



Synthesizing ZrO₂ Nanoparticle as a Catalyst Through Thermal Decomposition of Phenol-Zirconium Complexes in Order to Degradation of Harmful Organic Substances Under UV Light

Yahya Absalan*, Olga.V. Kovalchukova

General Chemistry

*Corresponding Author E-Mail: Yahyaabsalan2014@gmail.com

Abstract

This research was focused on synthesizing 3 zirconium complexes with phenol ligand and preparing ZrO₂ from synthesized complex through the method of thermal decomposition was the result of the work. Nanoparticles of ZrO₂ were synthesized after the complexes were decomposed in autoclaves at varies temperatures according to the different ligands.

FT-IR spectroscopy, UV-Vis spectroscopy, chemical analyzing and metal analyzing were used for investigating the complex as analyzing methods.

Furthermore, for the obtained nanoparticle, XRD, UV-Vis, FESEM and EDAX analyses were chosen for analyzing. Based on the result, synthesized ZrO₂ are able to remove harmful organic compounds under UV light.

Keywords: ZrO₂, ligand, phenol, catalyst, complex, nanoparticle

1. Introduction

Phenol is a toxic source for surface and ground water and it can be considered as a major pollution subject, so many methods have been suggested to remove this harmful substance, such as adsorption [1,2], chemical oxidation[3,4], photolysis[4,5] and electro photocatalysis[6].

Except of removing phenols and their derivatives, there is a way helping phenol not to be harmful but beneficial. Isolation metals by phenols make complexes to be used in many important areas, for instance complexes of phenol with S-block metals are useful for hydrogen storage [7], ion transport channels in biological systems [8], and carboxylation of an activated hydrogen in ketone [9], in the second group of metals, complex of metals with phenols as catalysts are applied for oxidation thin films made by dip coating [8] or organic chemical vapour deposition (OMCVD)[10]. In group 5 metals, they are used for catalytically active surface species [8], acting as precatalysts in process of polymers and catalysts for cyclohexene or cyclooctene epoxidation with H₂O₂ [8]. The application of the 6th group metal are categorized in Polymerization [11], and Conductive materials [8][12]. Group 7 is used for low temperature

applications[13] to be capable of selectively catalyzing the epoxidation of cyclic alkenes using O₂ and isobutyraldehyde. Group 8 is used as magnetism [14]and polymerization catalysis [8]. Complex of phenol with metals in group 9, 10, 11, 12 and 13 are able to be as catalyser [15–21]. Elements of group 3 are used as sensing and separations [19,22,23], voltammetric analysis of UO₂²⁺ by sulfonated calixarene derivatives electrostatically adsorbed onto gold electrodes[25], and aqueous extraction[24].

In this research, the focus is on complexation of zirconium which are very requested as catalysts in many industrial areas,

such as polymerization, oligomerization[25], hydrothermal stability of MOFs which is used also as catalyst [26,27], oxidation of organic compounds[28,29]

Some advantages of using these types of metals include low toxicity, non-endangered [30,31], easily prepared, less air-sensitive, huge economic benefit[29], and high selectivity[29], in addition, in an accurate investigation on activation of 4th group with bis-phenolate which has been done at Mitsui Chemicals developed, they illustrated the complexes are remarkably active for polymerization and copolymerization[32]beside of their high activation, the reactivity can be well controlled due to electron transfer ability to a variety of substrates[33], also in a particular experiment, Emmanuelle Despagnet-Ayoub and co-worker showed a switchable system by the cationic (bis-phenolate-Nheterocyclic carbene) zirconium complex which are able to be used for polymerization and oligomerization catalyst[34].

According to the recent researches, soft second-row donors are more useful than hard first-row donors for catalytic reactivity[35]. Kol et al. have focused on initial activity time of Titanium and Hafnium as catalyst for lactide polymerization and they showed the time can be reduced from 17 min for titanium (Ti) to 1 min for hafnium (Hf) [7], in addition, Okuda et al. showed zirconium complexes bearing tetradentate (OSSO)-type bis(phenolate) ligand are applied for ring opener for polymerization of lactide monomer.[36]

In this study, we synthesised new phenol-zirconium complexes and then their characterization and their application as catalyst were studied.

2. Experiment

2.1. Preparation of Complex



0.1 mol of $ZrCl_4$ was added to 10 ml of THF solvent at 25 C then the metal solution was added drop by drop to 0.2 mol of phenol solution which had stirred for 1 h in 10 ml THF (Room temperature) and then it was stirred for 12 h, then the solvent was vacuumed and extracted by CH_2Cl_2 after that again the solution was removed under vacuum to 2 ml and adding hexane was done to appear precipitation then to have bigger precipitates, it was put at -18 C for 1 day and it was filtered, the residual solid was washed three times with hexane and drying was carried out under vacuum. Obtained products were as follow: (72.0 mg (76%), pink powder for L1, 0,3556mg (65%), red powder L2, 72.0 mg (76%), brown powder L3)

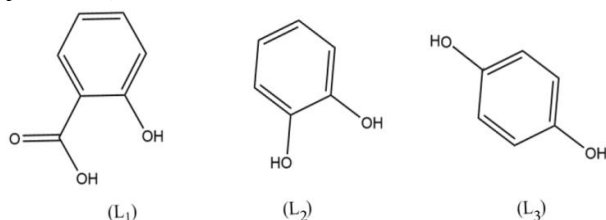


Fig.1. Ligands used in the experiment; (a)salicylate, (b)hydroquinone and (c) catechol

2.2. Preparing ZrO₂ Nanoparticle

The obtained complexes was decomposed at temperature between 25-700 °C. All complexes were decomposed in a dynamic mode, at a rate of 10 deg/min in platinum crucibles.

3. Characterization

3.1. CHN Analysis of Complex

The results of the chemical analysis with formulae of the complexes, are tabued (Table 1). The analyze was repeated two times.

Table 1. CHN analysis of the complexes

No	Substance	M, g/mol	Ti (Zr)	C	N (Cl)	H
1	$ZrCl_2(L^1)_2$	434,34	21,00/ 21,34	38,71/38,93	16,33/ 16,47	1,86 / 3,33
2	$ZrCl_2(L^2)_2$	378,32	24,11/ 23,76	38,10/38,45	18,74/ 18,87	2,13 / 2,65
3	$ZrCl_2(L^3)_2$	378,32	24,11/ 23,98	38,10/38,24	18,74/ 18,92	2,13 / 2,78

3.2. FT-IR Spectroscopy of Complex

The displacement of absorption bands of ligand in IR spectra during the transition from uncoordinated organic molecules to zirconium complexes (Fig. 2) indicates the coordination bonds are formed. The low-frequency change of the $\nu(C=O)$ band from 1659 cm^{-1} in the H2L1 spectrum to 1617 cm^{-1} in the $ZrCl_2(L^1)_2$ spectrum (Fig. 2) confirms the deprotonation of the carboxyl group. The strong hygroscopicity of the compounds leads to the appearance in the peaks of metal complexes of an intense broad absorption band in the 3600-3000 cm^{-1} region.

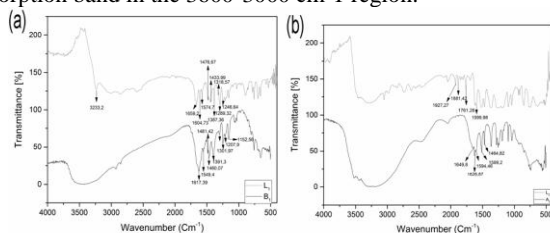


Fig. 2. IR absorption spectra: (a) H2L1 (gray line) and $ZrCl_2(L^1)_2$ (black line), (b) H2L2 (gray line) and $ZrCl_2(L^2)_2$ (black line)

3.3. UV-Vis analysing of complexes

Changes in the electronic spectra of the organic ligands H2L1 and H2L3 with the gradual addition of $ZrCl_4$ are observable in Fig. 3. As can be seen, the addition of an ethanol solution of $ZrCl_4$ to H2L1 and H2L3 solutions, it leads to a shift in absorption band of the ligands. Being isobestic points indicates the equilibrium of complexation reactions. Consequently, zirconium (IV) also forms complex compounds with aromatic hydroxyl-containing ligands in ethanol solutions.

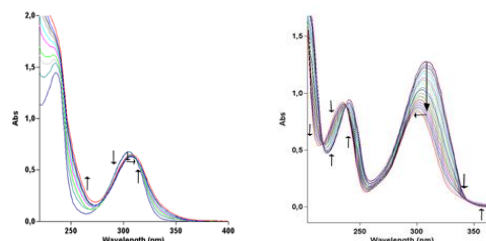


Fig. 3. UV-Vis absorption of ethanol solutions of compounds; (a) H2L1 and (b) H2L3 with an ethanol solution of zirconium chloride

3.4.X-ray Analysis of Nanoparticles

X-ray diffraction spectra for the ZrO_2 system is observable in Fig. 4. The most intense peak is recognisable for Zr. It was found the obtained nanoparticles to be 19-24 nm. In all of the spectra the peaks of the ZrO_2 matrix in the cubic phase are evident. It illustrates moving of phase transition in the ZrO_2 matrix from the cubic phase to the baddeleyte phase (monoclinic system). This type of transition is suppressed in the analogous treatment in H2

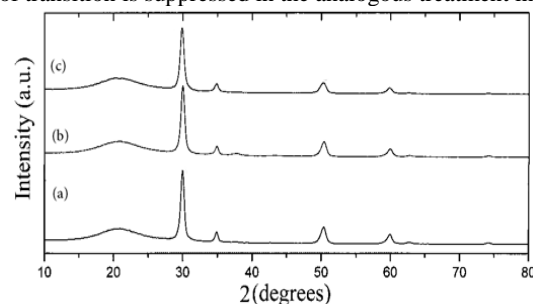


Fig. 4. XRD pattern of ZrO_2 nanoparticles; (a) $Zr(L^1)_2$, (b) $Zr(L^2)_2$, (c) $Zr(L^3)_2$

3.5. UV-Vis Spectra of Nanoparticles

The curves of $(\alpha h\nu)^2$ against $h\nu$ was calculated to obtain energy band-gap (E)(Fig.5). The ZrO_2 nanoparticles are able to absorb UV light (Fig.5). Because of being metal in the lattice, the λ_{max} goes to the red light. In addition, the absorption of light obeys the following charge-transfer transition; $O^{2-} \rightarrow Zr^{4+}$. The relativity of the energy band gap with the size of the obtained ZrO_2 is direct but here this relationship is not considered, it can be result in active surface of the samples, because increasing active surface leads E decreased.

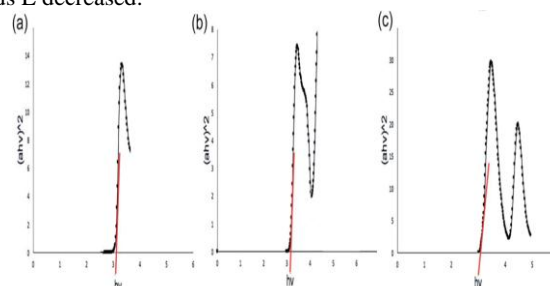


Fig. 5. Graph of energy band gap for ZrO_2 ; (a) $Zr(L^1)_2$, (b) $Zr(L^2)_2$, (c) $Zr(L^3)_2$

3.6. FESEM and EDAX Analysis

To study the morphology of the nanoparticles (ZrO_2) FESEM images were used (Fig.6). spherical shape can be observed in ZrO_2 . The size for all nanoparticles are between 24-27.5 nm but this size is not obtained for ZrL_2^2 with size between 19-22.5 nm. Some agglomeration is found which is caused in calcination nanoparticles. EDAX was applied to obtain the amount of the elements (Fig.6, right picture). Based on the amount of the elements (table Inserted Fig 6), synthesized ZrO_2 are in a proper stoichiometric ratio. The Zr and O peaks are observable in the pattern (Fig.6)

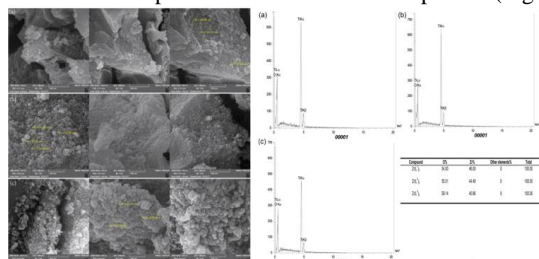


Fig. 6. FESEM and EDAX pattern of ZrO_2 ; (a) $Zr(L^1)_2$, (b) $Zr(L^2)_2$, (c) $Zr(L^3)_2$

4. Conclusion

ZrO_2 nanoparticle was prepared by three phenol-zirconium complexes and analyzing was done for both complex and nanoparticle.

In complex, purity and stability were found in all complexes, zirconium is coordinated by ligands with two atoms of oxygen in all cases. ZrO_2 were obtained at low temperature which is in industry has to be thought and in addition, it's enough uniform. Photocatalytic ability of the nanoparticles and ability in receiving UV light were proved by the result of the UV-Vis light and energy band gap.

Acknowledgement

The publication was prepared with the support of the «RUDN University Program 5-100»

References

- [1] A.S. H.T. Muhammad Saada, Jawariya Khanb, Uzma Hameedb, Ultrason. Sonochem. 34 (2017) 600–608.
- [2] M.A.M.-M. V.H.-M. I.A. Aguayo- Villarreal, N.A. Rangel-Vázquez, J. Mol. Liq. 196 (2014) 326 – 333.
- [3] C.Y. H.S. Fuat Güzel, Gülbahar Akkaya Saygılı, Filiz Koyuncu, J. Clean. Prod. (2017).
- [4] J. Saini, V.K. Garg, R.K. Gupta, N. Kataria, J. Environ. Chem. Eng. 5 (2017) 884–892. doi:10.1016/j.jece.2017.01.012.
- [5] S. Aliouche, K. Djebbar, T. Sehili, Water Treat. 3994 (2015). doi:10.1080/19443994.2015.1090915.
- [6] A. Cruz-Rizo, S. Guti??rrez-Granados, R. Salazar, J.M. Peralta-Hern??ndez, Sep. Purif. Technol. 172 (2017) 296–302. doi:10.1016/j.seppur.2016.08.029.
- [7] E. Sergeeva, J. Kopilov, I. Goldberg, M. Kol, Inorg. Chem. 49 (2010) 3977–3979. doi:10.1021/ic100390x.
- [8] Y. Li, K. Zhao, C. Redshaw, C. Road, B.A.M. I. T.A. Hanna, F. Worth, PATAI's Chem. Funct. Groups. (2014). doi:10.1002/9780470682531.pat0616.
- [9] S.J.D. Marco Coletta, Euan K. Brechin, 2016. https://link.springer.com/chapter/10.1007/978-3-319-31867-7_25.
- [10] I.S.A. and A.I.K. D. R. Sharafutdinova, O. B. Bazanova, A. A. Murav'ev, S. E. Solov'eva, Russ. Chem. Bull. Int. Ed. 64 (2015) 1823–1828.
- [11] C. Redshaw, D. Homden, D.L. Hughes, A. Wright, M.R.J. Elsegood, Dalt. Trans. (2009) 1231–1242. doi:10.1039/b813313a.
- [12] T.M.S. A. Vigalok, Adv. Mater. (2002) 368–371. doi:10.1002/1521-4095(20020304)14:5<368::AID-ADMA368>3.0.CO;2-I.
- [13] E.K.B. Georgios Karotsis, Chemie Int. Ed. 48 (2009) 9928–9931. doi:10.1002/anie.200905012.
- [14] S.J.D. and E.K.B. Sergio Sanz, Kerry Ferreira, Ruairaidh D. McIntosh, Chem. Commun. 47 (2011) 9042–9044. doi:10.1039/c1cc13055b.
- [15] E. Bukhaltsev, L. Frish, Y. Cohen, A. Vigalok, Org. Lett. 7 (2005) 5123–5126. doi:10.1021/ol051741d CCC.
- [16] R.V.S. G A Evtugyn, E E Stoikova, Russ. Chem. Rev. 79 (2010) 1071–1097. doi:10.1070/RC2010v079n12ABEH004107.
- [17] N.D. Bahram Mokhtari, Kobra Pourabdollah, J Incl Phenom Macrocycl Chem. 69 (2011) 1–55. doi:10.1007/s10847-010-9848-7.
- [18] K.P. Bahram Mokhtari, J. Coord. Chem. 64 (2011) 3081–3091. doi:10.1080/00958972.2011.613462.
- [19] N.D. Bahram Mokhtari, Kobra Pourabdollah, Chromatographia. 73 (2011) 829–847. doi:10.1007/s10337-011-1954-1.
- [20] N.D. Bahram Mokhtari, Kobra Pourabdollah, J Radioanal Nucl Chem. 287 (2011) 921–934. doi:10.1007/s10967-010-0881-1.
- [21] D.M. Roundhill, I.B. Solangi, S. Memon, M.I. Bhangar, M. Yilmaz, Pak. J. Anal. Environ. Chem. 10 (2009) 1–13.
- [22] S.P. (Founding E. Jacob Zabicky (Editor), Zvi Rappoport (Series Editor), Joel F. Liebman (Series Editor), Ilan Marek (Series Editor), The Chemistry of Metal Phenolates, Wiley Authenticity Guarantee, United States, 2014.
- [23] V. Arora, H.M. Chawla, S.P. Singh, ARKAT USA, Inc. 2007 (2007) 172–200. <http://pdf.easechem.com/pdf/21/4bca107e-b2df-4aa2-a995-db3c15b02f94.pdf>.
- [24] D.K.S. and K.N.R. Chengbao Ni, Chem. C Ommun. 47 (2011) 6392–6394. doi:10.1039/c1cc11329a.
- [25] C. Boulho, H.S. Zijlstra, A. Hofmann, P.H.M. Budzelaar, S. Harder, Chem. - A Eur. J. 22 (2016) 17450–17459. doi:10.1002/chem.201602674.
- [26] G. Mouchaham, L. Cooper, N. Guillou, C. Martineau, E. Elkaïm, S. Bourelly, P.L. Llewellyn, C. Allain, G. Clavier, C. Serre, T. Devic, Angew. Chemie - Int. Ed. 54 (2015) 13297–13301. doi:10.1002/anie.201507058.
- [27] A.J. Howarth, Y. Liu, P. Li, Z. Li, T.C. Wang, J.T. Hupp, O.K. Farha, Nat. Rev. Mater. (2016) 15018. doi:10.1038/natrevmats.2015.18.
- [28] R. Yu, F.-S. Xiao, D. Wang, J. Sun, Y. Liu, G. Pang, S. Feng, S. Qiu, R. Xu, C. Fang, Catal. Today. 51 (1999) 39–46. doi:10.1016/S0920-5861(99)00006-1.
- [29] S. Khare, P. Shrivastava, R. Chokhare, J.S. Kirar, S. Parashar, J. Porous Mater. 24 (2017) 855–866. doi:10.1007/s10934-016-0325-6.
- [30] E. Le Roux, 2015.
- [31] M.D. Jones, 2015.
- [32] S. Chen, X. Zhang, H. Ma, Y. Lu, Z. Zhang, H. Li, Z. Lu, N. Cui, Y. Hu, J. Organomet. Chem. 690 (2005) 4184–4191. doi:10.1016/j.jorganchem.2005.06.029.
- [33] S. Barroso, P. Adão, A.M. Coelho, J.C. Pessoa, A.M. Martins, J. Mol. Catal. A Chem. 412 (2016) 107–116. doi:10.1016/j.molcata.2015.11.021.
- [34] E. Despagne-Ayoub, M.K. Takase, L.M. Henling, J.A. Labinger, J.E. Bercaw, Organometallics. 34 (2015) 4707–4716. doi:10.1021/acs.organomet.5b00472.
- [35] M.K. and J.O. Andreas Sauer, Andreas Kapelski, Christophe Fliedel, Samuel Dagorne, J. Dalt. Trans. 42 (2013) 9007–9023. doi:10.1039/C3DT00010A.
- [36] J.-C. Buffet, A.N. Martin, M. Kol, J. Okuda, Polym. Chem. 2 (2011) 2378. doi:10.1039/c1py00266j.