Journal of Applied Chemical Research, 10, 3, 111-118 (2016)

www.jacr.kiau.ac.ir

New and Simple Strategy for Dechlorination of Nitrochlorobenzene over Ni/La-Al_2O_3 Nanocatalyst

Ebrahim Babaei[1*], **Nader Rostameizadeh**[2]

[1]*Department of Chemistry, Qaemshar Branch, Islamic Azad University, Qaemshar, Iran*

[2]*Department of Chemistry, Dezfoul Branch, Islamic Azad University, Dezfoul,Iran*

(Received 20 Mar. 2016; Final version received 16 May 2016)

Abstract

In this study simple catalytic test experiment was performed in a flask of rotary evaporator for dechlorination of nitrochlorobenzene (NCB) over two samples of Ni/LaAl_2O_3 nanocatalysts (C1 and C2). In the reaction, Ni acts as a catalyst to collect hydrogen gas in aqueous solution and dissociate it to produce active hydrogen atoms for replacing the chlorine. The catalysts were characterized by scanning electron microscope (SEM), X-ray fluorescence (XRF), X-ray diffraction (XRD), BET specific surface area, and particle size analysis (PSA) techniques. The Ni/La-Al_2O_3 catalyst prepared by aluminium nitrate exhibits greater specific surface area and higher dechlorination efficiency compared to sample prepared through aluminium triisopropoxide precursor.

Keywords: *Nitrochlorobenzene, Dechlorination, Ni/La-Al_2O_3 nanocatalyst.*

Introduction

Nickel based catalysts are known for the hydrogenation, CO_2 hydrogenation, reverse water gas shift (RWGS) and biomass gasification processes [1-3]. The key focus of this paper is the nickel based catalyst used in dechlorination process. Nitroaromatic (NAC) compounds are of interest to environmental scientists because of their danger and distribution in the environment. NACs are widely used in the manufacture of herbicides, insecticides, chemical feedstock, dyes and explosives. The extensive use of these compounds has resulted in the intentional and accidental introduction of NACs into the environment. NACs are readily absorbed by contact with the skin and by inhalation of vapors. It affects the central nervous system

---

****Corresponding author:*** *Dr. Ebrahim Babaei, Department of Chemistry, Qaemshar Branch, Islamic Azad University, Qaemshar, Iran. E-mail:e.babaei@yahoo.com.*

and produces fatigue, headache, vertigo, vomiting, general weakness, unconsciousness, and coma, so it is listed as a priority pollutant [4]. Concern about the NACs as environmental contaminants has led to extensive and varied approaches to the remediation of these materials.

The most widely studies have been reported for dechlorination of chlorinated hydrocarbons (CHC) including photocatalytic degradation, steam reforming [5], hydrodechlorination [6,7], and catalytic oxidation [8–12]. Transition metal oxide catalysts including oxides of V, Cr, Mn, Fe, Co, Ni, and Cu have shown significant reactivity toward CHC and higher resistance to chlorination and poisoning by Cl2 and HCl[13]. In recent years, numerous bimetallic catalysts have been used for the degradation of chlorinated organic compound. In bimetallic particles, (Pd, Pt, Ni or Ag) acts to produce active hydrogen atoms to be the real reductant [14-18]. The aims of this work are summarized as follows: I) Ni/La-Al_2O_3 as a new catalyst was demonstrated for nitrochlorobenzene dechlorination process, II) Introducing a simple method to evaluate the catalyst for the dechlorination of nitrochlorobenzene.

Experimental

Materials

Aluminium triisopropoxide (Al $(C_3H_7O)_3$), Aluminium nitrate nonahydrate ($Al(NO_3)_3.9H_2O$), Nickel nitrate hexahydrate ($Ni(NO_3)_2.6H_2O$) and Lanthanum nitrate hexahydrate ($La(NO_3)_3.6H_2O$) were purchased from the Merck company. Ammonia 28% (NH_3) and NCB (99%) were provided from the Aldrich Company.

Preparation of catalysts

According to our previous work two samples of catalyst were synthesized [19].

Preparation of supports

A:

30 g aluminium triisopropoxide with a rate of 2 g/min was added into bottom-round flask containing 100 mL aqueous solution of lanthanum nitrate (5 g), at 75°C. The reaction mixture while continuously stirred was refluxed for half an hour. The resulting suspension was kept at 90ºC for 2 h to extract the alcohol resulted from hydrolysis. The obtained sol was washed with distilled water several times and then used for preparation of the first catalyst (C1).

B:

A solution including 55 g aluminium nitrate along with 5 g lanthanum nitrate in 100 ml distilled water was prepared (pH 4). The ammonia was dropwise added to the solution while continuously stirring to reach pH to 10. After 2 h, the resulting sol was filtered and washed with distilled water and then used to prepare the second catalyst (C2).

Preparation of C1 and C2

After gelation of A and B support precursors for 2h, two same solution including 3 g nickel nitrate salt in 20 mL distilled water were added to gels and the resulting mixtures were aged for 12 h, washed with deionized water, then dried at 120°C and finally calcined at 650°C in air for 6 h with heat rate of 5°C/min, to produce porous catalysts (C1and C2).

Batch experimental procedure

Batch experiments were performed in a flask of rotary evaporator. Mixture of water and nitrochlorobenzene (1:4, V/V) was added into the flask, which was contained 3 g catalyst, each time one of the catalysts C1 and C2. The total volume of the solution was 100 ml. The reactions were carried out at 185 °C by oil bath, without vacuum with rotating at a rate of 200 rpm. Produced aniline volumes were separately measured for C1 and C2 catalysts every half hour and it was calculated volume ratio of aniline to nitrochlorobenzene as reaction efficiency at 3 h. Produced aniline was characterized by IR spectroscopy. Performances of the catalysts were determined by using following formula:

$$\text{Dechlorination efficiency (\%)} = (V_{aniline} / V_{NCB}) \times 100$$

Catalyst characterization

In this work, the calcined catalysts were characterized for powder X-ray diffraction (XRD) analysis in order to identify the component phases by PW1800 Philips system with copper cathode (kα), the BET surfacearea, pore size and pore volume by Quantachrome instrument (model Nova 2000), powder X-ray fluorescence analysis to determine the percentage combination of available phases by PW1480 Philips system, determination of catalyst surface morphology using scanning electron microscope (SEM) by S-360 system and determination of size ranges of particles using particle size analyzer (PSA) by Horiba LB550 system.

Results and discussion

Powder X-ray diffraction (XRD)

In XRD patterns related to the catalysts powders of C1 calcined at 650ºC (figure 1) and C2 calcined at 650 ºC (figure 2) and 850ºC (figure 3), the broad diffraction peaks at 2θ = 31.9, 37.6, 46 and 67º are attributed to γ-Al_2O_3 amorphous phase [20]. The broad peaks of amorphous gamma alumina have been covered lanthanum and nickel oxides phases. To verify this topic, one of the samples was calcined at 850ºC and studied again by XRD. The obtained pattern shows that increase in the temperature causes to progress in phase conversion and growth of particle, so the peaks are more clarity. On the other hand, the XRD peaks intensities of lanthanum and nickel oxides phases is very low due to their low amounts in the samples

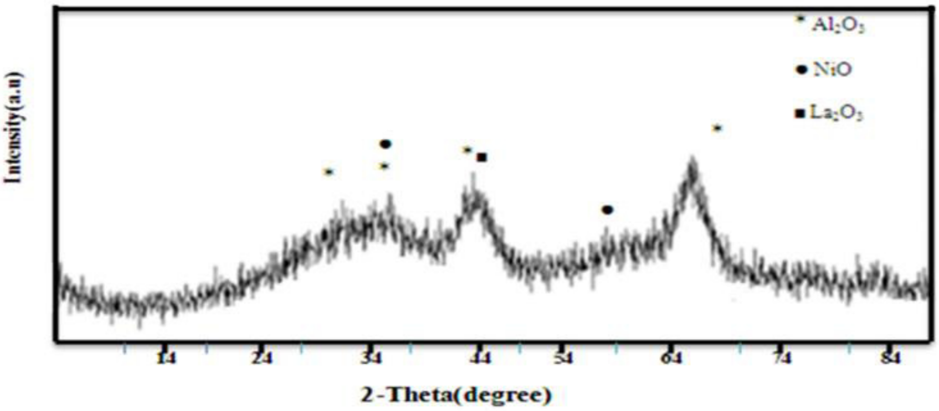

Figure 1. XRD pattern of C1 catalyst Powder at calcination temperature of 650°C.

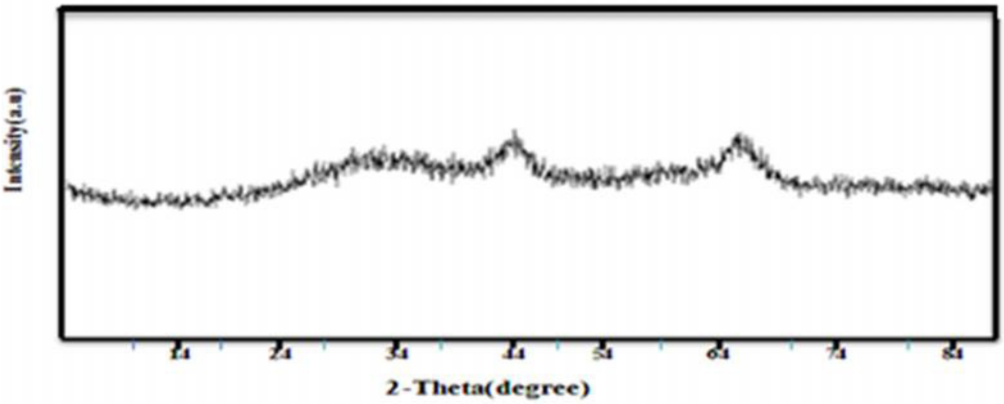

Figure 2. XRD pattern of C2 catalyst Powder at calcination temperature of 650°C.

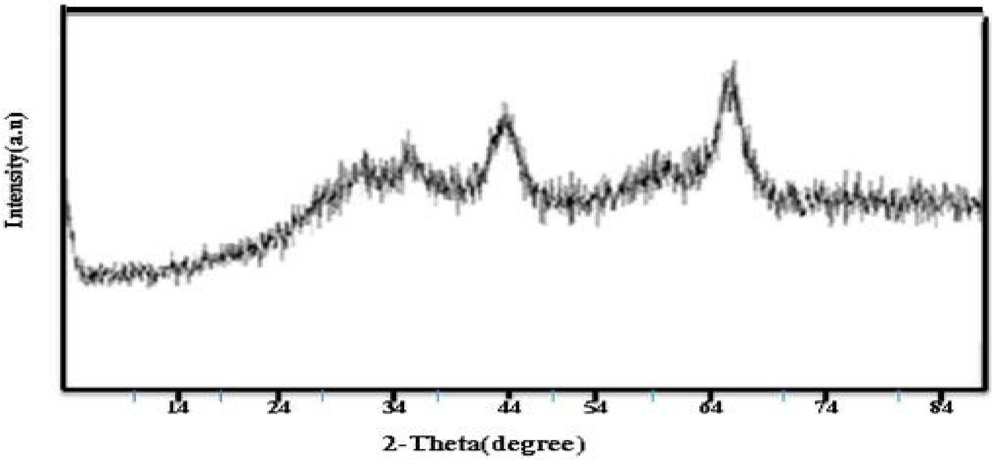

Figure 3. XRD pattern of C2 catalyst Powder at calcination temperature of 850°C.

Surface area and morphology

The results obtained from the BET technique are presented in table 1. The results show that the values of specific surface area, pore size and pore volume of catalyst prepared by aluminium nitrate precursor are greater than those of catalyst prepared via alkoxide precursor. SEM images of C1 and C2 catalysts are illustrated in figures 5 and 6, respectively. The images show that using different precursors for prepared catalysts makes a difference in their morphologies. In addition, large pores and good distribution of the active phase on the support surface, which cause to significant increase of effective surface area are observable.

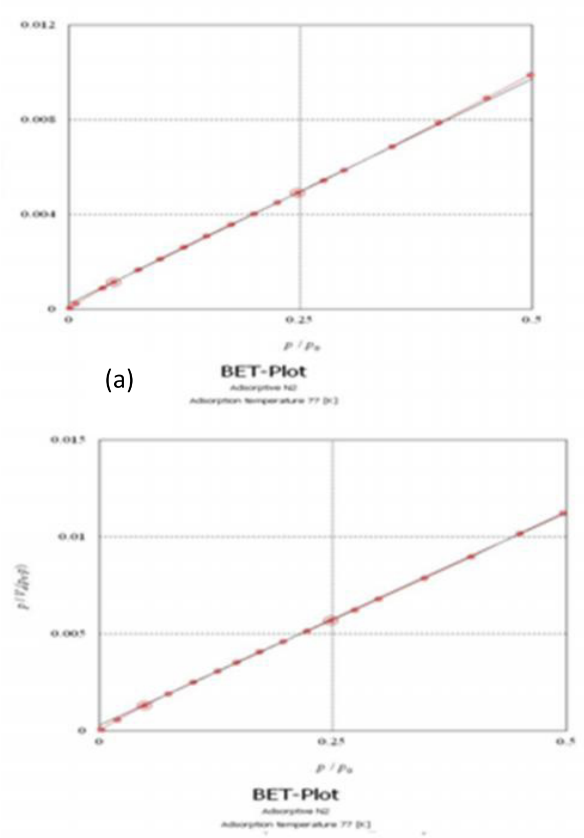

Figure 4. BET plots forC1(a) and C2(b) catalysts.

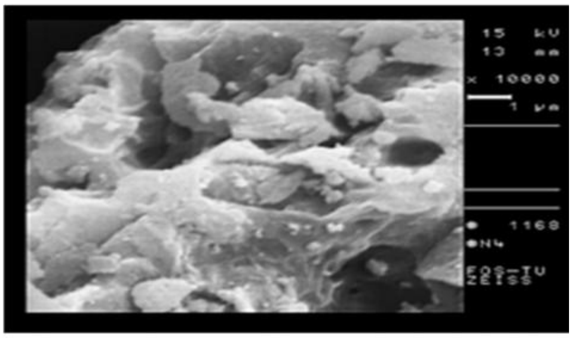

Figure 5. SEM image C1 catalyst powder.

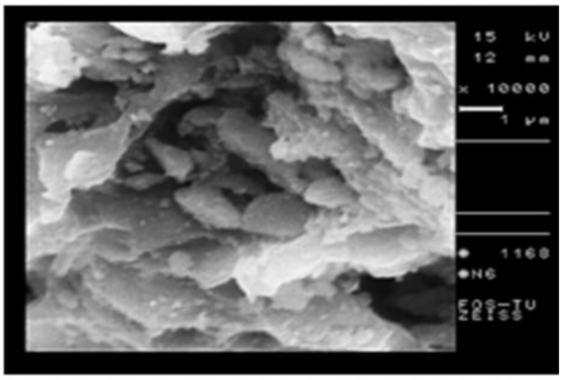

Figure 6. SEM image C1 catalyst powder.

Table 1. Data of BET technique for catalysts C1 and C2.

sample	Surface area (m^2/g)	Pore size (nm)	Pore volume (cm^3/g)
C_1	186	6.02	0.29
C_2	203	6.8	0.39

XRF and PSA analysis

The XRF technique was used to specify C2 catalyst composition. The obtained results are summarized in Table 2. It can be observed from Table 2, C2 catalyst is composed of 26.02 wt% La_2O_3 and 7.37 wt% NiO. Table 3 displays results obtained from PSA analysis for C1 and C2 catalysts. As observed from Table 3, average particle size is about 561 nm for C1 and 532 nm for C2 catalysts, respectively.

Table 2. Data obtained from XRF technique for catalyst C2.

Sample	%Al_2O_3	%La_2O_3	%NiO	%other
C2	64.63	26.02	7.37	~2

Table 3. Data obtained from PSA technique for catalyst C1.

Sample	The average particle size	Particle size range
C1	561nm	435-754 nm
C2	532 nm	403-734 nm

Dechlorination of NCB

Recently, metallic oxide modifiers such as γ-Al_2O_3 and calcined boehmite AlO(OH) have been known as a good way to generate hydrogen [21]. Moreover, Ni acts as a catalyst to collect hydrogen gas in aqueous solution and dissociate it to produce active hydrogen atoms for replacing the chlorine of nitrochlorobenzene and produce aniline and chlorine ions [22]. Therefore, following mechanism is proposed for the dechlorination process:

$$2\,H_2O \xrightarrow{Al_2O_3} H_2 + 2OH^-$$

$$H_2 \xrightarrow{Ni} 2H\,*$$

$$2H\,* + C_6H_4ClNO_2 \longrightarrow C_6H_5NO_2 + Cl^- \xrightarrow{H^+} C_6H_5NH_2 + H_2O$$

In this project , according to the strategy chosen for the testing of catalyst, reaction temperature was set on 185 ºC to remove produced aniline from the reaction zone and was collected by the rotary system condensor. Catalytic test results over C1 and C2 catalysts are shown in Figure 7 and tables (4 and 5). The results show that increasing the effective area of the catalyst, dechlorination efficiency increases.

Table 4. Catalytic test results for C1.

Time (h)	$V_{aniline}$ (ml)	($V_{aniline}$ / V_{NCB}) ×100
0.5	13.5	16.8
1	16.5	21
1.5	19	24
2	22	27.5
2.5	24	30
3	24.5	30.5

Table 5. Catalytic test results for C2.

Time (h)	**$V_{aniline}$ (ml)**	**($V_{aniline}$ / V_{NCB}) ×100**
0.5	15.5	19
1	23	29
1.5	28	35
2	31.5	39
2.5	32	40
3	32	40

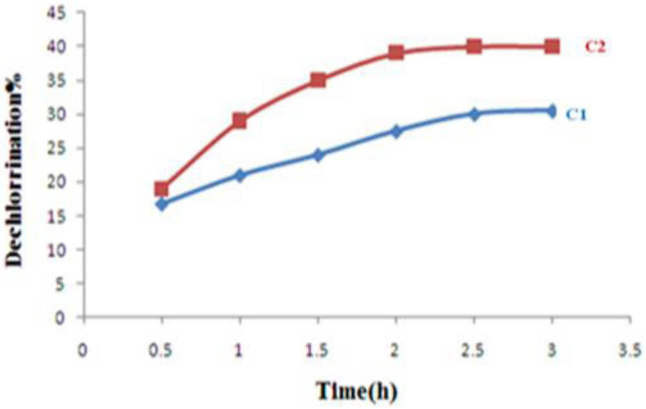

Figure 7. catalytic dechlorination of NCB over C1 and C2 catalysts.

Conclusion

1. The obtained results in this research show that using sol-gel assisted method, the catalyst support of gamma alumina with exclusive characteristics (high effective surface, narrow porous range and high porous volume) can be achieved.

2. The method applied in this research can be an efficient and flexible method to change the percentage compound of catalyst components as well as an appropriate approach to have the suitable distribution of the effective particles on the support of the catalyst.

3. The Ni/La-Al_2O_3 catalyst prepared by aluminium nitrate exhibits greater specific surface area and higher dechlorination efficiency compared to sample prepared through aluminium triisopropoxide precursor.

Acknowledgement

It is an acknowledgement to the respected Research Deputy of Islamic Azad University, Qaemshahr Branch for their financial supports to this research.

References

[1] R. Malyala, C. Rode, M. Arai, S. Hedge, R. Chaudhari, *Appl. Catal. A. Gen*., 193, 71 (2000). [2] Y. Liu, D .Liu, *Int. J. Hydrogen Energy* ,24, 351 (1999).

[3] F. L. Chan, A. Tanksale, *Sustainable Energy Rev.,* 38, 428 (2014).

[4] D.S. Bhatkhande, V.G. Pangarkar and A.A.C.M.Beenackers, *Water Res*., 37, 1223

(2003).

[5] N. Coute, J. D. Ortego, J. T. Richardson, M. V.Twigg, *Appl. Catal. B: Environ.*, 19, 175 (1998).

[6] A. G. F. de Souza, A. M. P. Bentes Jr., A. C. C. Rodrigues, L. E. P. Borges, J. L. F. Monteiro, Catal. Today, 107, 493 (2005).

[7] F. Murena, F. Gioia, *Catal. Today*, 75, 57 (2002).

[8] M. Taralunga J. Mijoin, P. Magnoux, *Appl. Catal. B: Environ.*, 60, 163 (2005).

[9] S. P. Decker, J. S. Klabunde, A. Khaleel, K. J. Klabunde, *Environ. Sci. Technol.*, 36, 762 (2002).

[10] S. Lomnicki, J. Lichtenberger, Z. Xu, M. Waters, J.Kosman, *Appl. Catal. B: Environ.*, 46, 105 (2003).

[11] D. P. Debecker, F. Bertinchamps, N. Blangenois, P. Eloy, E. M. Gaigneaux, *Appl. Catal. B: Environ.*, 74, 223 (2007).

[12] M.C. Galván, B. Pawelec, *Appl. Catal. B: Environ.*, 51, 83 (2004).

[13] X. Xu, Z. Turgut, *J. Desalination*, 242, 256 (2005).

[14] Z. Zhang, Q. Shen, N. Cissoko, J. Wo, X. Xu*, J. Hazard. Mater.*, 142, 253 (2010).

[15] R. Cheng, W. Zhou, Y, Qian, *J. Hazard. Mater.*, 180, 79 (2010).

[16] Y. Han, W. Li, M. Zahan, K. Toa, *Chemosphere*, 72, 53 (2008).

[17] Z. Zhang, S. Hu, S. A. Baig, J. Tang, X. Xu, *J. Colloid Interf. Sci.,* 385, 160 (2012).

[18] D. H. Kim, *Catal. Lett.*, 70, 35 (2000).

[19] E. Babaei, N. Rostamizadeh, F. Razmjou, F. Sobhani, *J. Particle. Sci. Tech.*, 54, 113 (2015).

[20] H. T. Teng, T. Y. Lee, Y. K. Chen, H. W. Wang, G.Cao, *J. Power Sources*, 219, 16 (2012).

[21] Y. Han, W. Li, M. Zhang, K. Tao, *Chemosphere*, 72, 53 (2008).

[22] H. Gocmez, O. Özcan, *Mater. Sci. Eng*. A, 475, 20 (2008).