



A sol-gel based method for preparation of Ni/La-Al₂O₃ as a new catalyst for dechlorination of monochlorobenzene

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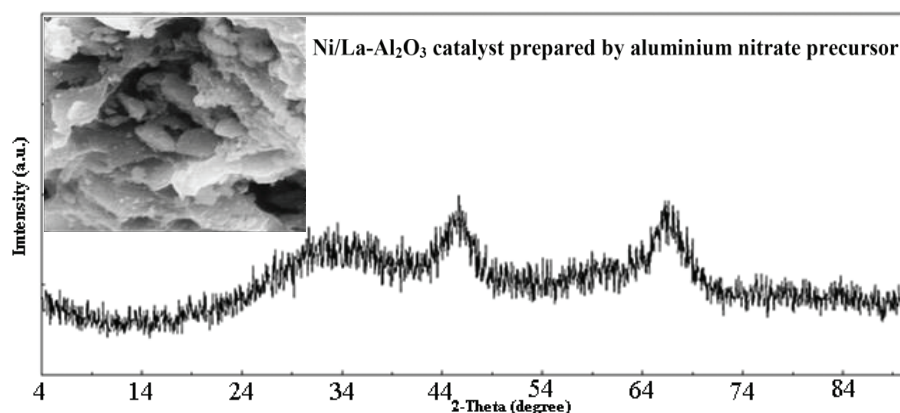
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HIGHLIGHTS

- Two new Ni/La-Al₂O₃ catalysts were prepared via a sol-gel method.
- The Ni/La-Al₂O₃ catalysts prepared by two different aluminium salts as precursors.
- The catalysts were evaluated for the dechlorination of monochlorobenzene (MCB).
- Compared to aluminium triisopropoxide, aluminium nitrate makes a more active catalyst.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 8 January 2015

Received in revised form

6 May 2015

Accepted 17 May 2015

Keywords:

Monochlorobenzene (MCB)

Dechlorination

Ni/La-Al₂O₃ catalyst

Sol-gel

ABSTRACT

In this study, two new Ni/La-Al₂O₃ catalysts were prepared by a sol-gel method, with different aluminium precursors (aluminium triisopropoxide and aluminium nitrate). 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 BET results showed that the particles obtained from the aluminium nitrate precursor had a larger surface area (203 m²/g). The PSA data showed particle size distributions between 435 and 754 nm for the catalyst prepared from aluminium triisopropoxide. Finally, the catalysts were evaluated for the dechlorination of monochlorobenzene (MCB).

1. Introduction

Nickel based catalysts are known for the hydrogenation, CO₂ hydrogenation, reverse water gas shift (RWGS) and biomass gasification processes [1-4]. The key focus of this paper is the nickel based catalyst used in dechlorination process. Dechlorination process can be examined from two important views. In the first, the necessity of formation and development of this process considered for recycling different chlorinated compounds which have many domestic and industrial applications, to reduce environmental damages of these compounds. In second view, dechlorination is a part of industrial process such as oil refinement industry in which the presence of chlorinated compounds is regarded as an undesired factor to continue the industrial process, so should be removed. Dechlorination of the feedstock entering the hydrogen production unit in refinery can be an example for this view. Hydrogen unit in the refinery produces the required hydrogen for isomax unit. The feedstock should be dechlorinated and desulphureted before entering the reformer and shift conversion, since chlorinated and sulphureted compounds are as poison for the catalysts of two above-mentioned processes [5-11].

The most widely studies have been reported for dechlorination of chlorinated hydrocarbons (CHC) including photocatalytic degradation, steam reforming [12], hydrodechlorination [13,14], and catalytic oxidation [15-19]. 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 [20].

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 [21-25].

The aims of this work are summarized as follows: I) Presentation of a facile and flexible method based on sol-gel technique to prepare Ni/La-Al₂O₃ as a new catalyst for monochlorobenzene dechlorination process, II) The use of lanthanum oxide as a known promoter to improve the thermal and mechanical properties of catalyst support [26-27], III) Introducing a simple method to evaluate the catalyst for the dechlorination of chlorobenzene as one of the components in feedstock of hydrogen unit.

2. Experimental

2.1. Materials

Aluminium triisopropoxide (Al(C₃H₇O)₃), Aluminium nitrate nonahydrate (Al(NO₃)₃·9H₂O), Nickel nitrate hexahydrate (Ni(NO₃)₂·6H₂O) and Lanthanum nitrate hexahydrate (La(NO₃)₃·6H₂O) were purchased from the Merck company. Ammonia 28% (NH₃) was provided from the Aldrich company.

2.2. 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 90°C 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).

2.3. Preparation of catalysts

C1 and C2:

After gelation of A and B support precursors for 2 h, 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 (C1 and C2).

2.4. Batch experimental procedure

Batch experiments were performed in a flask of rotary evaporator. Mixture of water and monochlorobenzene (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 reactions were carried out at 353 K

without vacuum with rotating at a rate of 200 rpm. Produced benzene volumes were separately measured for C1 and C2 catalysts every half hour and it was calculated volume ratio of benzene to monochlorobenzene as reaction efficiency at 3 h. Produced benzene was characterized by IR spectroscopy. Performances of the catalysts were determined by using following formula:

$$\text{Dechlorination efficiency (\%)} = (V_{\text{benzene}} / V_{\text{MCB}}) \times 100$$

2.5. 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 ($k\alpha$), the BET surface area, 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.

3. Results and discussion

According to the primary materials, there are two important approaches to prepare boehmite sol (pseudo-boehmite).

In this present work, by simplification and modification of the previous reported and conventional methods, both approaches are used to prepare the sol using aluminium salts. Finally, using an innovative method to reach the appropriate distribution of Ni particles on the catalyst supports, Ni salt solution was added to gel in aging step. Among supports, $\gamma\text{-Al}_2\text{O}_3$ is an appropriate option due to particular mechanical and thermal characteristics. With adding lanthanum Oxide, thermal resistance to sintering of $\gamma\text{-Al}_2\text{O}_3$ support improves, especially at high temperature catalytic processes. The Nickel and Palladium are known as active phases to produce active atoms of hydrogen. In this study, Ni was used as an active phase because it is more inexpensive compared to Pd. [28-30].

It should be noted that because of the strong interaction of the alkoxide with water, hydrolysis reaction with cold or hot water can take place. The experi-

mental work was performed in both conditions. If the cold water (25°C) uses for hydrolysis, one night after decoagulation, some white deposit will observe at the bottom of the container that is due to the lack of stable sol as after a while the reaction product becomes bayerite ($\beta\text{-Al}(\text{OH})_3$) with larger particles [31]. Whereas if hot water (approximately 75°C) uses for hydrolysis, the obtained sol will be stable for several months. In the following, a summary of the performed reactions at low and high temperatures is shown.



The value of water is one of the effective factors during hydrolysis process. Increasing the value of water will lead to the faster hydrolysis reaction. It should be considered that high values of water cause to prolong the conversion time of sol into gel and the drying time. Therefore the optimum ratio of water to alkoxide should be twelve to one [32-33].

3.1. Powder X-ray diffraction (XRD)

In XRD patterns related to the catalysts powders of C1 calcined at 650°C (Fig. 1) and C2 calcined at 650°C (Fig. 2) and 850°C (Fig. 3), the broad diffraction peaks at $2\theta = 31.9, 37.6, 46$ and 67° are attributed to $\gamma\text{-Al}_2\text{O}_3$ amorphous phase [34]. 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 850°C 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.

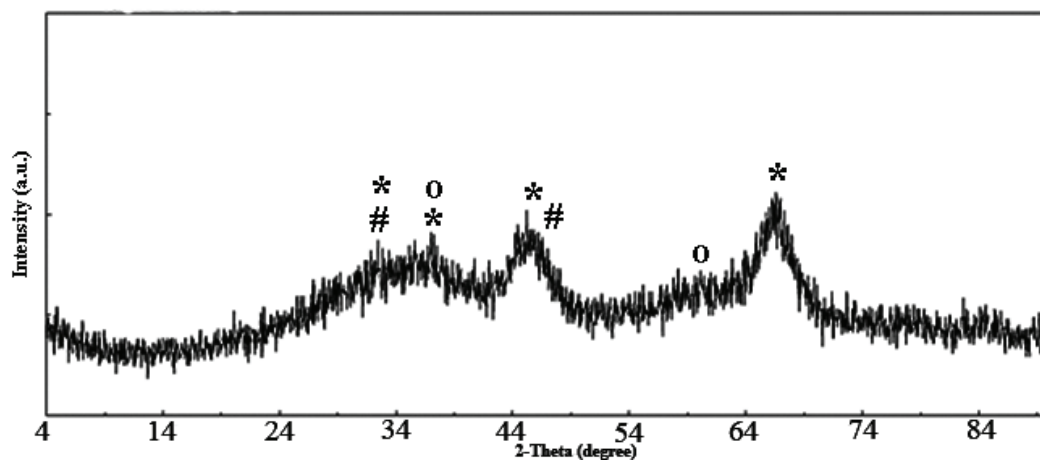


Fig. 1. . XRD pattern of C1 catalyst calcined at 650°C; (*) γ - Al_2O_3 , (o) NiO, (#) La_2O_3 .

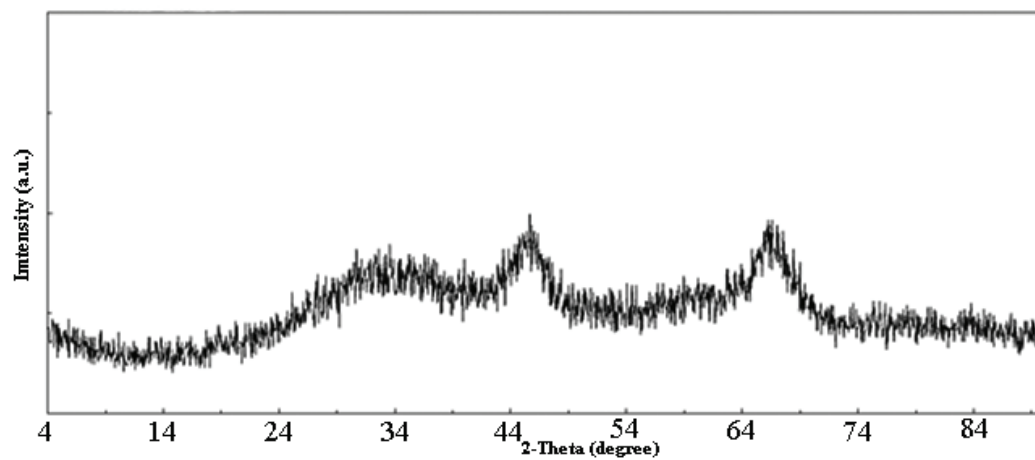


Fig. 2. XRD pattern of C2 catalyst calcined at 650°C.

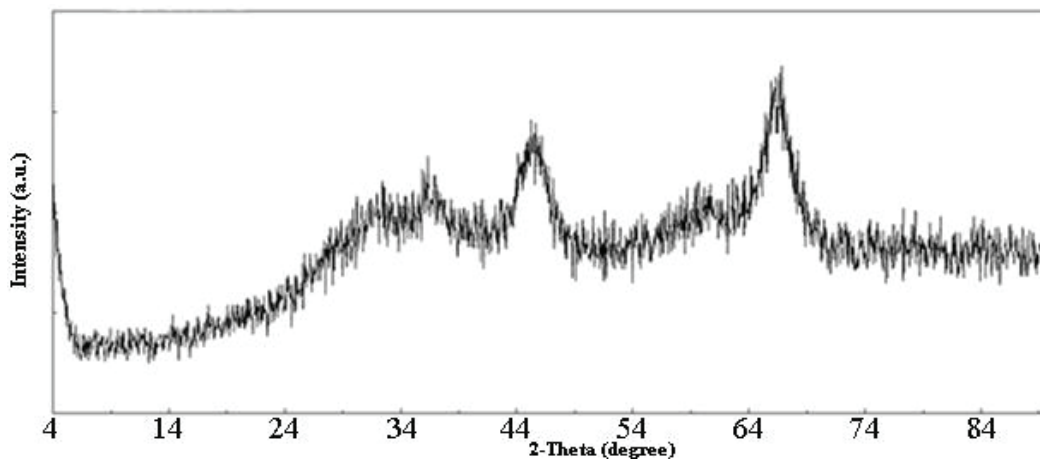
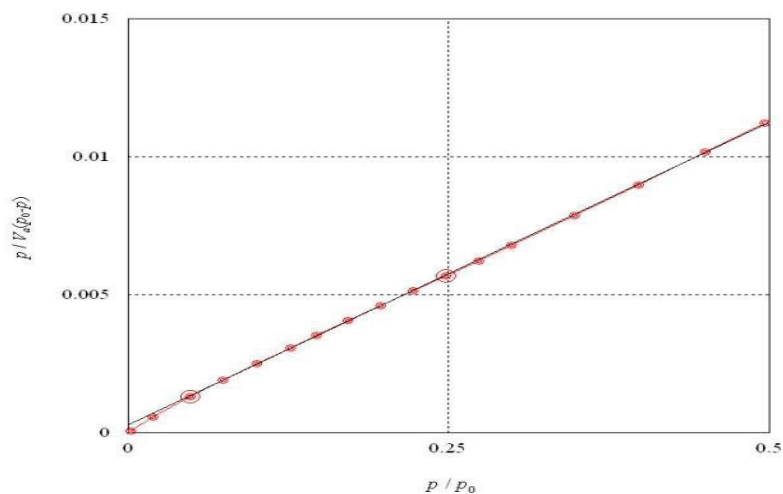


Fig. 3. XRD pattern of C2 catalyst calcined at 850°C.

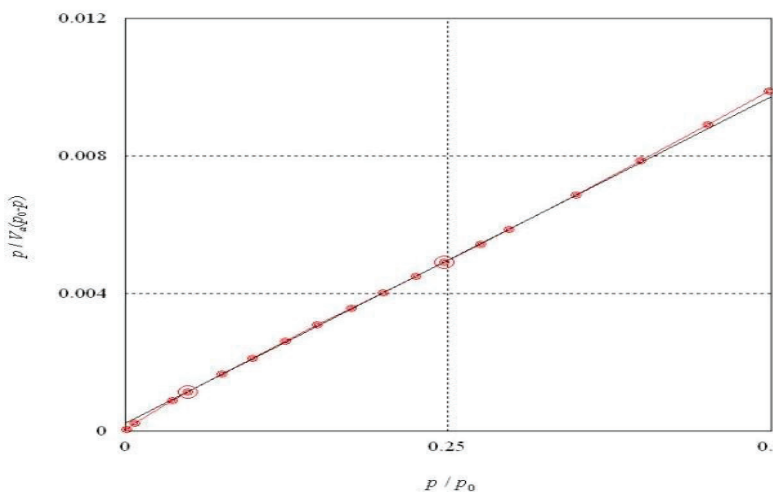
3.2. Surface area and morphology

The results obtained from the BET technique are presented in Table 1 and Fig. 4. 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.



(a)

BET-PlotAdsorptive N2
Adsorption temperature 77 [K]

(b)

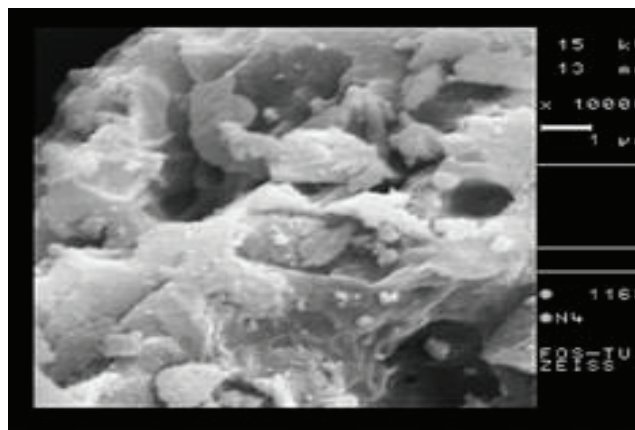
BET-PlotAdsorptive N2
Adsorption temperature 77 [K]

Fig. 5. SEM image of C1 catalyst powder.

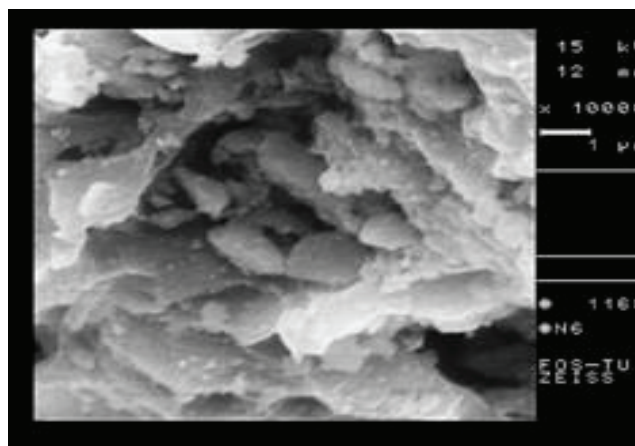


Fig. 6. SEM image of C2 catalyst powder.

Fig. 4. BET plots for C1 (a) and C2 (b) catalysts.

Table 1.

Textural properties for C1 and C2 catalysts.

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

3.3. 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 catalyst. As observed from Table 3, average particle size is about 561 nm for C1 catalyst.

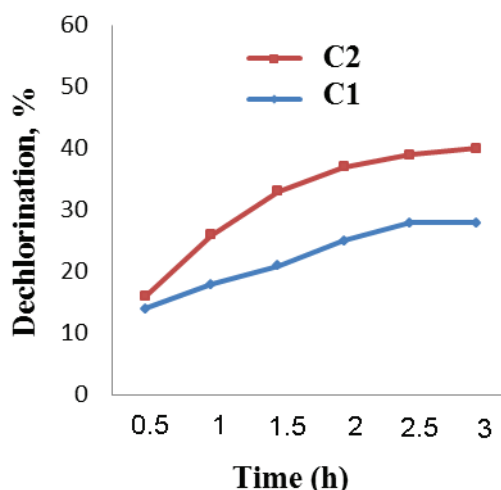


Fig. 7. catalytic dechlorination of MCB over C1 and C2 catalysts.

Table 2.

Composition of C2 catalyst (resulted from XRF technique).

sample	Al_2O_3 (wt%)	La_2O_3 (wt%)	NiO (wt%)	Other (wt%)
C2	64.63	26.02	7.37	1.98

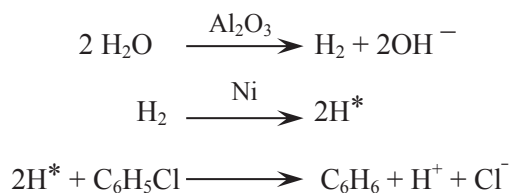
Table 3.

Data obtained from PSA technique for C1 catalyst.

sample	Average particle size (nm)	Particle size range (nm)
C1	561	435-754

3.4. Dechlorination of MCB

Recently, metallic oxide modifiers such as $\gamma\text{-Al}_2\text{O}_3$ and calcined boehmite $\text{AlO}(\text{OH})$ have been known as a good way to generate hydrogen [35]. 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 chlorobenzene and produce benzene and chlorine ions [36]. Therefore, following mechanism is proposed for the dechlorination process:



In this study, according to the strategy chosen for the testing catalyst, to removal of chlorine and to collect produced benzene from the reaction zone, reaction temperature is set at 80°C . The catalytic test results over C1 and C2 catalysts are shown in Fig. 7 and Tables 4 and 5. The results show

Table 4.

Catalytic test results for C1 catalyst.

Time (h)	V_{benzene} (ml)	$(V_{\text{benzene}} / V_{\text{MCB}}) \times 100$
0.5	10.5	14
1	13.5	18
1.5	16	21
2	19	25
2.5	21	28
3	21	28

Table 5.

Catalytic test results for C2 catalyst.

Time (h)	V_{benzene} (ml)	$(V_{\text{benzene}} / V_{\text{MCB}}) \times 100$
0.5	12	16
1	20	26
1.5	25	33
2	28	37
2.5	29.5	39
3	30	40

4. Conclusions

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

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

3. The Ni/La-Al₂O₃ catalyst prepared by aluminium nitrate exhibits greater specific surface area and higher dechlorination efficiency compared to sample prepared through aluminium triisopropoxide precursor.

4. In the future research can be examined the effective parameters on dechlorination efficiency such as temperature, pH and amount and particle size of nickel.

Acknowledgement

It is acknowledgement to the respected research deputy of Islamic Azad university, Qaemshar branch for financial support of this research.

References

- [1] R. Malyala, C. Rode, M. Arai, S. Hedge, R. Chaudhari, Activity, selectivity and stability of Ni and bimetallic Ni-Pt supported on zeolite Y catalysts for hydrogenation of acetophenone and its substituted derivatives, *Appl. Catal. A. Gen.* 193 (2000) 71-86.
- [2] Y. Liu, D. Liu, Study of bimetallic Cu-Ni/ γ -Al₂O₃ catalysts for carbon dioxide hydrogenation, *Int. J. hydrogen energy* 24 (1999) 351-354.
- [3] A. Trovarelli, Catalytic properties of ceria and CeO₂-containing materials, *Catal. Rev. - Sci. Eng.* 38 (1996) 439-520.
- [4] F. L. Chan, A. Tanksale, Review of recent developments in Ni-based catalysts for biomass gasification, *Renew. Sustainable Energy Rev.* 38 (2014) 428-438.
- [5] F. Mohammad, Thermal and catalytic decomposition behavior of PVC mixed plastic waste with petroleum residue, *J. Anal. Appl. Pyrol.* 74 (2005) 282-289.
- [6] E. L. Grabowska, J. Yperman, G. Gryglewicz, S. Hoste, R. Carleer, Study on hydrodechlorination of polychlorinated biphenyls during reductive pyrolysis in the presence of a catalyst, *Fuel* 85 (2006) 374-381.
- [7] Y. Ukisu, Complete dechlorination of DDT and its metabolites in an alcohol mixture using NaOH and Pd/C catalyst, *J. Hazard. Mater.* 152 (2008) 287-292.
- [8] H. Yi, L. Wei, Z. Minghui, T. Keyi, Catalytic dechlorination of monochlorobenzene with a new type of nanoscale Ni(B)/Fe(B) bimetallic catalytic reductant, *Chemosphere* 72 (2008) 53-58.
- [9] B. Lv, G. Zhao, D. Li, C. Liang, Dechlorination and oxidation for waste poly(vinylidene chloride) by hydrothermal catalytic oxidation on Pd/AC catalyst, *Polym. Degrad. Stabil.* 94 (2009) 1047-1052.
- [10] I-M. Chen, W. Wanitchapichat, T. Jirakittayakorn, S. Sanohniti, W. Sudjarid, C. Wantawin, J. Voranisaraku, J. Anotai, Hexachlorobenzene dechlorination by indigenous sediment microorganisms, *J. Hazard. Mater.* 177 (2010) 244-250.
- [11] S. Gómez-Quero, F. Cárdenas-Lizana, M. A. Keane, Liquid phase catalytic hydrodechlorination of 2,4-dichlorophenol over Pd/Al₂O₃: Batch vs. continuous operation, *Chem. Eng. J.* 166 (2011) 1044-1051.
- [12] N. Coute, J. D. Ortego, J. T. Richardson, M. V. Twigg, Catalytic steam reforming of chlorocarbons: trichloroethane, trichloroethylene and perchloroethylene, *Appl. Catal. B: Environ.* 19 (1998) 175-187.
- [13] A. G. F. de Souza, A. M. P. Bentes Jr., A. C. C. Rodrigues, L. E. P. Borges, J. L. F. Monteiro, Hydrodechlorination of carbon tetrachloride over PtNaX zeolite: Deactivation studies, *Catal. Today* 107 (2005) 493-499.
- [14] F. Murena, F. Gioia, Catalytic hydrotreatment of water contaminated by chlorinated aromatics, *Catal. Today* 75 (2002) 57-61.
- [15] M. Taralunga J. Mijoin, P. Magnoux, Catalytic Oxidation of Chlorobenzene and PCDD/Fs with Ozone over Transition Metal Oxides, *Appl. Catal. B: Environ.* 60 (2005) 163-171.
- [16] S. P. Decker, J. S. Klabunde, A. Khaleel, K. J. Klabunde, Catalyzed Destructive Adsorption of Environmental Toxins with Nanocrystalline Metal Oxides. Fluoro-, Chloro-, Bromocarbons, Sulfur, and Organophosphorus Compounds, *Environ. Sci. Technol.* 36 (2002) 762-768.
- [17] S. Lomnicki, J. Lichtenberger, Z. Xu, M. Waters, J. Kosman, Catalytic oxidation of 2,4,6-trichlorophenol over vanadia/titania-based catalysts, *Appl. Catal. B: Environ.* 46 (2003) 105-119.

- [18] D. P. Debecker, F. Bertinchamps, N. Blangenois, P. Eloy, E. M. Gaigneaux, On the impact of the choice of model VOC in the evaluation of V-based catalysts for the total oxidation of dioxins: Furan vs. chloro benzene, *Appl. Catal. B: Environ.* 74 (2007) 223-232.
- [19] M.C. Galván, B. Pawelec, Formaldehyde/methanol combustion on alumina-supported manganese-palladium oxide catalyst, *Appl. Catal. B: Environ.* 51 (2004) 83–91.
- [20] X. Xu, Z. Turgut, De-colorization of direct dye in textile wastewater by ozonation in a semi-batch bubble column reactor, *J. Desalination* 242 (2005) 256-263.
- [21] Z. Zhang, Q. Shen, N. Cissoko, J. Wo, X. Xu, Catalytic dechlorination of 2,4-dichlorophenol by Pd/Fe bimetallic nanoparticles in the presence of humic acid, *J. Hazard. Mater.* 142 (2010) 253-259.
- [22] R. Cheng, W. Zhou, Y. Qian, Dechlorination of pentachlorophenol using nanoscale Fe/Ni particles: Role of nano-Ni and its size effect, *J. Hazard. Mater.* 180 (2010) 79-85.
- [23] Y. Han, W. Li, M. Zahan, K. Toa, catalytic dechlorination of monochlorobenzene with a new type of nanoscale Ni(B)/Fe(B) bimetallic catalytic reductant, *Chemosphere* 72 (2008) 53–58.
- [24] Z. Zhang, S. Hu, S. A. Baig, J. Tang, X. Xu, Catalytic dechlorination of Aroclor 1242 by Ni/Fe bimetallic nanoparticles, *J. Colloid Interf. Sci.* 385 (2012) 160-165.
- [25] D. H. Kim, The role of lanthanum oxide on Pd-only three-way catalysts prepared by co-impregnation and sequential impregnation methods, *catal. Lett.* 70(2000) 35-41.
- [26] R. Craciun, N. Dulamita, Influence of La₂O₃ promoter on the structure of MnOx/SiO₂ catalysts. *Catal. Lett.* 46 (1997) 229-234.
- [27] B. Béguin, E. Garbowski, M. Primet, Stabilization of alumina by addition of lanthanum, *Appl. Catal.* 75 (1991) 119–132.
- [28] W. Zhang, X. Quan, J. Wang, Z. Zhang, S. Chen, Rapid and complete dechlorination of PCP in aqueous solution using Ni–Fe nanoparticles under assistance of ultrasound, *Chemosphere* 65 (2006) 58-64.
- [29] N. Dilsiz, G. Akoval, Study of sol–gel processing for fabrication of low density alumina microspheres, *Mater. Sci. Eng.: A* 332 (2002) 91-96.
- [30] B. E. Yoldas, Microstructure of Monolithic Materials Formed by Heat Treatment of Chemically Polymerized Precursors in the Al₂O₃-SiO₂ Binary, *Ceram. Bull.* 59 (1980) 479-483.
- [31] B. E. Yoldas, *Us. Patent*. No 3, 681, 113 (issued August 1, 1972).
- [32] H. S. Potdar, K. W. Jun, J. W. Bae, S. M. Kim, Y. J. Lee, Synthesis of Nano-Sized Porous γ -alumina powder via a precipitation/digestion route, *Appl. Catal. A: Gen.* 321 (2007) 109-116.
- [33] T. F. Baumann, A. E. Gash, S. C. Chin, A. M. Sawvel, R. S. Maxwell, J. H. Satcher, Synthesis of High Surface Area Alumina Aerogels without the use of Alkoxide Precursors, *Chem. Mater.* 17 (2005) 395-401.
- [34] H. T. Teng, T. Y. Lee, Y. K. Chen, H. W. Wang, G. Cao, Effect of Al(OH)₃ on the hydrogen generation of aluminum–water system, *J. Power Sources* 219 (2012) 16-21.
- [35] Y. Han, W. Li, M. Zhang, K. Tao, Catalytic dechlorination of monochlorobenzene with a new type of nanoscale Ni(B)/Fe(B) bimetallic catalytic reductant, *Chemosphere* 72 (2008) 53-58.
- [36] H. Gocmez, O. Özcan, Low temperature synthesis of nanocrystalline α -Al₂O₃ by a tartaric acid gel method, *Mater. Sci. Eng. A* 475 (2008) 20-22.