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Environmentally Friendly Room Temperature Synthesis of 1-Tetralone over Layered Double Hydroxide-Hosted Sulphonato-Salen-Nickel(II) Complex

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Abstract

1-Tetralone, a useful synthetic intermediate in the manufacture of pharmaceuticals, agrochemicals and dyes, can be prepared by liquid phase catalytic oxidation of tetralin. Selective oxidation of tetralin to 1-tetralone is still a big challenge with low-temperature processes using environmentally friendly routes even after decades of research. Herein, we demonstrate room-temperature oxidation of tetralin to 1-tetralone over layered double hydroxide-hosted sulphonato-salen-nickel(II) complex, LDH-[Ni-salen]. The layered double hydroxide-hosted sulphonato-salen-nickel(II) compound was characterized by powder X-ray diffraction, Fourier transform infrared spectrometer (FTIR), UV-Visible diffuse reflectance spectra, scanning electron microscopy (SEM) and elemental analysis. The theoretical calculations of free sulphonato-salen-nickel(II) complex using Density Functional Theory/CAM-B3LYP at the 6-311++ G(d,p) level of theory were also used to determine the orientation of the Ni-salen compound within the layered structure. The immobilized compound, LDH-[Ni-salen] was found to be an effective reusable catalyst for the oxidation of tetralin to 1-tetralone using a combination of trimethylacetaldehyde and molecular oxygen (14.5 psi) and at 25˚C. At 45.5% conversion, tetralin was converted to 1-tetralone with 77.2% selectivity at room temperature and atmospheric pressure after 24 h. The catalyst recycles test and hot filtration experiment showed that oxidation proceeded through Ni(II) sites in LDH-[Ni-salen]. The catalysts were reused several times without losing their catalytic activity and selectivity. The present results may provide a convenient strategy for the preparation of 1-tetralone using layered double hydroxide-based heterogeneous catalyst at ambient temperature for industrial application in near future.

Keywords

Sulphonato-Salen-Nickel(II), Layered Double Hydroxide, Tetralin Oxidation, Room Temperature, 1-Tetralone

1. Introduction

Selective tetralin oxidation to 1-tetralone is a useful synthetic intermediate in the manufacture of fine chemicals [1] [2]. The product can also be applied as additive to increase the cetane number of diesel fuels for cleaner combustion [3]. Various heterogeneous catalysts viz., Fe/MgO [4], Mn octahedral molecular sieves [5], Cr-containing molecular sieves (CrAPO-5 and CrAPO-11), Cr-containing hierarchical material (H-CrAPO-5), Cr-exchanged zeolite-Y, CrMCM-41, CrZSM-5 [6]-[16] and Cu(II) immobilized γ-Fe_2O_3@SBA-15 [17] have been studied. Cr-containing materials provided good catalytic activity and selectivity to 1-tetralone, however, metal leaching from the material in the catalytic reaction creates a serious problem [10] [16]. As a consequence, Ahn *et al.* reported that mesoporous chromium terephthalate MOF, MIL-101, showed an excellent heterogeneous catalyst for tetralin oxidation with very high selectivity (86% - 93%) using t-BuOOH or trimethylacetaldehyde-O_2 as an oxidant system at 80˚C [18]. The layered double hydroxide hosted salen-nickel(II) compounds also exhibited good activity (72.3%) and selectivity (72%) for oxidation of tetralin to 1-tetralone using a combination of trimethylacetaldehyde and dioxygen at 70˚C [19]. It has been reported that the above catalytic systems are reusable and do not suffer from active metal ions leaching in the catalytic reaction. However, these catalytic systems also generally required high temperature to achieve high catalytic activity.

Hydrotalcite-like compounds (HTLs) are a class of anionic clays comprising hydroxides of common metals, such as zinc and aluminum, and can be prepared at room temperature and atmospheric pressure from water medium without using organic solvents. Hydrotalcite-based materials are green materials appealing to interest to many research groups owing to their use in various areas in recent years, such as catalyst and catalyst precursors, hosts for drugs controlled delivery, CO_2 capture, contaminant and heavy elements removal [20]-[28].

Recently, Bhattacherjee *et al.* [29] reported the synthesis of a novel chiral sulphonato-salen-mangenese (III) immobilized into an LDH host, which showed higher catalytic conversion and selectivity for the oxidation of R-(+)-limonene and (−)-α-pienene than those of zeolite-entrapped Mn-salen Jacobsen's catalyst or other metal-salen systems. Furthermore, it has been shown that hydrotalcite-based catalysts prevent the active metal leaching in the catalytic reaction and also reusable catalysts without loss of efficiency [29] [30] [31].

Studies on tetralin oxidation at room temperature using non-leaching heterogeneous catalysts are spare. Boltz *et al.* reported on room-temperature tetralin oxidation over polyoxometalate-hosted mononuclear Cu(II) bipyridine/phenantroline complexes [32]. The materials exhibited low tetralin conversion (16%) and selectivity to 1-tetralone (56%) after 136 h. In continuation of our ongoing research program on the development of room temperature catalytic system for fine chemical preparation [33], recently, we reported the room temperature tetralin oxidation using chromium-containing microporous aluinophosphate, CrA-PO-5, using atmospheric pressure dioxygen and trimethylacetaldehyde as an oxidant [34]. The catalyst exhibited high 1-tetralone selectivity (92.2%) and 58.2% tetralin conversion at 25˚C after 24 h. These results incited us to examine the efficacy of LDH-supported-nickel (II)-sulfonato-salen compounds as catalyst under the environmentally friendly and safe strategy for the selective oxidation of tetralin to 1-tetralone at ambient conditions. The present work describes the oxidation of tetralin to 1-tetralone at ambient temperature using in-situ generated acrylperoxy radicals from trimethylacetaldehyde and dioxygen (1 atm) as an oxidant over LDH-[Ni-salen] as an efficient, reusable, and stable catalyst. Using DFT/CAM-B3LYP at the 6-311++ G(d,p) level of theory we have calculated the molecular modeling of Ni-salen compound which helps in understanding the orientation of [Ni-(sulfonato-salen)]$^{2-}$ anion into LDH host.

2. Materials and Methods

2.1. Materials

Salicylaldehyde (98%, Aldrich), aniline (99.5%, Aldrich), 1,2-ethylenediamine (TCI), zinc(II) nitrate tetrahydrate (Aldrich), aluminum(III) nitrate nonahydrate (Aldrich), nickel(II) perchlorate hexahydrate (Aldrich), tetralin (Sigma, 99%) and trimethylacetaldehyde (Aldrich, 96%) were obtained commercially and used without further purification.

2.2. Synthesis of Catalyst

The LDH-supported-nickel (II)-sulfonato-salen (**1**), benzoate immobilized on the LDH (**2**) and nickel (II)-sulfonato-salen (**3**) were prepared as described in our earlier work [19]. In a typical synthesis, benzoate immobilized onto Zn(II)-Al(III) layered double hydroxide compound **2** (1.0 g) was added to an aqueous solution of Ni(II)-(sulfonate-salen) **3** (0.4 g) with constant stirring under N_2 atmosphere at 25˚C for 10 h which gave an orange product. After filtration, the material was washed with water and ethanol and dried at 60˚C for 12 h. Analytical data found (calculated values) for **1**: Zn, 22.05; Al, 4.84; Ni, 3.62; N, 1.74; S, 3.99; for **2**: Zn, 22.16; Al, 4.93; for **3**: C, 34.40 (34.02); H, 2.79 (2.83); N. 4.69 (4.96); S, 11.12 (11.35); Ni, 10.30 (10.39).

2.3. Characterization

Powder X-ray diffraction patterns of the prepared materials in solid state were recorded on a Rigaku Miniflex diffractometer using CuKα (λ = 1.54 Å) at 0.5˚

min^{-1}. FTIR spectra of the samples were measured using KBr disks on an IR Prestige (Shimadzu) spectrometer. Solid-state UV-Vis diffuse reflectance spectra were obtained on a Varian CARY 3E double-beam spectrophotometer using MgO as a reference at ambient temperature. SEM micrographs were taken on a Hitachi S-4200, two-sided carbon tape fixed to an SEM sample stub and the powder was sprinkled on the surface of the carbon tape. Elemental analyses were performed using an Elementar vario Micro cube. Metal contents were measured by atomic absorption spectroscopy using Perkin-Elmer AAS AAnalyst 200, samples for the measurements were dissolved in a mixture of HCl, HNO_3 and hydrogen peroxide (1:2:1). Tetralin conversion and product selectivity were measured using a GC (Clarus 500, Perkin-Elmer) fitted with a high-performance HP-1 capillary column and FID using dodecane as an internal standard.

2.4. Computational Details

The geometries of the $[Ni\text{-}(sulfonato\text{-}salen)]^{2-}$ complex was optimized using DFT/CAM-B3LYP/6-311++g(d,p) level of theory. The effective core potential (ECP) LANL2DZ was used for nickel metal. Gauss View 6.0.16 [35] and Gaussian 16 [36] simulation package were applied for the calculations. Geometry optimization was achieved when the highest force and maximum displacement to threshold values were 0.00045 Hartree/Bohr and 0.0018 Bohr, respectively. Without imaginary frequency confirmed the minimum geometry structures. The individual geometry species of ligand, metal and metal-complexes were optimized. The entire calculations were performed without any geometric constraint.

2.5. Tetralin Oxidation Reaction

Tetralin oxidation reactions were carried out using a combination of trimethylacetaldehyde and dioxygen as the oxidant. In a typical reaction, a mixture of tetralin (2 mmol), trimethylacetaldehyde (4 mmol), acetonitrile (10 cm^3), and catalyst (0.01 g) were placed into a two-necked round-bottomed flask with a reflux condenser. The mixture was stirred at 25˚C while bubbling molecular oxygen at atmospheric pressure. After completion of the reaction, the catalyst was filtered off and the conversion and selectivity were identified by GC analysis.

Catalyst hot filtration experiments were performed by separation of the catalyst from the reaction mixture after 9 h of reaction. The filtrate mixture was then stirred for a further 15 h at room temperature.

3. Results and Discussion

3.1. Characterization of the Catalyst

A sulfonato-salen-nickel(II) compound was intercalated into the Zn(II)-Al(III) layered double hydroxide structure in an aqueous medium reaction between benzoate hosted LDH (LDH-[C_6H_5COO]) and sulfonato-salen-nickel(II) compound through ion exchange of the benzoate ion at 25˚C. The material was characterized by

FTIR, UV-Visible diffuse spectrum, XRD, SEM, and elemental analysis. Elemental measurement showed that the unit formula of LDH-[Ni-(sulfonato-salen)] compound was in good agreement with the formula $[Zn_{1.96}Al_{1.04}(OH)_6][\text{Ni-sulfonato-salen}]_{0.36}[C_6H_5COO]_{0.32}\cdot 6H_2O$.

The FTIR spectra of free sulfonato-salen-nickel(II) and LDH-[Ni-(sulfonato-salen)] compounds exhibited two strong peaks at 1118 and 1037 cm^{-1}, and 1112 and 1033 cm^{-1}, respectively (**Figure 1(a)** and **Figure 1(b)**), due to the antisymmetric and symmetric modes of the SO_3 group [19] [37]. These bands are not present in the spectrum of the LDH-$[C_6H_5COO]$ (**Figure 1(c)**), indicating the sulfonato-salen-nickel(II) complex intercalated into layered double hydroxide host. **Figure 2** shows the UV-Visible diffuse spectrum of free sulfonato-salen-nickel(II) and LDH-[Ni-(sulfonato-salen)] compounds. The sulfonato-salen-nickel(II) compound displays two absorption maxima above 400 nm (**Figure 2(a)**), of which band at 535 nm represents the lowest energy d-d transition of Ni(II) [19]. The VU-Vis spectrum of LDH-[Ni-(sulfonato-salen)] compound (**Figure 2(b)**) showed a similar feature to the free complex, suggesting that the coordination environment of sulfonato-salen-nickel(II) remains the same during the exchange process. **Figure 3(a)** and **Figure 3(b)** present SEM images of LDH-$[C_6H_5COO]$ and LDH-[Ni-(sulfonato-salen)] compounds. Both images showed identical agglomerates with a granular morphology. These results provide support that no morphological change occurs during the partial substitution of intercalated C_6H_5COO ions by the sulfonato-salen-nickel(II) ions.

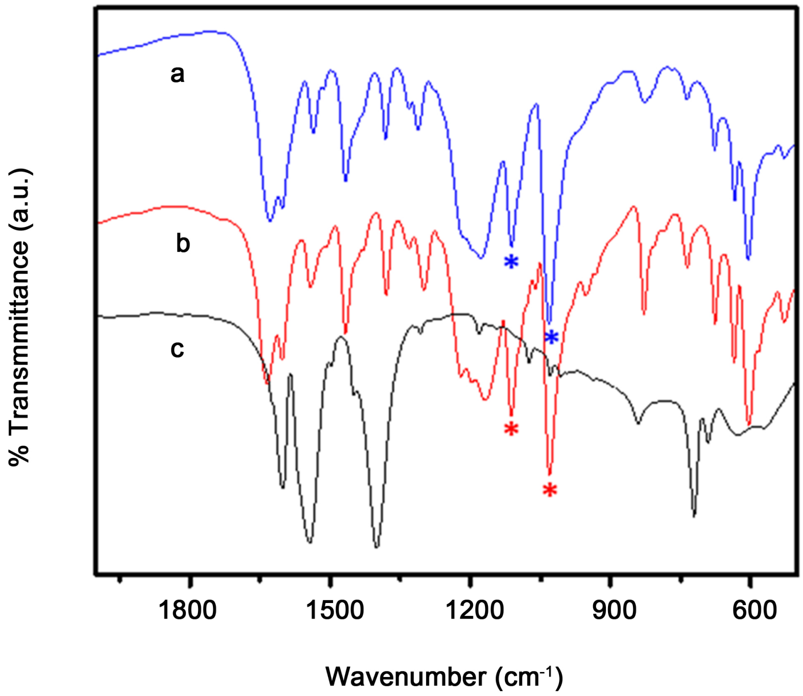

Figure 1. FTIR spectra of (a) free sulfonato-salen-nickel(II), (b) LDH-[Ni-(sulfonato-salen)] and (c) LDH-$[C_6H_5COO]$.

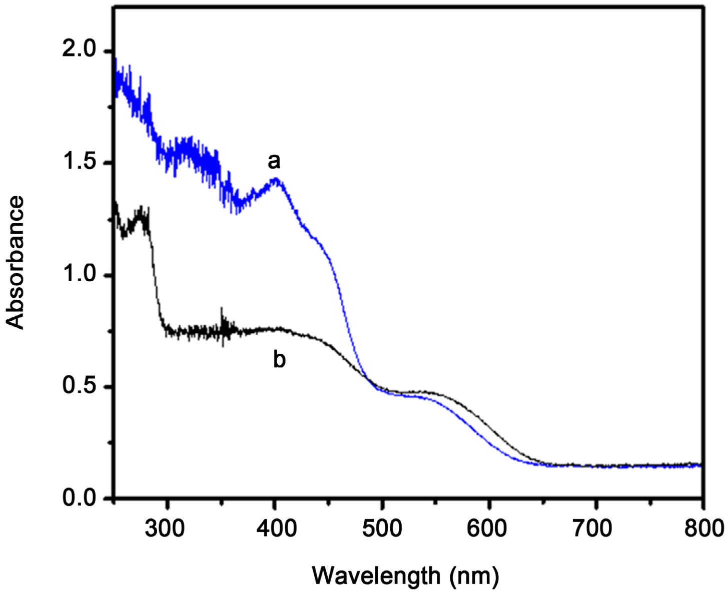

Figure 2. UV-Visible diffuse reflectance spectra of (a) free sulfonato-salen-nickel(II) and (b) LDH-[Ni-(sulfonato-salen)].

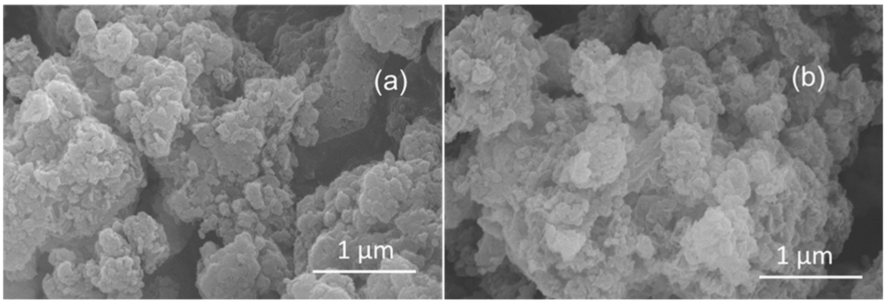

Figure 3. Scanning electron micrographs of (a) LDH-[C_6H_5COO] and (b) LDH-[Ni-(sulfonato-salen)].

3.2. Structure Calculation of [Ni-(Sulfonato-Salen)]$^{2-}$ and LDH-[Ni-(Sulfonato-Salen)]

To assess the orientation of [Ni-(sulfonato-salen)]$^{2-}$ anion into LDH host, LDH-[Ni-(sulfonato-salen)] compound was examined by DFT/CAM-B3LYP/6-311++g(d,p) level of theory and powder X-ray diffraction. The theoretical optimized minimum energy structure of [Ni-(sulfonato-salen)]$^{2-}$ anion is shown in Figure 4 and the geometrical parameters are listed in Table 1. Choudhary *et al.* described the molecular structure of [Ni(II)L] [L = (N,N'-bis(5-hydroxy-salicylidene)ethylenediamine)] using DFT [38]. The value for Ni-N bond length and O-Ni-N bond angle of [Ni(II)L] are 1.87 Å and 94.0˚, respectively. The calculated Ni-N1/Ni-O1 bond lengths and O1-Ni-N1/O2-Ni-N2 bond angles of the present [Ni-(sulfonato-salen)]$^{2-}$ complex displayed identical bond lengths and bond angles values of 1.87 Å and 93.13˚, respectively (Table 1) to the previously reported values of [Ni(II)L] [L = (N,N'-bis(5-hydroxy-salicylidene)ethylenediamine)] [38], confirming that these are structurally similar materials.

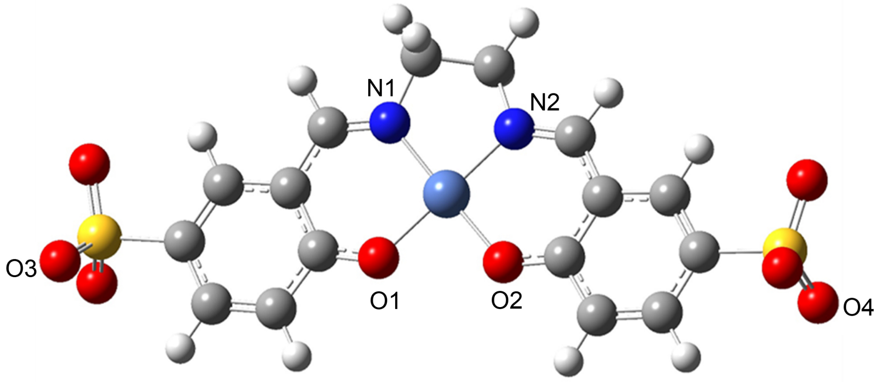

Figure 4. Calculated structure of [Ni-(sulfonato-salen)]$^{2-}$ anion. Red, blue, yellow, grey and white circles represent oxygen, nitrogen, sulfur, carbon and hydrogen, respectively.

Table 1. Selected bond lengths (Å) and angles (˚) for [Ni-(sulfonato-salen)]$^{2-}$ anion.

Labels	Bond lengths (Å)	Labels	Bond angles (˚)
Ni-N1	1.877	O1-Ni-N1	93.132
Ni-N2	1.876	O2-Ni-N2	93.130
Ni-O1	1.860	O1-Ni-O2	88.295
Ni-O2	1.860	N1-Ni-N2	85.592
End to end distance	15.09 - 15.46		

The XRD of LDH-[C_6H_5COO] and LDH-[Ni-(sulfonato-salen)] compounds are shown in **Figure 5**. The basal spacing of LDH-[C_6H_5COO] was increased from 15.4 Å to 19.5 Å for LDH-[Ni-(sulfonato-salen)] during the ion exchange process. The gallery height of sulfonato-salen-nickel(II) compound hosted LDH is 14.8 Å when the thickness of the brucite layers (4.7 Å) are subtracted. The longest distance of salen-nickel(II) compound of general formula [Ni(II)L] [L = (N,N'-bis(5-hydroxy-salicylidene)ethylenediamine)] was ~14.3 Å [38]. The calculated end-to-end distance of sulfonato-salen-nickel(II) compound is ca. 15.09 - 15.46 Å (**Table 1**). The observed gallery height of sulfonato-salen-nickel(II) compound hosted LDH from experimental XRD is in good agreement with the longest dimension of sulfonato-salen-nickel(II) compound, suggesting that the sulfonato-salen-nickel(II) compound was orientated with long axis perpendicularly to the LDH layers. Based on experimental and calculated results, the postulated configuration of the intercalated sulfonato-salen-nickel(II) compound in the interlayer space of the LDH is shown in **Figure 6**.

3.3. Catalysis Studies on the Oxidation of Tetralin

We recently reported that mesoporous chromium terephthalate MOF, MIL-101, and LDH-[Ni-sulfonato-salen] compounds exhibited good conversion and 1-tetralone selectivity in the oxidation of tetralin at 80˚C using *tert*-butyl hydroperoxide (*t*-BuOOH) or in-situ generated acylperoxy radicals from pivalaldehyde

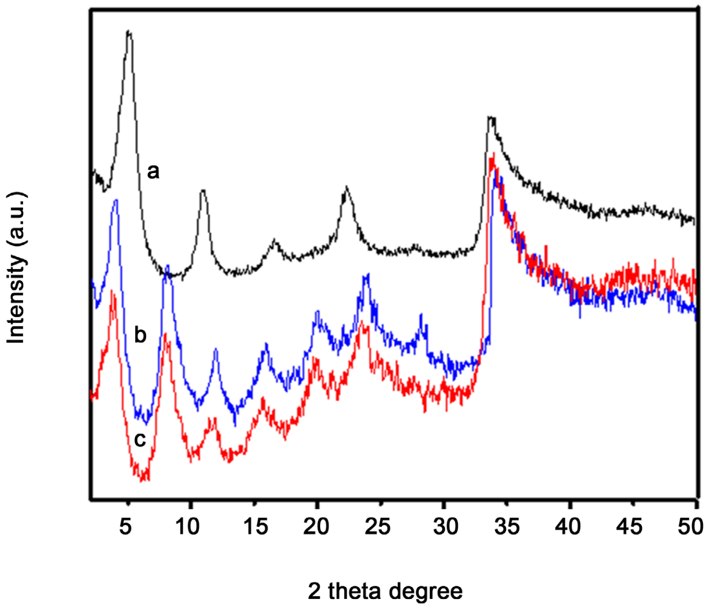

Figure 5. X-Ray powder patterns of (a) LDH-[C_6H_5COO], (b) fresh LDH-[Ni-(sulfonato-salen)] and (c) reused catalyst after fourth run.

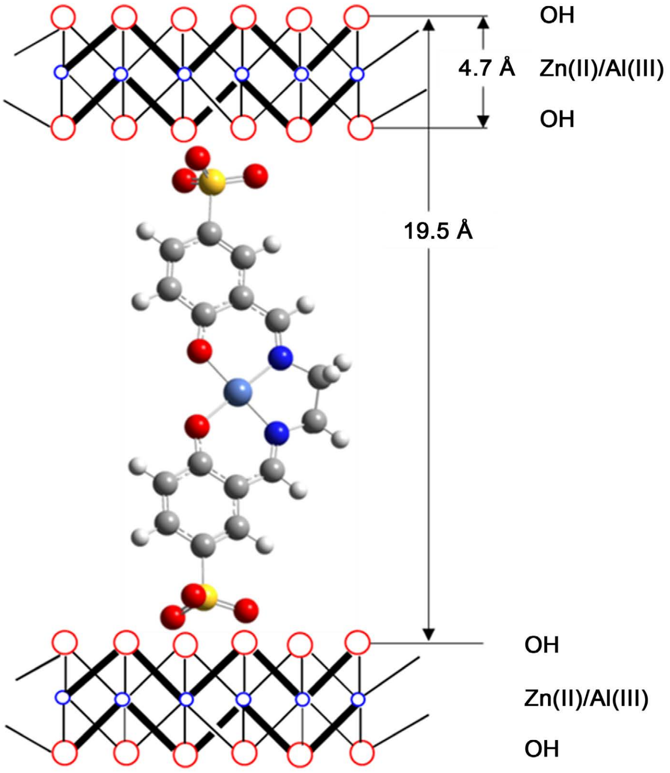

Figure 6. Postulated orientation of sulfonato-salen-nickel(II) anion in the interlayer space of the LDH.

and molecular oxygen [18] [19]. Among these, the later oxidant system showed a more efficient route than the former oxidant system. Based on our previous experimental results, LDH-hosted, LDH-[Ni-salfonato-salen] compounds were tested in the oxidation of tetralin using pivalaldehyde and molecular oxygen at atmospheric pressure in acetonitrile at 25˚C under identical reaction conditions as described previously [18] [19]. The results are summarized in **Table 2**. At 25˚C, tetralin was converted into 1-tetralone with 45.5% conversion and 77.2% selectivity to 1-tetralone after 24 hrs over LDH-[Ni-salfonato-salen] as catalyst (**Table 2**). The reaction profile as a function of reaction time is shown in **Figure 7**. The tetralin conversion increases continuously with increasing reaction time, while the product selectivity remained fairly constant at ca. 77.2% during this period.

Table 2. The temperature, reaction time, catalytic activity and catalyst recycling with different heterogeneous catalysts in tetralin oxidation.

Catalyst	Temp., ˚C (Time, h)	Conv. (%)	Product selectivity (%)[b]				Ref.
			Tlone	Tlol	Nthol	Nlene	
LDH-[Ni-sulfonato-salen][a]	25 (24)	45.5	77.2	22.2	0.4	0.2	Present work
		45.4[c]	77.3	21.7	0.7	0.3	
	70 (8)	72.3	72.2	21.0	-	-	19
CrAPO-5	25 (24)	58.2	92.2	5.1	1.9	0.8	34
Cu-phen/POM	25 (136)	16.0	56.0	-	-	-	32
MIL-101(Cr)	80 (8)	66.0	93.7	1.5	3.4	1.4	18
Cu/γ-Fe_2O_3@SBA-15	90 (6)	64.0	85.0	10.0	-	2.0	17
MnO_x-CoO_y/γ-Al_2O_3	120 (8)	68.0	75.0	16.0	-	-	38

[a] Reaction conditions: 2 mmol tetralin, 4 mmol pivalaldehyde, 10 ml acetonitrile, molecular oxygen (1 atm) and 0.01 g catalyst for 24 h. [b] 1-Tetralone, 1-tetralol, 1-naphthol and naphthalene are denoted as Tlone, Tlol, Nthol and Nlene, respectively. [c] Fourth run.

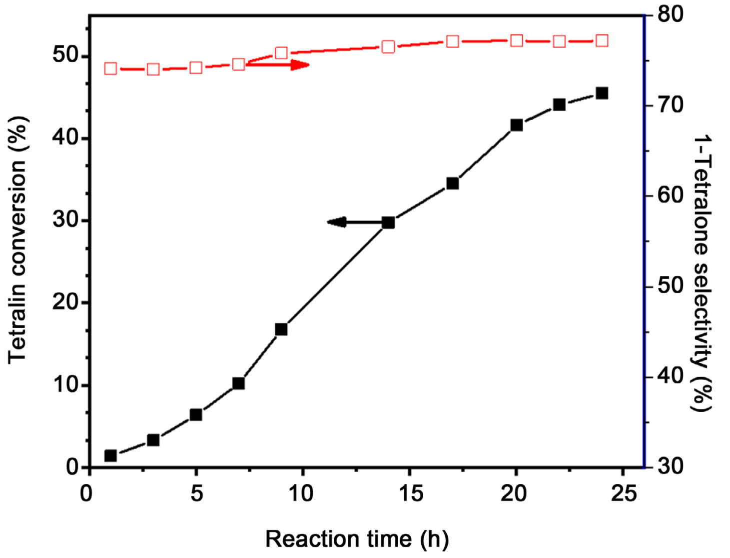

Figure 7. Conversion of tetralin and selectivity to 1-tetralone as a function of reaction time at 25˚C over LDH-[Ni-sulfonato-salen].

It is important to examine the stability of a solid catalyst under given reaction conditions since the observed catalytic reaction can be progressed in a homogeneous phase with leached active metal ions [16] [39]. To examine the heterogeneity of present material in liquid phase tetralin oxidation, a hot filtering technique and catalyst recyclability run over the spent catalyst were performed. As shown in **Figure 8**, in a hot filtering experiment using LDH-[Ni-salen], the catalyst was quickly separated from the reaction mixture after 9 hrs and then the filtrate mixture was stirred for a further 15 hrs at 25˚C. No increase in conversion was observed after the removal of the catalyst, indicating that the reaction proceeded through the framework Ni sites in LDH-[Ni-salen].

The catalyst reusability test of the catalyst was carried out on the tetralin oxidation by consecutive reuse of the catalyst in the same manner as described above. At the end of each run, the catalyst was filtered off, washed with solvent, dried, and reused. The results are summarized in **Table 2**. The catalysts were reused several times without losing their catalytic activity and selectivity. There is no leaching of Ni ions in filtrate solution over the recycled catalyst evidenced by atomic absorption spectroscopy. The XRD pattern of reused LDH-[Ni-salfonato-salen] (**Figure 5(c)**) was identical to that of fresh catalyst (**Figure 5(b)**), indicating that the structure of the catalyst was retained during the catalysis reaction.

Some of the published data for tetralin oxidation using various catalysts are listed in **Table 2**. A slightly higher 1-tetralone selectivity but the lower conversion was found for present LDH-[Ni-sulfonato-salen] catalyst at 25˚C using atmospheric pressure of molecular oxygen and pivalaldehyde when compared with

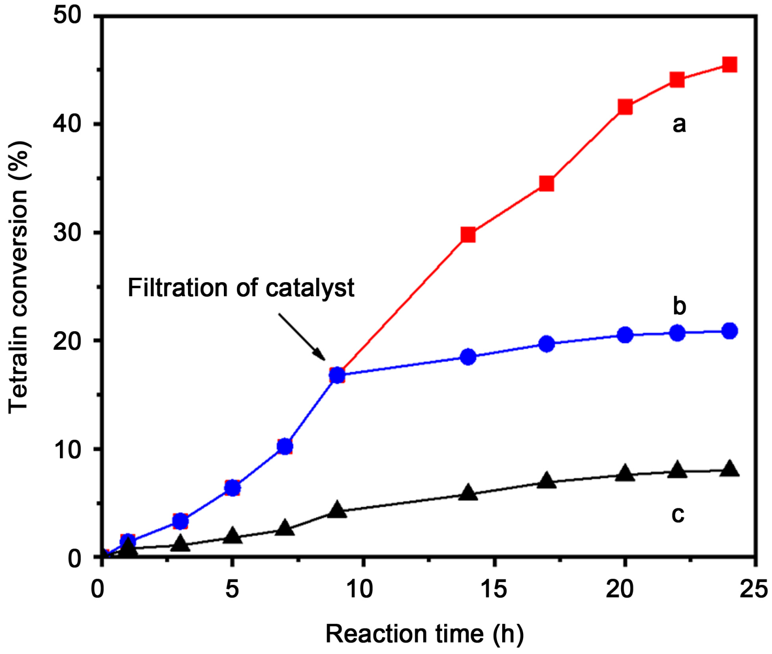

Figure 8. Tetralin oxidation at 25˚C: (a) with LDH-[Ni-sulfonato-salen] catalyst and (b) filtrate (catalyst separated out after 9 hrs reaction) and (c) without catalyst (in the presence of pivalaldehyde and molecular oxygen).

same catalyst using higher temperature (at 70˚C) under same reaction conditions [19]. At ambient temperature, LDH-[Ni-sulfonato-salen] exhibited higher conversion and selectivity than previously reported for Cu(phenantroline)(Cl_2)/POM [32]. Chromium-incorporated microporous aluminophosphate, CrAPO-5 provided higher activity and selectivity to 1-tetralone than the present catalyst LDH-[Ni-sulfonato-salen] at ambient temperature under identical reaction conditions [34]. The present catalyst, LDH-[Ni-sulfonato-salen] afforded lower conversion and product selectivity at ambient temperature than those reported for MIL-101(Cr) [18], Cu/γ-Fe_2O_3@SBA-15 [17] and MnOx-CoOy/γ-Al_2O_3 [40], where the reaction occurred at a higher temperature.

4. Conclusion

In summary, heterogeneous catalysts for the selective oxidation of tetralin to 1-tetralone using LDH-hosted sulfonate-salen-nickel(II) compound at ambient temperature under mild reaction conditions were developed. The experimental gallery height of sulfonato-salen-nickel(II) compound hosted LDH and theoretical geometric parameters suggest that the sulfonate-salen-nickel(II) complex was orientated with a long axis perpendicularly to the LDH layers. The catalyst was found to be highly active and selective for the preparation of 1-tetralone compared with that obtained for well-known chromium-containing molecular sieve CrAPO-5 at ambient temperature using trimethylacetaldehyde and molecular oxygen as an oxidant. This solid catalyst could be recycled several times without losing the initial high activity and product selectivity. The present results may provide a convenient strategy for the preparation of 1-tetralone using heterogeneous catalyst at ambient temperature for industrial application in near future.

Acknowledgements

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Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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