

# Synthesis of Ag/Ni(OH)<sub>2</sub> Catalyst Generated from LDH for the Selective Hydrogenation of Citral

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**Abstract.** The Ag nanoparticles with no need for reduction supported on MgAl-layered double hydroxide (LDH) were prepared. Ag nanoparticles (NPs) were achieved in the LDH support by in situ reduction, meanwhile, metal nickel generated by the reaction mechanisms of hydrogenation of citral. Silver generates highly mobile atomic hydrogen, which reduces nickel by abstracting H from the surface support, and nickel nanoparticles formed after reaction. The action of silver and nickel are conducive to higher selectivity to unsaturated aldehyde in Ag-[Ni(OH)<sub>2</sub>]<sub>x</sub>/LDH. The effects of support and silver were explained by TEM, SEM, XRD and H<sub>2</sub>-TPR.

**Keywords.** in-situ reduction, layered double hydroxide, citral hydrogenation

## 1. Introduction

Citral is 3, 7-dimethyl-2, 6-octadienal, which is a typical  $\alpha$ ,  $\beta$  -unsaturated aldehyde. It is difficult to selectively hydrogenate only one of the functional groups of citral to obtain a single product because it has three hydrogenated double bonds: the isolated C=C bond and the conjugated C=O and C=C bond. Citral and other substances with similar molecular structure have a special lemon flavor, and it is an important raw material for spices and pharmaceutical intermediates, and its hydrogenation products have a wider range of uses [1]. The selectivity of citral is directly affected by the activation ability of the catalyst surface to the carbon-carbon double bond and carbonyl group and the adsorption capacity of the reactant molecule. The difficulty of catalytic hydrogenation lies in that C=C is easier to hydrogenate in thermodynamics than C=O, but it is difficult to prepare a catalyst that can not only select hydrogenated conjugate C=C but also maintain the stability of the product [2]. Therefore, it is of great academic significance and economic value to develop an economical and highly selective catalyst. Layered double hydroxides (LDH) are assembled from the positively charged host laminate and interlayer anions by the interaction of non-covalent bonds [3]. Its chemical composition can be expressed as  $[M_{1-x}^{2+}M_x^{3+}(\text{OH})_2](A^{n-})_{x/n} \cdot m\text{H}_2\text{O}$ , in which  $[\text{Mg}_6\text{Al}_2(\text{OH})_{16}\text{CO}_3] \cdot 4\text{H}_2\text{O}$  as classical structure. It can serve as a good candidate for

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heterogeneous catalysts and supports, which are performed unique properties: tunable basicity, homogeneous [4-6]. At present, many authors reported Compared with other precious metals, Ag has the advantages of low price, abundant reserves, high selectivity and easy reduction, and however, Ag-based catalysts have disadvantages, such as low activity, high loading or complex synthesis. Nickel-based catalysts are widely used in catalytic hydrogenation due to their low price, easy availability and high activity, but their reaction conditions are not mild enough. Consequently, in this work, a supported Ag catalyst is designed meanwhile impregnated with transition metals nickel without reduction, and the in-situ reduction catalyst with activity and special selectivity was obtained by taking advantage of the properties of Ag and metal (Ni) as well as the characteristics of the support itself.

## 2. Experimental

### 2.1. Preparation of Ag-Ni/MgAl-LDH Catalyst

MgAl-LDH were first pre-synthesized by coprecipitation method. A solution containing metal nitrates and an alkaline solution (methol: water=1:1) were simultaneously added in a three-necked round-bottomed. A certain amount of NaOH and Na<sub>2</sub>CO<sub>3</sub> were dissolved together to give a base solution ( $[\text{CO}_3^{2-}] = 2.0[\text{Al}^{3+}]$ ,  $[\text{OH}^-] = 1.8([\text{Mg}^{2+}] + [\text{Al}^{3+}])$ ). Ag nanoparticles were loaded onto MgAl-LDH through impregnation method. First, LDH powder was dispersed in the water solution and under continuous stirring for 1 h at room temperature. Then a known amount of AgNO<sub>3</sub> and Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O, which was adjusted to yield catalysts containing 1.2 wt% Ag and different Ni content and then dried in an air at 100°C. The dry powder was then calcined at 150°C for 3h. Then after filtered and extensive washing with deionized water and ethyl alcohol, the samples were dried at room temperature.

### 2.2. Catalytic Test

The catalytic experiments were performed in a stainless steel autoclave (50 mL), which equipped with electric heating and magnetic stirring functions. The catalyst (100 mg) and the reaction solution (3 mmol citral in 15 ml ethanol) were mixed in the reaction reactor. The air in the reactor was excluded completely by repetitively filling H<sub>2</sub> for five times, and then the pressure of H<sub>2</sub> was kept at 3.0 Mpa. The reaction temperature was heated to 120°C under the stirring rate of 800 rpm, after 120min, the reaction solution were extracted out and analyzed by an Agilent7890 GC.

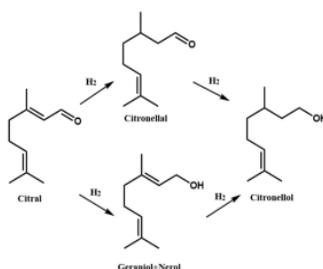
### 2.3. Catalyst Characterization

TEM experiments were performed with JEM-2100(JEOL Co., Japan), X-ray powder diffraction (XRD) analysis were carried by D8-Advance, scanning at a rate of 2°min<sup>-1</sup>, with an angle range of 5°~90°, metal content determined by ICP-OES (Agilent Technologies 5100), H<sub>2</sub>-TPR testing by chemisorption analyzer (Micromeritics AutoChem II 2920).

### 3. Results and Discussion

#### 3.1. Catalytic Performance

Citral is a typical unsaturated aldehyde and its hydrogenation can lead to various products. Figure 1 shows the main reaction pathways involved in the hydrogenation of citral. It is evident that citral contains three unsaturated bonds, of which the C=O is preferentially reduced to give geraniol and nerol (UALC), and the C=C is preferentially reduced to give mainly the selective reduction product citronellal (CAL). Subsequently, further hydrogenation of UALC or citronellal lead to an increase in citronellol yield. Finally, 3,7-dimethyloctanol was produced completely.



**Figure 1.** Hydrogenation route of citral over [Ag-Ni(OH)<sub>2</sub>]/LDH catalyst.

The catalytic performances of Ag-based catalysts are shown in table 1. Remarkably, the [Ag-Ni(OH)<sub>2</sub>]<sub>8,12</sub>/LDH catalyst demonstrates 95% conversion of citral and 90% selectivity of citronellal. However, when the catalyst is only loaded with metal silver or nickel hydroxide, there is no catalytic activity. As a comparison, the supported Ag/Ni(OH)<sub>2</sub> catalyst was synthesized by using the wet impregnation method. This result indicated Ag and Ni(OH)<sub>2</sub> are mainly common work for citral reaction. Because of the heterogeneity of citral hydrogenation products, it is difficult to stay in just one step to obtain high yield of citronellal.

**Table 1.** Hydrogenation performance of Mg<sub>3</sub>Al-LDH supported catalysts for citral.

Catalysts <sup>a</sup>	Conversion	Selectivity (%)			Yield (%)
		CAL	COL	UALC	
Ag/LDH	0	0	0	0	0
Ag[Ni(OH) <sub>2</sub> ] <sub>5,2</sub> /LDH	82	33	35	32	27
Ag[Ni(OH) <sub>2</sub> ] <sub>8,12</sub> /LDH	95	89	7	4	85
Ag[Ni(OH) <sub>2</sub> ] <sub>9,04</sub> /LDH	100	19	76	5	19
[Ni(OH) <sub>2</sub> ]/LDH	0	0	0	0	0
Ag/[Ni(OH) <sub>2</sub> ] <sub>8,12</sub> <sup>b</sup>	54	82	0	18	44

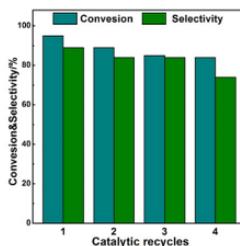
Reaction conditions: P(H<sub>2</sub>) = 3 MPa, t = 2h, T = 120°C

a) Determined by ICP-AES analysis, content of Ag and Ni of entry 1 and entry 5 same as Entry 3.

b) Ni(OH)<sub>2</sub> synthesis like the method in this work .

In this experiment, the stability of the catalyst was tested by recovering the Ag[Ni(OH)<sub>2</sub>]<sub>8,12</sub>/LDH sample via centrifugal washing in ethanol. As can be seen in figure 2, the yield of citronellal decreased from 85 % to 74 % after four cycles of the experiment. To investigate the reason for the decrease in activity, the elemental analysis results by ICP-AES reveals that the loss of Ag in Ag[Ni(OH)<sub>2</sub>]<sub>8,12</sub>/LDH

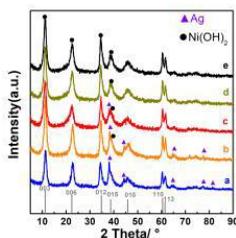
decreased from 1.2 % to 0.8 % after four cycles. The reduced catalytic activity was attributed to lower silver content.



**Figure 2.** Recyclable catalytic of Ag[Ni(OH)<sub>2</sub>]<sub>8.12</sub>/LDH sample for the selective hydrogenation of citral.

### 3.2. The Structure of the Ag[Ni(OH)<sub>2</sub>]<sub>x</sub>/LDH Catalysts

XRD patterns are shown in figure 3. The XRD patterns of the support are in good agreement with the LDH rhombohedral crystals, which corresponding with reflections of planes (003), (006), (012), (015), (018), (110) and (118) [7-8]. For reference, the XRD pattern of LDH support is also given. In the XRD pattern, the peaks appearing around 38.2°, 44.6° can be attributed to the characteristic diffraction peaks of metallic silver. It is obvious that the diffraction peaks of Ag gradually weakened with the increase of Ni content at a certain Ag content. Particularly, the diffraction peaks of Ni(OH)<sub>2</sub> were matching with the hexagonal phase Ni(OH)<sub>2</sub> at 2θ values of 11.2°, 22.2°, and 38.6° (PDF #38-0715) [9].

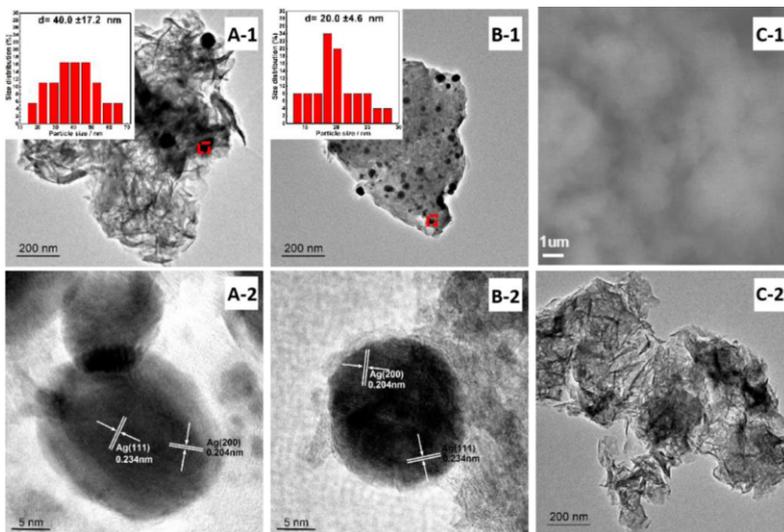


**Figure 3.** XRD patterns of the Ag[Ni(OH)<sub>2</sub>]<sub>x</sub>/LDH catalysts. (a) Ag/LDH (b) Ag[Ni(OH)<sub>2</sub>]<sub>5.2</sub>/LDH, (c) Ag[Ni(OH)<sub>2</sub>]<sub>8.12</sub>/LDH, (d) Ag[Ni(OH)<sub>2</sub>]<sub>9.04</sub>/LDH, (e) Ni(OH)<sub>2</sub>/LDH. The grey straight line in (A) refers to LDH characteristic diffraction peaks.

### 3.3. The Morphology of the Ag[Ni(OH)<sub>2</sub>]<sub>x</sub>/LDH Catalysts

As shown in figure 4, the morphology and microstructure of Ag/LDH and representative Ag-[Ni(OH)<sub>2</sub>]<sub>8.12</sub>/LDH samples can be observed. The observation of HRTEM images shows that the lattice spacing can be observed in all three samples with a good match to 0.204 nm on the Ag(111) crystal plane and 0.234 nm on the Ag(200) crystal plane, proving that only Ag is present as a monomer in our samples. In the Ag/LDH sample, a large number of nanoparticles with a particle size of about 41.08 nm were found to be unevenly distributed on the surface. The overall microstructure of the samples was similar to that of LDH, while it exhibits a typical lamellar structure. After introducing Ni with the silver catalyst, the Ag[Ni(OH)<sub>2</sub>]<sub>8.12</sub>/LDH catalyst sample has smaller silver nanoparticles with an average particle size of 20.21 nm. While for the

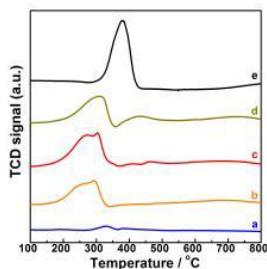
Ni(OH)<sub>2</sub>/LDH sample, as shown in figure 4, several layers of folded structures were exhibited, and no nanoparticles were detected [10].



**Figure 4.** TEM and SEM results of the Ag[Ni(OH)<sub>2</sub>]<sub>x</sub>/LDH samples, TEM images of A(Ag/LDH), B(Ag[Ni(OH)<sub>2</sub>]<sub>8.12</sub>/LDH), C(Ni(OH)<sub>2</sub>)/LDH.

### 3.4. The H<sub>2</sub>-TPR profiles of Ag[Ni(OH)<sub>2</sub>]<sub>x</sub>/LDH Catalysts

The H<sub>2</sub>-TPR curves of Ag/LDH and various [Ag-Ni(OH)<sub>2</sub>]<sub>x</sub>/LDH with different nickel loadings are shown in figure 5. For Ag/LDH(a), no peak was observed basically, which means that Ag in the Ag/LDH sample is all in zero valence state. It consistent with the XRD results of Ag-[Ni(OH)<sub>2</sub>]<sub>5.2</sub>/LDH. However, the H<sub>2</sub>-TPR curve shows that a peak of Ni(OH)<sub>2</sub>/LDH is observed at 300°C~380°C (e). Therefore, the peaks in the curve are mainly attributed to the reduction of Ni(OH)<sub>2</sub> species rather than metallic Ag species. It is obvious that with the decrease in Ag/Ni ratio in Ag-Ni(OH)<sub>2</sub> /LDHs (from b to e), the reduction temperature of Ni decreases significantly, indicating a Ag-promoted reduction of Ni species. It enhances the catalytic activity of the catalyst material, which has also been reported in other similar reduction processes [11].



**Figure 5.** H<sub>2</sub>-TPR profiles of the Ag-[Ni(OH)<sub>2</sub>]<sub>x</sub>/LDH catalysts.

a) Ag/LDH; b) Ag-[Ni(OH)<sub>2</sub>]<sub>5.2</sub>/LDH; c) Ag-[Ni(OH)<sub>2</sub>]<sub>8.12</sub>/LDH; d) Ag-[Ni(OH)<sub>2</sub>]<sub>9.04</sub>/LDH; e) Ni(OH)<sub>2</sub>/LDH.

#### 4. Conclusion

In summary, we have developed in situ generated Ag (0) and Ni (0) as active catalyst for the selective hydrogenation of citral to citronellal. The results show that the Ag/Ni(OH)<sub>2</sub> material generated by LDH can obtain highly selective liquid phase hydrogenation catalyst of citral under mild conditions. Besides, the characterization results demonstrated that the addition of Ag helped to improve the catalytic activity by initiating hydrogen in the catalyst surface. The presence of silver also increased the reducibility of Ni(OH)<sub>2</sub> species. Only in the presence of Ag, partial reduction of Ni<sup>2+</sup> into Ni<sup>0+</sup> is observed. The proportion of Ag and nickel on the surface of the [Mg<sub>6</sub>Al<sub>2</sub>(OH)<sub>16</sub>CO<sub>3</sub>]·4H<sub>2</sub>O is controlled, a new material with good activity and special selectivity was prepared.

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