



SILVER NANOPARTICLES SUPPORTED ON ALUMINUM PILLARED CLAY (Ag/Al-B) FOR CYCLOHEXENE OXIDATION

(This article was presented first to the PPM2017, then submitted to JOTCSB as a non-peer-reviewed article)

A.Hakkoum^(1,2,*a) R.Bachir¹, S.Bedrane¹, A.Choukchou-Braham¹,
1-Laboratoire de Catalyse et Synthèse en Chimie Organique, Département de Chimie
université de Tlemcen -Algérie BP 119 Tlemcen 13000 Algérie
2-Université Hassiba Benbouali de Chlef Algérie

Abstract: The silver nanoparticles supported on aluminum pillared Clay (Ag/Al-B), with Ag content of about 1%, were used for the free catalyzed oxidation of cyclohexene with hydrogen peroxide (H₂O₂). The structure of the material was subsequently studied by IR, BET, and X-ray diffraction analysis. The silver supported on aluminium pillared clay (Au / Al-B) catalyst gives a high activity relative to the clay purified.

Cite this: Hakkoum A, Bachir R, Bedrane S, Choukchou-Braham A. Silver nanoparticles supported on aluminum pillared clay (Ag/Al-B) for cyclohexene oxidation. JOTCSB. 2017;1(sp.is.2): 1-8.

Corresponding author. E-mail: hakkoum_abdelkader@yahoo.fr

INTRODUCTION

In the last decade, silver (Ag) nanoparticles have attracted extensive attention due to their potential utility in catalysis (1-8). However, it is difficult to separate the Ag nanoparticle catalysts from the reacting mixtures. In order to reuse the catalysts simply and/or enhance their catalytic activities (9), Ag nanoparticles had been immobilized onto the various supports such as silica (10-14), MCM and zeolite (15,16), carbon nanotubes and activated carbon (17-20), alumina (21-23), ceria (24,25), titania (26), polymeric materials (27,28), CaCO₃ (29), silica-alumina (30), and tungsten oxide (31) or encapsulated by the other materials (32-35). The immobilized catalysts have the strongpoint of producing more easily compared with the encapsulated catalysts.

Clay minerals have always been commonly used in industry and laboratory applications either at their natural form or after modification. Clay minerals supported silver as catalysts are attracting the attention of P. Djomgoue et al(36).

In the present work, montmorillonite was used as the supports of the preparation of the immobilized silver nanoparticles catalyst and used for the catalyzed oxidation of cyclohexene. The study of the oxidation of cyclohexene catalyzed in the presence of hydrogen peroxide was investigated.

EXPERIMENTAL

Materials and reagents

Natural bentonite was obtained from career of Roussel, Maghnia (Algeria) which has been previously separated by particle size (<2 mm) and homoionized with a 1N NaCl solution followed by filtering. The pillared clay (Al-B) was prepared as described in detail elsewhere (37). The clay was pillared with an oligomeric solution made from (AlCl₃.6H₂O) and NaOH. After washing and freeze-drying, the solid was calcined at 400 °C, for 4 hours after a ramp of 5 °C/min.

Silver was introduced into the pillared bentonite by the ion exchange method. One gram of the pillared clay was added to 100 mL of the 0.02 mol of silver nitrate solution. The vigorously stirred suspension of the pillared Bentonite was left in contact with the solution of silver nitrate at 50°C for 3 h. The silver modified bentonite is separated, washed and dried at 100°C for 24 h and then calcined at 300°C for 6 h.

Characterization methods

The specific surface area, pore volumes and micropore volumes of the samples were determined from N₂ adsorption isotherms at 77 K using Quantachrome Nova 1000^e instrument. The pore size distribution was calculated by BJH method for desorption branch. Micropore volume and micropore surface area were calculated by t-plot method using de Boer method. Prior to the physisorption measurements, the samples were outgassed at 250 °C for 3 h under vacuum.

The FT-IR of modified montmorillonite clay catalysts were recorded using absorbance accessory at room temperature on Cary 640 FT-IR spectrometer., the IR spectrum was recorded in the spectral range 1650 and 1350 cm⁻¹ using KBr background.

Powder X-ray diffractograms (XRD) of the materials were recorded on a Rigaku D/max 2500 diffractometer, Ni-filtered Cu K α radiation, $\lambda=1.541874$ Å, between 2.5 and 70° (2 θ) at scanning speed 1 step per second with step size 0.03°. The diffractometer operates at 40 kV and 80 mA.

Catalytic experiments

Liquid phase oxidation of cyclohexene by using hydrogen peroxide (H₂O₂, 30%) to AA was performed in a 25 mL three-neck round-bottomed flask equipped with a reflux condenser, a magnetic stirrer, and an adjusted temperature water bath.

Then, 19 mmol (2 mL) of cyclohexene was added to 8 mL of oxidant (H₂O₂, 30%). The mixture was heated to 80 °C under vigorous stirring, and then the catalyst (20 mg) was added (time zero). The reaction products were identified by comparison with authentic products and the course of reactions was followed by gas chromatography (GC), using SHIMADZU GC 14-B equipped with capillary column "Agile HP-FFAP" and flame ionization detector (FID).

On the other hand, to control the remaining H₂O₂, an iodometric titration was performed at the end of the reaction (after 6 h) by analyzing the aqueous phase.

$$\text{conversion} = \left[\frac{\text{moles of initial cyclohexene} - \text{moles of remaining cyclohexene}}{\text{moles of initial cyclohexene}} \right] * 100$$

$$\text{selectivity} = \left[\frac{\text{moles individual product}}{\text{moles of converted cyclohexene}} \right] * 100$$

RESULTS AND DISCUSSION

Figure 1 presents the XRD patterns recorded for the raw bentonite and its modifications. Position of the (001) peak allows determination of the interlayer distance. The raw clay exhibited a reflection at 2θ about 7.15° , which was assigned to the basal spacing $d_{001} = 12.36 \text{ \AA}$. A disappearance of the (001) peak after pillaring of the parent bentonite with aluminum suggests that the obtained material is characterized by a delaminated structure (non parallel ordering of the clay layers).

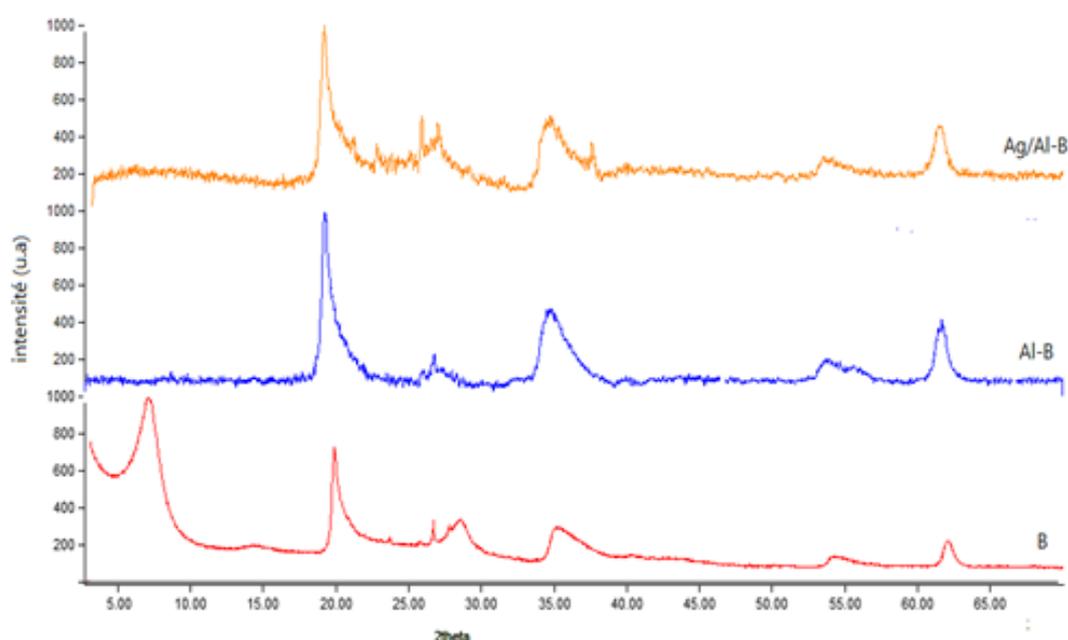


Figure 1: X-ray diffraction patterns of bentonite and its modifications.

Modification of the pillared bentonite with Ag^+ cations results in an appearance of a new peak at about 38.2° , which is assigned to the presence of metallic silver Ag (111) with diameter of 20.91 nm using Scherrer formula (35). During the ion-exchange procedure, silver was deposited in the clay material in the form of separate cations and metal oxide clusters, which were thermally reduced to metallic silver (Ag) during the calcination process. A disappearance of the (001) peak, observed in the case of the Ag/Al-B sample, suggests that silver clusters are localized partially in the interlayer space. Probably, these metal particles, which have various sizes, disturb ordering of Clay layers. The BET surface areas, pore volumes, micropore volumes and pore diameters of the materials prepared are summarized in Table 1. The specific area of raw clay is $80 \text{ m}^2 \text{ g}^{-1}$. Therefore we note a

decrease of surface area after incorporation of aluminum where they pass from 80 to 79.244 $\text{m}^2 \text{g}^{-1}$, which indicate the incorporation of aluminum oxide into pores framework.

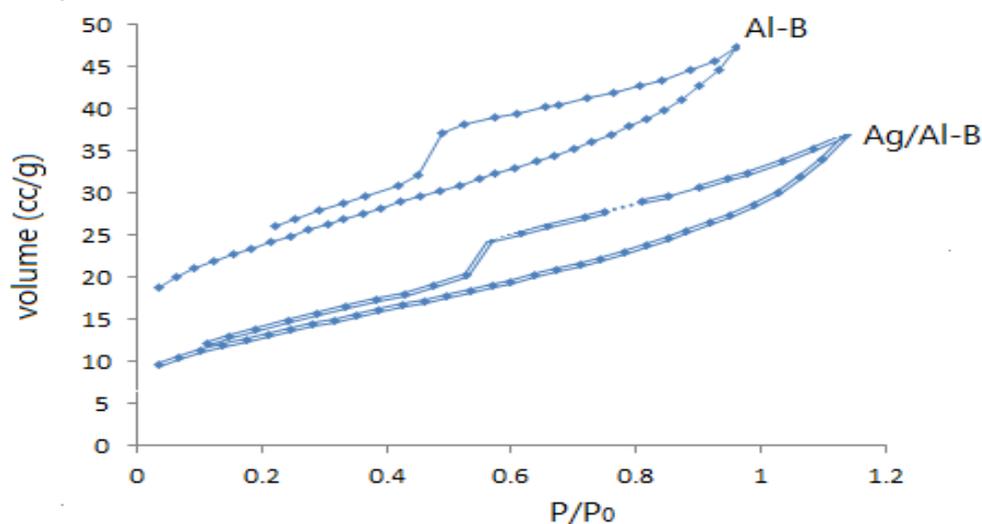


Figure 2: N_2 adsorption-desorption isotherms.

After impregnation of Al-B with amount of silver the BET surface area increase sharply. This effect can be explained by the deposition of the silver (Ag) metal on the surface of support (Al-B). The micropore volume also increased sharply with the deposition of silver. The profile of the adsorption isotherms shown in Fig. 2 was identical for both samples and of type IV, which is characteristic of solids that include both mesopores and micropores.

Table 1 Textural properties

	S_{BET}	V_t	$V_{\mu\text{p}}$	d_p
	$/\text{m}^2 \text{g}^{-1}$	$/\text{cm}^3 \text{g}^{-1}$	$/\text{cm}^3 \text{g}^{-1}$	$/\text{nm}$
B	80	-	-	-
Al-B	79.244	0.073	0.042	3.07
Ag/Al-B	115.779	0.12	0.08	3.79

S_{BET} surface area V_t Total pore volume $V_{\mu\text{p}}$ micropore volume d_p pore diameter

FTIR spectra of samples are shown in Figure 3. The band around 1040 cm^{-1} is due to asymmetric stretching vibrations of SiO_2 tetrahedra. A band around 800 cm^{-1} is due to stretching vibration of Al^{IV} tetrahedra, and absorption at $526\text{-}471 \text{ cm}^{-1}$ is due to bending of Si-O vibration (38). The band at 1629 cm^{-1} is attributed to less strongly hydrogen bonded

water and corresponds to the position of the water bending mode of liquid water (39). No peak of oxides of Ag is present showing presence of silver in the reduced form.

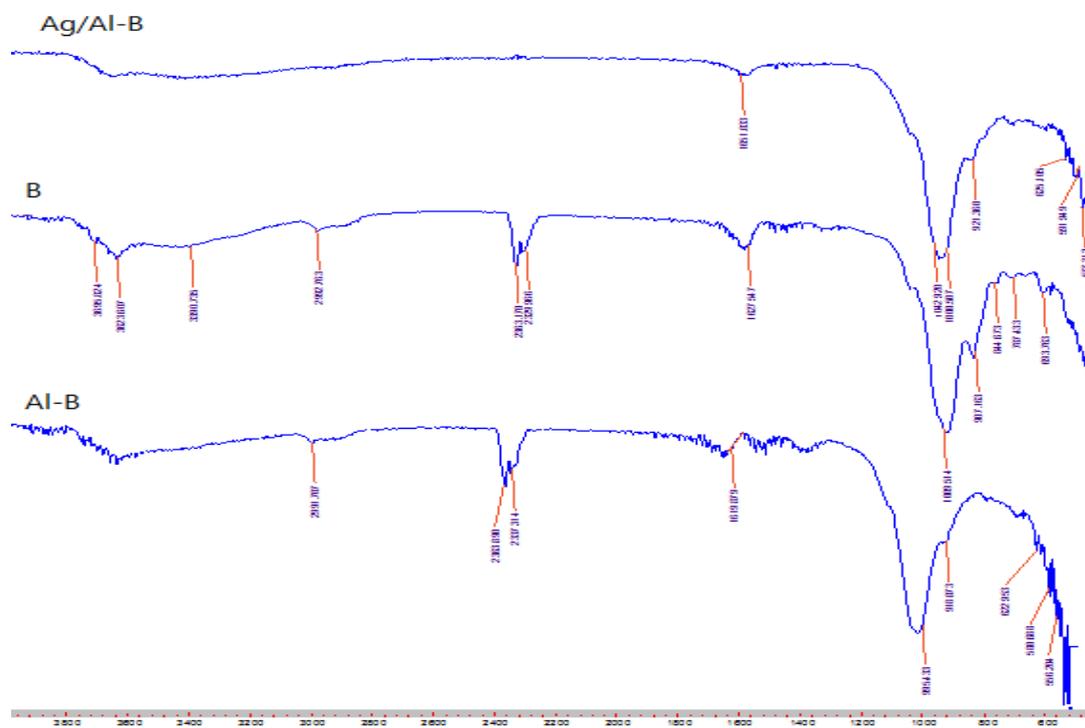


Figure 3: FT-IR spectra of the clay before and after modifications.

Table 2: Effect of Silver content.

Catalysts	Cyclohexene conversion (%)	H ₂ O ₂ consumption (%)	Selectivity (%)					
			Epoxide	One	Ol	Enone	Enol	Diol
B	0.0	0	-	-	-	-	-	-
Al-B	29	13	11	-	-	-	-	26
Au/Al-B	33	20	1	-	-	10	-	46

Conditions: 20 mg catalyst; /cyclohexene = 4.3; T = 80 °C; 20; reaction time 8 h.

Catalytic activity

Table 2 shows the results of cyclohexene epoxidation with supports and catalyst. We observe that our support (B) is inactive toward the oxidation of cyclohexene. After insertion of aluminum (Al-B), we note a conversion of 29% with selectivity in cyclohexane-diol (26%) and epoxide (11 %). After impregnation of Al-B with silver, we observe that the conversion increases slightly and we note also increasing in selectivity in cyclohexane-diol (46%). We note also low consumption of H₂O₂ for the two materials.

CONCLUSIONS

In conclusion, in the present work we prepared nano-silver supported over Aluminum pillared montmorillonite clay to test it in the oxidation of cyclohexene reaction. The characterization shows the deposition of silver on the modified bentonite with an average diameter of 20 nm.

The aluminum-pillared clay modified with silver (Ag/Al-B) was the most active catalyst for cyclohexene oxidation by H₂O₂, and selectivity towards cyclohexane-diol.

REFERENCES

1. H. Rashid, T.K. Mandal, J. Phys. Chem. C 111 (2007) 16750.
2. G. Merga, R. Wilson, G. Lynn, B.H. Milosavljevic, D. Meisel, J. Phys. Chem. C 111 (2007) 12220.
3. G.N. Pascal, F.C. Mertens, P. Vandezande, X.P. Ye, F. Verpoort, I.F.J. Vankelecom, D.E. De Vos, Appl. Catal. A: Gen. 325 (2007) 130.
4. W.J. Yan, R. Wang, Z.Q. Xu, J.K. Xu, L. Lin, Z.Q. Shen, Y.F. Zhou, J. Mol. Catal. A: Chem. 255 (2006) 8.
5. S.H. Choi, Y.P. Zhang, A. Gopalan, K.P. Lee, H.D. Kang, Colloid Surf. A: Physicochem. Eng. Aspects 256 (2005) 165.
6. J.P. Zhang, P. Chen, C.H. Sun, X.J. Hu, Appl. Catal. A: Gen. 266 (2004) 49.
7. S. Kundu, S.K. Ghosh, M. Mandal, T. Pal, New J. Chem. 27 (2003) 656.
8. Y. Shiraishi, N. Toshima, Colloid Surf. A: Physicochem. Eng. Aspects 169 (2000) 59.
9. S. Rojluechai, S. Chavadej, J.W. Schwank, V. Meeyoo, Catal. Commun. 8 (2007) 57.
10. Z.P. Qu, W.X. Huang, M.J. Cheng, X.H. Bao, J. Phys. Chem. B 109 (2005) 15842.
11. A. Sarkany, I. Sajo, P. Hargittai, Z. Papp, E. Tombacz, Appl. Catal. A: Gen. 293 (2005) 41.
12. Y. Sawayama, H. Shibahara, Y. Ichihashi, S. Nishiyama, S. Tsuruya, Ind. Eng. Chem. Res. 45 (2006) 8837.
13. L. Jin, K. Qian, Z.Q. Jiang, W.X. Huang, J. Mol. Catal. A: Chem. 274 (2007) 95.
14. H.J. Zhai, D.W. Sun, H.S. Wang, J. Nanosci. Nanotechnol. 6 (2006) 1968.
15. H.H. Patterson, R.S. Gomez, H.Y. Lu, R.L. Yson, Catal. Today 120 (2007) 168.

16. W. Gac, A. Derylo-Marczewska, S. Pasieczna-Patkowska, N. Popivnyak, G. Zhkocinski, J. Mol. Catal. A: Chem. 268 (2007) 15.
17. S.T. Zhang, R.W. Fu, D.C. Wu, W. Xu, Q.W. Ye, Z.L. Chen, Carbon 42 (2004) 3209.
18. S.J. Park, B.J. Kim, J. Colloid Interf.Sci. 282 (2005) 124.
19. D.J. Guo, H.L. Li, Carbon 43 (2005) 1259.
20. X. Lu, T. Imae, J. Phys. Chem. C 111 (2007) 2416.
21. P. Bera, K.C. Patil, V. Jayaram, M.S. Hegde, G.N. Subbanna, J. Mater. Chem. 9 (1999) 1801.
22. P. Bera, K.C. Patil, M.S. Hegde, Phys. Chem. Chem. Phys. 2 (2000) 373.
23. S. Bhattacharyya, A. Gabashvili, N. Perkasa, A. Gedanken, J. Phys. Chem. C 111 (2007) 11161.
24. P. Bera, K.C. Patil, M.S. Hegde, Phys. Chem. Chem. Phys. 2 (2000) 3715.
25. L. Kundakovic, M. Flytzani-Stephanopoulos, J. Catal. 179 (1998) 203.
26. L.S. Zhong, J.S. Hu, Z.M. Cui, L.J. Wan, W.G. Song, Chem. Mater. 19 (2007) 4557.
27. A. Murugadoss, A. Chattopadhyay, Nanotechnology 19 (2008) 015603.
28. J.L. Chen, X.F. Tang, J.L. Liu, E.S. Zhan, J. Li, X.M. Huang, W. Shen, J. Chem. Mater. 19(2007) 4292.
29. J.Q. Lu, J.J. Bravo-Suarez, A. Takahashi, M. Haruta, S. Ted Oyama, J. Catal. 232 (2005) 85.
30. W.L. Dai, Y. Cao, L.P. Ren, X.L. Yang, J.H. Xu, H.X. Li, H.Y. He, K.N. Fan, J. Catal.228 (2004) 80.
31. S. Ghosh, S. S. Acharyya, S. Adak, L. N. SivakumKonathala, Sasaki and R. Bal, Gre. Chem 16(2014)2826
32. T. Ung, L.M. Liz-Marzan, P. Mulvaney, J. Phys. Chem. B 103 (1999) 6770.
33. T. Hirakawa, P.V. Kamat, J. Am. Chem. Soc. 127 (2005) 3928.
34. X.M. Sun, Y.D. Li, Langmuir 21 (2005) 6019.
35. L. Chmielarz, M. Zbroja, P. Kuoetrowski, B. Dudek, A. Rafalska-Łasocha and R.Dziembaj. Them.Anal.and Cal 77 (2004) 115
36. P. Djomgoue, D. Njopwouo, J. Surf.Eng Mat. and Adv. Tech.3(2013) 275
37. D.I. Nistor, N.D. Miron, I.Siminiceanu, sci.study and Reserch.3 (2006) 1582.
38. N.N. Binitha, S. Sugunan, Micro. Meso.mate, 93(2006)82.
39. S. Shoval, S. Yariv, K. Michaelian, I. Lapidés, M. Bou- deuille and G. Panczer, J. Coll. and Inter- f. Sci, 21(1999)523.