the studied substrates. Although the reaction rate and reaction conditions depend on



Fig. 4. The hot-filtration experiment.

the chemical structure of alkylarenes, it can be concluded that the prepared Ni<sub>2</sub>Mn-LDH catalyst provides an efficient and simple method for the transformation of alkylarenes to carbonyl compounds.

#### 3.4. The stability and recyclability of Ni<sub>2</sub>Mn-LDH

The stability for the catalyst was then investigated under the selected conditions. To examine the leaching of metallic ions, a hot-filtration experiment has been conducted. When the reaction proceeded about 30 min (about 40 % conversion), the catalyst was filtered off, and the filtration was continuously stirred under the same reaction conditions. The plots for the conversion depicted in Fig. 4 show that no further transformation took place without catalyst, suggesting that no leaching of the active site happened.

Reaction conditions: diphenylmethane 1 mmol, Ni\_2Mn-LDH 0.2 g, dodecane 2 mL, 120 °C, O\_2 (1 atm).

The recyclability of the Ni<sub>2</sub>Mn-LDH catalyst was subsequently tested with a reaction time of 80 min. Almost no reduction of activity could be observed for the catalyst even after eight runs (Fig. S2). XRD pattern for the reused catalyst indicates that the layered structure was completely preserved after several reuses (Fig. 5A). ICP analysis of regenerated catalyst revealed that Ni and Mn contents almost did not change after the reaction. XPS spectra for the Mn 2p suggest that the distribution of Mn<sup>n+</sup> active site remained unaltered (Fig. 5B and Table S3). N<sub>2</sub>adsorbtion/desorption also demonstrate no significant variation of the physic-chemical properties (Fig. 5C, D and Table S3). These observations strongly indicate the excellent structurally and catalytic stability of the Ni<sub>2</sub>Mn-LDH catalyst during the aerobic oxidation of diphenylmethane under the present conditions.

# 3.5. Kinetic and thermodynamic analysis for the catalytic oxidation of diphenylmethane over Ni<sub>2</sub>Mn-LDH

Kinetic study is an important aspect for one catalytic reaction and it has also been conducted in the present research. After elimination of internal and external diffusion (the calculation details can be found in the Supporting Information) [33,39,65,66], the experiments were investigated under different temperatures to study the kinetic aspects of the aerobic oxidation of diphenylmethane. The fitting results indicate that the oxidation is a first order reaction (Fig. 6).

Reaction conditions: diphenylmethane 2 mmol, Ni\_2Mn-LDH 0.2 g, dodecane 3 mL, O\_2 (1 atm).

The *k* values can be correlated by an Arrhenius-type expression, and the parameters of Arrhenius equation (Eq. 2) can be deduced via the plot of lnkto the 1/T.



Fig. 5. XRD pattern (A), Mn 2p XPS spectra (B) and N2 adsorption/desorption isotherms (C and D) of the recycled Ni2Mn-LDH.



Fig. 6. First order kinetics fit of aerobic oxidation of diphenylmethane under different temperatures ( $X_A$  is the value of diphenylmethane conversion).

$$\ln k = \ln A_0 - E_a / RT \tag{2}$$

where  $E_a$  is the energy of activation (kJ mol<sup>-1</sup>) and  $A_0$  is the preexponential factor (min<sup>-1</sup>).

A multiple regression analysis with this expression of the constants against temperature was depicted in Fig. 7. The slope and the intercept of the equation can be obtained as -10303.29808 and 21.31649, respectively. And the values of the apparent activation energy ( $E_a$ ) and the pre-exponential factor ( $A_0$ ) can be calculated through Eq. (2), and they are 85.7 kJ mol<sup>-1</sup> and 1.8  $\times$  10<sup>9</sup> min<sup>-1</sup>, respectively.

Thermodynamic characteristics of the catalytic oxidation were calculated according to the Eyring-Polanyi equation (Eq. 3) [67–69].

$$\ln(k/T) = -\Delta H^{\neq}/RT + \ln(k_{\rm b}/T) + \Delta S^{\neq}/R$$
(3)



Fig. 7. Arrhenius plot for the aerobic oxidation of diphenylmethane over  $\rm Ni_2Mn\text{-}LDH.$ 

where *k* is the rate constant at temperature T,  $\Delta H^{\neq}$  (kJ mol<sup>-1</sup> K<sup>-1</sup>) is the change in enthalpy of activation,  $\Delta S^{\neq}$  (J mol<sup>-1</sup> K<sup>-1</sup>) is the change in entropy of activation,  $k_b$ , *h* and *R* are Boltzmann, Planck, and universal gas constant, respectively.

The Eyring-Polanyi plot for the aerobic oxidation of diphenylmethane over Ni<sub>2</sub>Mn-LDH is shown in Fig. S4. The slope and the intercept of the equation can be obtained as -9905.4 and 14.3303, respectively. And the values of the  $\Delta H^{\neq}$  and  $\Delta S^{\neq}$  can be calculated through Eq. (3) to be -82.4 kJ mol<sup>-1</sup> K<sup>-1</sup> and -183.2 J mol<sup>-1</sup> K<sup>-1</sup>, respectively. A value of -10.4 kJ mol<sup>-1</sup> K<sup>-1</sup> for the change in Gibbs energy ( $\Delta G^{\neq}$ ) can be determined by the Eq. (4), indicating the reaction is exergonic.

The results for the controlled experiments.

Entry	Catalyst	Additive	Conv. (%)	Sel. (%)
1	Ni <sub>2</sub> Mn-LDH	_	>99	>99
2 <sup>a</sup>	Ni2Mn-LDH	-	56	>99
3 <sup>b</sup>	Ni2Mn-LDH	-	11	>99
4	-	-	2	>99
5	Ni <sub>2</sub> Al-LDH	-	3	>99
6	MnCO <sub>3</sub>	-	5	>99
7	MnCl <sub>2</sub> ·4H <sub>2</sub> O	-	3	78
8	MnO <sub>2</sub>	-	8	>99
9	Ni2Mn-LDH	BHT <sup>c</sup>	46	>99
10	Ni <sub>2</sub> Mn-LDH	TEMPO <sup>c</sup>	94	48

Reaction conditions: diphenylmethane 1 mmol,  $Ni_2Mn$ -LDH 0.2 g, dodecane 2 mL, 100 min, 120 °C, O<sub>2</sub> (1 atm).

<sup>a</sup> Air atmosphere (1 atm).

<sup>b</sup> Nitrogen atmosphere (1 atm).

<sup>c</sup> 2 Equiv. of substrate.



Fig. 8. The catalytic activity of Mn species with different valences and the first order kinetics fit of the oxidation of diphenylmethane.

$$\Delta G^{\neq} = \Delta H^{\neq} - T \Delta S^{\neq} \tag{4}$$

# 3.6. Discussion of reaction pathways for the catalytic oxidation of diphenylmethane over $Ni_2Mn$ -LDH

To get further insight into the catalytic system and structure-activity relationship, some controlled experiments were performed and the results are summarized in Table 5.

When the oxygen was replaced by air or nitrogen, significantly decreased conversions were obtained, indicating the necessity of the molecular oxygen (entries 2-3). Without catalyst, only a 2% conversion was observed, suggesting that the catalyst is critical for the oxidation of diphenylmethane (entry 4). To distinguish the effect of Ni and Mn species, we have tried to prepare NiAl and MnAl hydrotalcites through coprecipitation method. From the XRD pattern for the two samples (Fig. 1), it is observed that Ni<sub>2</sub>Al-LDH has been successfully synthesized, but only MnCO3 phase formed during the coprecipitation of MnCl2 and Al(NO<sub>3</sub>)<sub>3</sub> solutions. The two samples only gave  $\leq$ 5% conversions in the oxidation of diphenylmethane (entries 5-6), implying that Mn species in hydrotalcite structure is essential for the catalytic function. The results also demonstrated that Ni played a key role in forming Mn-contained hydrotalcite compound in the present system, suggesting that Ni and Mn in Ni<sub>2</sub>Mn-LDH might have synergistic effects in the reaction. According to the XPS analysis of the prepared Ni<sub>2</sub>Mn-LDH, the Mn cation in the LDH structure existed in different valences (Fig. 2). To determine the

active site for the oxidation, commercial MnCl<sub>2</sub>.4H<sub>2</sub>O and MnO<sub>2</sub>, having  $Mn^{2+}$  and  $Mn^{4+}$  cations, respectively, have been tested in the reaction for comparison. Quite low conversions were obtained (entries 7–8), suggesting that the active site for the aerobic diphenylmethane oxidation might be  $Mn^{3+}$ , which is not stable and prone to transform to  $Mn^{2+}$  and  $Mn^{4+}$ . In the Ni<sub>2</sub>Mn-LDH sample, Ni<sup>2+</sup> can stabilize the  $Mn^{3+}$  cations in the hydrotalcite structure through hybridization of the Mn(3d) orbitals with the Ni(3d) orbitals to yield an average d electron configuration per metal atom greater than 4 [34].

To further study the catalytic activity of the Mn cations with different valences in the oxidation, the investigation of catalytic activity of Mn<sup>2+</sup>,  $\mathrm{Mn}^{3+}$  and  $\mathrm{Mn}^{4+}$  has been tried using  $\mathrm{MnCO}_3, \mathrm{Ni}_2\mathrm{Mn}\text{-}\mathrm{LDH}$  and  $\mathrm{MnO}_2$  as the represents, respectively. Although the evaluation methodology is rough, it can reflect the relative catalytic activity of these species to some extent. The contribution of Mn<sup>2+</sup> and Mn<sup>4+</sup> has been subtracted in the case of Ni<sub>2</sub>Mn-LDH, because it contains all the three species. From the curves of conversion of diphenylmethane against reaction time in Fig. 8, it is obvious that  $Mn^{3+}$  shows significantly high catalytic activity than Mn<sup>2+</sup> and Mn<sup>4+</sup> in the oxidation. The fitting results for the kinetic profiles indicate that the oxidations under the three Mn species are all first order reactions (inserted plots in Fig. 8). The reaction rate constants for Mn<sup>2+</sup>, Mn<sup>3+</sup> and Mn<sup>4+</sup> were calculated to be 1.5  $\times$  10<sup>-4</sup> s<sup>-1</sup>, 210  $\times$  $10^{-4}$  s<sup>-1</sup> and 0.51  $\times$   $10^{-4}$  s<sup>-1</sup>, respectively, further verifying the highest catalytic activity of Mn<sup>3+</sup>. The result should be related to the higher standard reduction potential of  $Mn^{3+/2+}$  (~1.54 V) than  $Mn^{4+/2+}$  $(\sim 1.22 \text{ V})$ , that is, Mn<sup>3+</sup> species has a stronger oxidation ability toward diphenylmethane [51,70].

Reaction conditions: diphenylmethane 1 mmol,  $Mn^{n+}$  (n = 2, 3 and 4) 0.47 mmol, dodecane 2 mL, 120 °C, O<sub>2</sub> (1 atm).

The reaction mechanism for the oxidation over  $Ni_2Mn$ -LDH was then investigated in detail. The possibility of involvement of a radical intermediate was examined by introduction of BHT (2,6-di-*tert*-butyl-4methylphenol) and TEMPO (2,2,6,6-tetramethylpiperidine-1-oxyl), which are common radical scavengers, in the catalytic reaction. BHT could significantly suppress the reaction, while the selectivity almost did not change (Table 4, entry 9). In contrast, the conversion decreased slightly in the case of TEMPO, but the selectivity decreased to only 48 % (Table 4, entry 10). In addition, small amount of 1,1,2,2-tetraphenylethane was observed in the reaction by GC–MS analysis (compound I). These results suggest that radical intermediate might be involved in the catalytic reaction, and 1,1,2,2-tetraphenylethane might form through coupling of two diphenylmethane radical.



To further elucidate the possibility of the single-electron transfer (SET) mechanism in the activation of diphenylmethane in the catalytic system, the aerobic oxidation 4-ethylanisole (compound II) and 4-iso-propylanisole (compound III) were conducted under the catalysis of Ni<sub>2</sub>Mn-LDH to distinguish the SET and hydrogen-atom transfer (HAT) mechanism. The difference in reactivity between the above two substrates can reflect the reaction pathways. For the SET reactions, the relative rate of C–H oxidation is  $2^{\circ}>3^{\circ}$ , whereas it is  $3^{\circ}>2^{\circ}$  for HAT reactions [32,71,72]. As shown in Fig. S5, the initial rate for the oxidation of 4-ethylanisole was apparently higher than that for 4-isopropylanisole. Therefore, the aerobic oxidation of alkylarenes over Ni<sub>2</sub>Mn-LDH is suggested to be initiated mainly by the SET process [32, 71,72].

In the aerobic oxidation of alkylarenes, Mars-van Krevelen mechanism and oxidative nucleophilic substitution are also possibly involved



Fig. 9. The variation of the concentration of diphenylmethane and products in the reaction.

in the reaction. To distinguish the process, the aerobic oxidation of diphenylmethane was conducted under the selected conditions in the presence of H<sub>2</sub><sup>18</sup>O. As a result, <sup>18</sup>O-lablled product increased at the first 5 min., and then decreased to a constant value as the reaction advanced (Fig. S6). The observation is significantly different from the Mars-van Krevelen-type mechanism, where the <sup>18</sup>O-lablled product would increase from zero at the low turnover number [32,72,73]. In contrast, the oxidative nucleophilic substitution mechanism is probably involved in the reaction, because the attack of H<sub>2</sub>O molecules to the benzylic cation should be fast. The formation of diphenylmethanol detected by GC-MS also verified the speculation. In addition, the reaction was also tested in the presence of 2 equivalent of acetic acid as an alternative nucleophile under the selected reaction conditions. The corresponding benzhydryl acetate (compound IV) was observed by GC-MS, further elucidating the formation of benzyl cations in the reaction. In a standard reaction, the formed carbocation intermediate could be trapped by active molecular H<sub>2</sub>O or hydroxyl species, which are generally contained in the interlayers of hydrotalcite material.



In the above discussed reaction pathways, either through radical intermediate or carbocation intermediate, alcohol should be produced as intermediate product. To further check the formation of alcohol, the alcohol and ketone were monitored during the oxidation under the optimized conditions, and the plot of their concentrations against the reaction time were depicted in Fig. 9. It could be found that the concentration of alcohol was quite low, and it almost could not be detected after 70 min. However, the observation does not exclude the formation of alcohol as the intermediate, because the rate of diphenylmethanol oxidation might be significantly higher than that of diphenylmethane oxidation under the selected conditions. To examine the speculation, a mixture of diphenylmethane and diphenylmethanol were introduced as the reactants under the selected conditions. The result in Fig. S7 obviously indicates that the oxidation rate of diphenylmethanol is evidently higher than that of the oxidation of diphenylmethane, suggesting that diphenylmethanol formed as the intermediate is reasonable in the oxidation of diphenylmethane to benzophenone. In addition, the alcohol might come from two pathways, namely the decomposition of peroxides and the nucleophilic attack of H<sub>2</sub>O or hydroxyl species to the cations.

Reaction conditions: diphenylmethane 1 mmol, Ni\_2Mn-LDH 0.2 g, dodecane 2 mL, 120 °C,  $O_2$  (1 atm).

Finally, plausible reaction pathways are suggested for the Ni<sub>2</sub>Mn-LDH-catalyzed alkylarenes oxidation with molecular oxygen based on the above experimental evidences and discussions (Scheme 1). Initially, a cation radical species is formed by a SET process from an alkylarenes substrate to  $Mn^{3+}$  species in the catalyst. Then, deprotonation of the cation radical species occurs to form an alkyl radical species, which might be accelerated by the Ni<sub>2</sub>Mn-LDH for its known surface basicity [35,36]. The radical species is then trapped by O<sub>2</sub> (path I) to form an alkylperoxy radical. The alkylperoxy radical can abstract a hydrogen from substrate to lead to a hydroperoxide, and then decomposes to ketone and alcohol. The formed alcohol can be further quickly oxidized to ketone under the catalysis of Ni<sub>2</sub>Mn-LDH. Alternatively, a second SET of the radical species in combination with the transformation of  $Mn^{3+}$  to



Scheme 1. The plausible reaction mechanism for the aerobic oxidation of diphenylmethane over Ni<sub>2</sub>Mn-LDH.

 $Mn^{2+}$  may occur to form a carbocation species, followed by nucleophilic trapping by the H<sub>2</sub>O or hydroxyl species in the catalyst (path II).

# 4. Conclusions

In summary, we have found that Ni<sub>2</sub>Mn-LDH can efficiently catalyze the oxidation of alkylarenes using molecular oxygen as the sole oxidant without any additive. The catalytic system can tolerate various substrates with different groups, and has excellent recyclability with the structure unchanged after several reuses. Study of the kinetic aspects indicates that the reaction is a first-order reaction over Ni<sub>2</sub>Mn-LDH, and the activation energy is 85.7 kJ mol<sup>-1</sup>. A value of -10.4 kJ mol<sup>-1</sup>  $K^{-1}$  for the  $\Delta G^{\neq}$  was determined based on Eyring-Polanyi equation, indicating the reaction is exergonic. The catalytically active site for the Ni<sub>2</sub>Mn-LDH catalytic oxidation of diphenylmethane is thought to be Mn<sup>3+</sup>, and a synergistic effect in the Ni<sub>2</sub>Mn-LDH catalyst has been observed. The mechanism study suggests that a SET process first takes place to produce an alkyl radical and carbocation species, and then molecular oxygen is directly introduced to the radical intermediate, or alternatively H<sub>2</sub>O or hydroxyl species are introduced to the cationic intermediate. The corresponding alcohol was thought to be formed as an intermediate product, which could be fast oxidized to ketone under the catalytic system.

Declaration of Competing Interest

The authors declare that there are no conflicts of interest.

#### **Declaration of Competing Interest**

The authors report no declarations of interest.

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# Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:https://doi.org/10.1016/j.mcat.2020.111276.

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