# Catalytic Hydrogenation of Benzaldehyde on Ni/Al₂O₃ or Co-Ni/Al₂O₃ Catalyst

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The Al₂O₃-supported Ni catalyst exhibits good activity for the catalytic hydrogenation of benzaldehyde. The activity and stability of the Ni/Al₂O₃ catalyst are affected by the amount of reductant, the conversion rate of Ni/Al₂O₃ and Co-Ni/Al₂O₃ catalyst achieving a maximum while the reductant is sufficient. Meanwhile, the reaction temperature and time show significant influence to the catalytic hydrogenation of benzaldehyde. The effect in catalytic hydrogenation of benzaldehyde on Co-Ni/Al₂O₃ catalyst is highest, it should be due to Co and Ni form to alloys and have the functional of the dual function catalyst, which is conducive to benzaldehyde was activated and forming benzyl alcohol. The conversion rate of benzaldehyde is close to 10.57 % while the reaction temperature reaches 80 ℃ and time is about 2 h.

**Key Words: Ni/Al₂O₃, Co-Ni/Al₂O₃, Hydrogenation, Benzaldehyde.**

## INTRODUCTION

Nickel catalytic hydrogenation system is widely used in laboratory and chemical industry, such as benzene and nitrobenzene were hydrogenated to cyclohexane and aniline, phenylamine and the hydrogenation reaction of aldehydes ketones and olefine aldehydes[1]. However, the surface area of unsupported Ni catalysts is rather low, thus dispersion of Ni on a high-surface support will be needed. The alteration of catalytic activity by the support may arise as a result of changes in dispersion and morphology of the component and possible metal-support interactions. There has been focused on developing the new supports for the preparation of Ni catalyst in recent years. It can be known from the literature that some supports, such as Al₂O₃[2], SiO₂[3], active carbon[4] and TiO₂[5] have been reported as supports of the Ni catalysts. Whereas macroporous Al₂O₃ is widely used as a support, it is well-known that it has strong adsorption, good chemical stability and thermal stability, moreover, which is a porous and high dispersive material, and its activity is not obvious in the chemical reaction. While the macroporous Al₂O₃ is used as a support of Ni catalysts, (1) the interference is small in their combination reaction, (2) Al₂O₃ can improve the dispersion of nickel catalyst, lead to more effective catalytic performance, (3) and also greatly reduce the dosage of the precious metal, thereby, reducing the economic cost of catalyst[6].

In this paper, Ni/Al₂O₃ catalyst was prepared by chemical reduction method, which using the NaBH₄ as reductant and used benzaldehyde as a model compound to explore tentatively the effect in catalytic hydrogenation of benzaldehyde under different time and temperature. Furthermore, Co was added as assistant to prepare Co-Ni/Al₂O₃ catalyst and study the hydrogenation reaction of benzaldehyde.

## EXPERIMENTAL

Al(NO₃)₃·6H₂O and Na₃Co(NO₃)₆ were purchased from Tianjin Chemical Reagent Co. Ltd. Ni(NO₃)₂·9H₂O were purchased from chongqing beibei Chemical Reagent Co. Ltd. All other chemicals were of analytical reagent grade.

Timing magnetic mixing equipment (90-2 type, jintan city in jiangsu province the earth automation instrument factory); Horse fee furnace (Shanghai songxian Ming experiment instrument factory); Gas chromatography (GC-2010, the Japanese island tianjin); Digital electronic balance (AR1140, Shanghai mettler Toledo instrument Shanghai Co. Ltd.).

**Preparation principle of Ni:** Preparation of Ni is based on the response equation as following[7]:

$$10Ni^{2+} + 8BH_4^+ + 17OH^- + 3H_2O \longrightarrow (3Ni_3B + Ni) + 5B(OH)^{2+} \qquad (1)$$
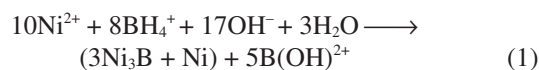
From reaction eqn. (1), it found that the reaction is processing in alkaline conditions, the best pH is 12[8]. The catalytic

principle benzaldehyde and isopropyl alcohol can be written as the following schematic reaction[9]:
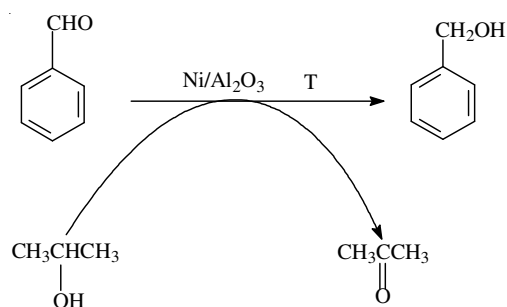


**Preparation of Al$_2$O$_3$:** Al$_2$O$_3$ were prepared by sol-gel method[10], 0.35 mol L$^{-1}$ Al(NO$_3$)$_3$.6H$_2$O and 0.91 mol L$^{-1}$ urea were mixed in 1:3 ratio, filtered the insoluble impurity and moved to the beaker (1000 mL). Then, the water was evaporated and the remaining solid product was dried at 150 ºC for 3 h, followed by calcinations in air at 400 ºC for 5 h, then cooled naturally and triturated.

**Preparation of Ni/Al$_2$O$_3$:** Ni/Al$_2$O$_3$ were prepared by dipping precipitation, in the first step, with Ni(NO$_3$)$_2$·9H$_2$O as raw materials and with $n_{Ni}/n_{Al} = 0.5$ for blending, adding ammonia solution to obtained the nickel-ammonia complex. In the second step, Al$_2$O$_3$ powder and nickel-ammonia complex mixed uniformly and sodium dodecyl sulfate was added as surfactant, 0.2 mol/L of NaOH solution was used to regulate the pH equal to 12; Followed by the addition of 0.2 mol/L NaBH$_4$ solution were slowly dropped into the mixture while stirring and reacted for 0.5 h. It was centrifuged and then washed with water and anhydrous alcohol three times, respectively. Subsequently the catalyst was dried at 150 ºC for 3 h and calcined at 400 ºC for 5 h, then cooled naturally and triturated.

**Ni-Co/Al$_2$O$_3$ preparation:** Firstly, weighed accurately 1.454 g Ni(NO$_3$)$_2$.9H$_2$O in beaker (100 mL) and added to 0.1003 g Al$_2$O$_3$ powder, their stock solution were prepared with ammonia; Secondly, 1.016 g Na$_3$Co(NO$_3$)$_6$ was dissolved in deionized water, mixed two solution uniformly, then sodium dodecyl sulfate was added as surfactant and 0.2 mol/L NaOH solution was used to regulate the pH near to 12. Finally, 0.2 mol/L NaBH$_4$ solution was slowly dropped into the mixture while stirring and reacted for 0.5 h. The collection step of Ni-Co/Al$_2$O$_3$ is consistent with the above.

**Catalytic performance study (A typical hydrogenation experiment[11]):** Weighed 0.010-0.020 g the prepared Ni/Al$_2$O$_3$ in a dry round bottom flask, 20 mL isopropyl alcohol and 5 mL distilled benzaldehyde were slowly dropped into flask with the graduated cylinder and pipette. The final solutions were stirred for 2 h at 40 ºC. The filtrates were collected by filtering and were taken on gas chromatography, using the normalization method in quantitative methods to calculate.

## RESULTS AND DISCUSSION

**Al$_2$O$_3$ test:** The beakers labeled A and B which contained 0.0105 g Al$_2$O$_3$ and 0.0102 g Al(OH)$_3$ and add to appropriate amount of HCl solution (pH = 3), then the final solutions were oscillated slightly, we can found that Al(OH)$_3$ was dissolved. But the Al$_2$O$_3$ powder were prepared by urea and Al(NO$_3$)$_3$.6H$_2$O

and calcinated, which was sink to the bottom of the beaker and didn't dissolve in HCl solution (pH = 3), indicating it was Al$_2$O$_3$ powder.

**Catalytic hydrogenation of benzaldehyde on Al$_2$O$_3$:** Because of the catalyst were composed of two components, namely Ni and Al$_2$O$_3$, the support whether can catalyze benzaldehyde hydrogenated must be considered. So the property in catalytic hydrogenation of benzaldehyde on pure Al$_2$O$_3$ was explored in Table-1.

| TABLE-1 |||
| :--: | :--: | :--: |
| CATALYTIC RATE OF BENZALDEHYDE ON Al$_2$O$_3$ |||
| Temp. (ºC) | Conversion rate of benzaldehyde (M %) | Selectivity of benzyl alcohol |
| 97 | 0 | - |
| 80 | 0 | - |
| 60 | 0 | - |
| 40 | 0 | - |
| Room temperature | 0 | - |
| Reaction conditions: fixed time, changing the reaction temperature, benzaldehyde and isopropyl alcohol were mixed in 1:20(volume ratio) |||

It can be seen that the conversion rate in catalytic hydrogenation of benzaldehyde on Al$_2$O$_3$ is zero, the selectivity of benzyl alcohol is zero (Table-1), indicating that the Al$_2$O$_3$ for hydrogenation of benzaldehyde.

**Catalytic hydrogenation of benzaldehyde on Ni/Al$_2$O$_3$ catalyst:** The amount of the reductant is a key factor to affect the catalyst's performance, changing the amount of reductant, the conversion rate of Ni/Al$_2$O$_3$ catalyst to catalyze benzaldehyde is different. To study the influence of the amount of reductant on the conversion of benzaldehyde, experiments using the different amount of reductant to prepared Ni/Al$_2$O$_3$ catalyst and explored the catalysis efficiency of benzaldehyde.

| TABLE-2 |||
| :--: | :--: | :--: |
| PROPERTIES IN CATALYTIC HYDROGENATION OF BENZALDEHYDE ON Ni/Al$_2$O$_3$ |||
| Temp. (ºC) | Conversion rate of benzaldehyde (M %) | Selectivity of benzyl alcohol |
| 97 | 1.74 | 100 |
| 80 | 1.23 | 100 |
| 60 | 1.15 | 100 |
| 40 | 0.30 | 100 |
| Room temperature | 1.19 | 100 |
| Reaction conditions: fixed time, changing the reaction temperature and benzaldehyde and isopropyl alcohol were mixed in 1:20 (volume ratio). Note: Ni/Al$_2$O$_3$ catalysts were prepared under the amount of NaBH$_4$ and Ni$^{2+}$ accord with chemical measurement relations system |||

As shown in Table-2, the amount of reducing agent is enough to reduce Ni$^{2+}$ to Ni, the catalyst have good catalytic and selectivity to benzaldehyde, indicating that the elemental Ni aggregated successfully on Al$_2$O$_3$. Furthermore, the reaction time is 2 h, with the temperature increasing, the conversion rate from 1.19 % (room temperature) change to 1.74 % (97 ºC). However, the catalyst (conversion rate) have occurred a trough at 60 ºC, it could be caused by Ni adsorbed on Al$_2$O$_3$ not uneven or the catalyst form to a stable intermediate in the catalytic reaction process. Because of the stability constant of the intermediate is high, causing it not easy to adsorb under the setted conditions, thus affecting the conversion rate.

The Ni/Al$_2$O$_3$ catalyst was obtained under reductant is not enough, its catalytic effect was explored in Table-3.

TABLE-3
PROPERTIES IN CATALYTIC HYDROGENATION
OF BENZALDEHYDE ON Ni/Al$_2$O$_3$

| Temp. (ºC) | Conversion rate of benzaldehyde (M %) | Selectivity of benzyl alcohol |
|---|---|---|
| 97 | 1.51 | 100 |
| 80 | 5.00 | 100 |
| 60 | 5.00 | 100 |
| 40 | 2.10 | 100 |
| Room temperature | 1.30 | 100 |

Reaction conditions: fixed time, changing the reaction temperature and benzaldehyde and isopropyl alcohol were mixed in 1:20 (volume ratio). Note: The Ni/Al$_2$O$_3$ catalyst was obtained under reductant not enough

In the catalyst preparation process, the amount of reductant not enough to reduce Ni$^{2+}$ to Ni, after calcinated, the nickel oxide will exist in catalyst and their catalytic effect were shown in Table-3. It is obvious that the conversion rate of benzaldehyde increases rapidly in the range of 60 ºC-80 ºC and were up to 5.00 %. It should be the internal structure of the catalyst have changed with the temperature increasing (for example, the NiO and Al$_2$O$_3$ reunion will wrap up the catalytic activity of Ni in the calcining process, or other reasons).

If the Ni/Al$_2$O$_3$ catalyst was obtained under reductant is excess, its catalytic effect was explored in the Table-4.

TABLE-4
PROPERTIES IN CATALYTIC HYDROGENATION OF
BENZALDEHYDE ON Ni/Al$_2$O$_3$

| Temp. (ºC) | Conversion rate of benzaldehyde (M %) | Selectivity of benzyl alcohol |
|---|---|---|
| 97 | $5.5 \times 10^{-4}$ | 100 |
| 80 | 6.50 | 100 |
| 60 | $6.7 \times 10^{-4}$ | 100 |
| 40 | $6.5 \times 10^{-4}$ | 100 |
| Room temperature | $5.6 \times 10^{-6}$ | 100 |

Reaction conditions: fixed time, changing the reaction temperature and benzaldehyde and isopropyl alcohol were mixed in 1:20(volume ratio). Note: the Ni/Al$_2$O$_3$ catalyst was obtained under reductant is sufficient

The amount of reductant is excess, Ni$^{2+}$ will be reduced fully, the catalytic effect of the Ni/Al$_2$O$_3$ appears great diversity at difference temperature, a largest conversion rate is 6.50 % at 70 ºC.

Because of the Ni/Al$_2$O$_3$ catalyst is not ideal, Co was added to prepare Co-Ni/Al$_2$O$_3$ catalyst and while the amount of reductant is sufficient, the catalytic results were shown in Table-5.

With the temperature increasing (from 40 ºC to 80 ºC), it is observed that the conversion rate in catalytic hydrogenation of benzaldehyde on Co-Ni/Al$_2$O$_3$ increased significantly, which is up to 10.57 % at 80 ºC. Obviously, cobalt can effectively improve the catalytic activity of the Co-Ni/Al$_2$O$_3$. It should be due to Co and Ni form to alloys and provide some electrons to Ni, so that the aggregation of Ni electronic degree increasing, thus the interaction or adsorption among the reactants were enhanced greatly, which is conducive to benzaldehyde was activated.

TABLE-5
PROPERTIES IN CATALYTIC HYDROGENATION
OF BENZALDEHYDE ON Co-Ni/Al$_2$O$_3$

| Temp. (ºC) | Conversion rate of benzaldehyde (M %) | Selectivity of benzyl alcohol |
|---|---|---|
| 97 | $3.2 \times 10^{-6}$ | 100 |
| 80 | 10.57 | 100 |
| 60 | 3.20 | 100 |
| 40 | 8.02 | 100 |
| Room temperature | - | 100 |

Reaction conditions: fixed time, changing the reaction temperature and benzaldehyde and isopropyl alcohol were mixed in 1:20 (volume ratio). Note: the Co-Ni/Al$_2$O$_3$ catalyst was obtained under reductant is sufficient

**Effect of reaction time on hydrogenation rate:** The reaction time plays an important role in catalytic hydrogenation. To study influence of the reaction time on the conversion rate of benzaldehyde on the Ni/Al$_2$O$_3$ catalyst was shown in Table-6.

As shown in Table-6, the reaction temperature is 70 ºC, it is obvious that the conversion of benzaldehyde is highest at the reaction time is 1h, it is up to 19.23%. But with the reaction time increasing, the conversion rate did not change significantly. It should be due to the reaction system formed the dynamic equilibrium. The dynamic equilibrium of catalytic hydrogenation of benzaldehyde can be written as the following:



TABLE-6
PROPERTIES IN CATALYTIC HYDROGENATION
OF BENZALDEHYDE ON Ni/Al$_2$O$_3$
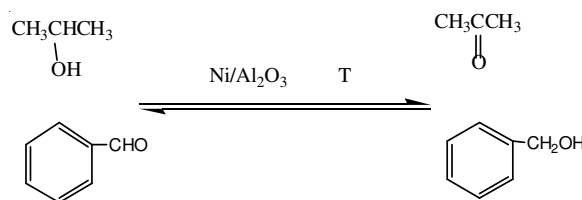
| Time (h) | Conversion rate of benzaldehyde (M %) | Selectivity of benzyl alcohol |
|---|---|---|
| 1 | 19.23 | 100 |
| 2 | 6.50 | 100 |
| 3 | 5.00 | 100 |
| 4 | 5.00 | 100 |
| 5 | 5.00 | 100 |
| 6 | 5.00 | 100 |
| 7 | 5.00 | 100 |
| 8 | 4.80 | 100 |
| 9 | 5.10 | 100 |
| 10 | 5.00 | 100 |

Reaction conditions: the reaction temperature is 70 ºC, benzaldehyde and isopropyl alcohol were mixed in 1:20(volume ratio). Note: the Co-Ni/Al$_2$O$_3$ catalyst was obtained under reductant is excess and the catalytic benzaldehyde hydrogenated under reflux temperature at 70 ºC

As shown in Table-7, while the reaction temperature was set out to 80 ºC, it is obvious that the conversion of benzaldehyde is highest at 2 h, the conversion rate is up to 10.57 %, it should be due to Co and Ni form to alloys and have the functional of the dual function catalyst, which is conducive to benzaldehyde was activated and forming benzyl alcohol. But with the reaction time increasing, the conversion rate did not change significantly.

TABLE-7
EFFECT IN CATALYTIC HYDROGENATION OF
BENZALDEHYDE ON Co-Ni/Al$_2$O$_3$

| Time (h) | Conversion rate of benzaldehyde (M %) | Selectivity of benzyl alcohol |
|---|---|---|
| 1 | $1.4 \times 10^{-3}$ | 100 |
| 2 | 10.57 | 100 |
| 3 | 5.00 | 100 |
| 4 | $7.00 \times 10^{-5}$ | 100 |
| 5 | $1.1 \times 10^{-5}$ | 100 |
| 6 | 5.00 | 100 |
| 7 | 5.00 | 100 |
| 8 | 5.00 | 100 |
| 9 | 5.00 | 100 |
| 10 | 5.00 | 100 |

Reaction conditions: the reaction temperature is 80 ºC and benzaldehyde and isopropyl alcohol were mixed in 1:20 (volume ratio). Note: the Co-Ni/Al$_2$O$_3$ catalyst was obtained under reductant is excess and the catalytic benzaldehyde hydrogenated under reflux temperature at 80 ºC

**Conclusion**

Al$_2$O$_3$ support has the advantages of high activity, good selectivity and strong anti-poisoning. Most of all, it can cause a strong interaction with metal, which induces unique catalyst activity and chemisorption properties compared to other supports. In this paper, Ni/Al$_2$O$_3$ catalyst was prepared by chemical reduction method, the results show that the optimum catalytic temperature is between 60 ºC and 80 ºC, the catalytic time is 1 h. While the reductant is sufficient, the conversion rate of Ni/Al$_2$O$_3$ catalyst is up to 6.50 % at 70 ºC. Furthermore, the effect in catalytic hydrogenation of benzaldehyde on Co-Ni/Al$_2$O$_3$ catalyst is highest, it should be due to Co and Ni form to alloys and have the functional of the dual function catalyst, which is conducive to benzaldehyde was activated and forming benzyl alcohol. The conversion of benzaldehyde is close to 10.57 % while the reaction temperature reaches 80 ºC and time is about 2 h.

**REFERENCES**

1. W.W. Lu and X.l. Xu, *Mol. Catal.*, **20**, 67 (2006).
2. S.J. Sawhill, K.A. Layman, D.R. Van Wyk, M.H. Engelhard, C. Wang and M.E. Bussell, *J. Catal.*, **231**, 300 (2005).
3. F. Sun, W. Wu, Z. Wu, J. Guo, Z. Wei, Y. Yang, Z. Jiang, F. Tian and C. Li, *J. Catal.,* **228**, 298 (2004).
4. Y. Shu and S.T. Oyama, *Carbon*, **43**, 1517 (2005).
5. D.Y. Li, X.Z. Yu, C.L. Cheng, N.P. Xu and Y.R. Wang, *J. Chem. Eng. Chin. Univ.*, **20**, 826 (2006).
6. J. Hong, W. Chu, M. Chen, X. Wang and T. Zhang, *Catal. Commun.*, **8**, 593 (2007).
7. Central China Normal University, Nanjing Normal University, Inorganic Chemistry, p. 582 (2003).
8. H.Y. Chen, N.T. Jiao, J. Xin and W.-B. Su, *J. Funct. Mater. Devices*, **11**, 495 (2005).
9. R.-A. Shelden, I. Arends and U. Hanefeld, *Green Chem. Catal.*, **12**, 91 (2007).
10. J. Huo, X.Q. Liu and Y. Li, *Powder Metal. Ind.*, **16**, 45 (2006).
11. T. Chen, R.G. Wang, G.M. Zhang, *et al.*, *Mol. Catal.*, **14**, 51 (2000).