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Research Article

Synthesis and characterization of bentonite-based zinc complexes

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ABSTRACT

In chemical reactions, the use of environmentally friendly catalysts obtained by transporting transition metals on solid or polymer carrier materials has become quite common recently. Studies in which zinc complexes are used as homogeneous and heterogeneous catalysts are frequently encountered in the literature. In addition to many advantages of homogeneous catalysts, disadvantages include difficulty separating from the reaction medium, recycling, and limited chemical-thermal stability. Solving problems can be solved by using solid catalyst support materials and transferring the active ingredients to these materials. Therefore, catalysts prepared by transporting transition metal complexes onto solid supports have become interesting for researchers. Natural or processed clays can be used as catalysts or catalyst carriers and have many uses due to their cheapness and abundance. In this study, natural Enez/Edirne bentonite was acid-activated (HB) and converted to organo-clay (HB/CTAB) with hexadecyltrimethylammonium bromide (CTAB). Then, heterogeneous catalysts were prepared by direct transport of the synthesized $[Zn(acac)_2H_2O]$ or $[Zn(p\text{-}H_2NC_6H_4COO)_2]1.5H_2O$ complexes onto modified clays separately. The catalysts have been characterized by X-ray diffraction, Fourier transform infrared spectroscopy, thermogravimetric analysis, surface scanning electron microscope, and Brunauer-Emmett-Teller specific surface analysis methods.

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1. INTRODUCTION

The heterogeneous catalyst preparation method by transporting transition metal complexes on solid support materials has become attractive in recent years due to ease of preparation, shape selectivity, recycling of catalysts, product purification, and more accessible transport properties [1, 2]. Metal complexes are used as homogeneous catalysts in various reactions. Although homogeneous catalysts have some advantages, they also have disadvantages as they cannot be used as a sustainable source for reasons such as separating the catalyst from the reaction medium, recycling the catalyst, and limited chemical and thermal stability [3, 4]. These problems can be solved using solid catalyst support materials consisting of inorganic or polymer matrices and transporting the active ingredients onto these support materials [5–7]. Methods such as placing on the support solid and trapping the complex have several advantages over non-covalent interactions [8–10].

Due to their cheapness and abundance, natural or modified clays are used for the chemical industry, agriculture, surface coating, and environmental purposes and directly as catalysts or catalyst carriers [11–13]. Bentonite is clay whose main component is the montmorillonite mineral and has a 2:1 layered structure. There is an octahedral alumina layer between the two tetrahedral silica layers. In montmorillonite containing a dioctahedral structure, 2/3 of the octahedral places are covered with Al^{3+} cations.

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As a result of the replacement of Al^{3+} ions with Mg^{2+} and Fe^{2+}/Fe^{3+} ions (isomorphic substitution), a net negative charge is formed on the surface. These negative charges are balanced by hydratable cations such as Na^+, Mg^{2+}, and Ca^{2+} between successive 2:1 layers [10, 14–18].

Studies on bentonite-based catalysts containing various zinc compounds such as zinc oxide and zinc sulfide have been seen in the literature [19–21], but no study has been found involving the transport of acetylacetonate and p-aminobenzoic acid-based zinc complexes onto bentonite.

This study it is aimed to develop new heterogeneous catalysts by transporting synthesized $[Zn(acac)_2H_2O]$ or $[Zn(p\text{-}H_2NC_6H_4COO)_2]1.5H_2O$ complexes directly onto bentonite and modified bentonite. For this purpose, Enez/Edirne bentonite was treated with acetic acid and acid-activated (HB), and this bentonite was converted into organo-clay (HB/CTAB) by interacting with hexadecyltrimethylammonium bromide (CTAB). Catalysts were prepared by transporting the synthesized zinc-based complexes onto the obtained modified clays separately. Characterization of the synthesized catalysts was performed by the methods such as Fourier transform infrared spectroscopy (FTIR), surface scanning electron microscope (SEM), X-ray diffraction (XRD), thermogravimetric analysis (TG/DTG), and Brunauer-Emmett-Teller (BET) specific surface analysis.

2. MATERIALS AND METHODS

2.1. Materials

Acetylacetone (2,4-pentadione) (Merck), zinc nitrate hexahydrate (Merck), zinc sulfate heptahydrate (Merck), ethyl acetate (Fluka), p-aminobenzoic acid (PABA) (Fluka), hexadecyltrimethylammonium bromide (CTAB) (Merck) and used other chemicals are analytical reagent grade and no purification was made before use. A natural clay Enez/Edirne bentonite was used in the study.

Refrigerating-heating circulator (Polyscience 9006), magnetic shaker (Heildolp MR 3001), grinder (Retsch PM 200), and pH meter (Denver 215) were used in the experiments.

2.2. Preparation of $[Zn(acac)_2H_2O]$ Complex

0.02 mol of acetylacetone (2,4-pentadione) and 0.02 mol sodium hydroxide were dissolved in 10 mL of ultrapure water. This solution was slowly added to a 0.01 mol zinc sulfate heptahydrate solution dissolved in 10 mL of water. The resulting mixture was stirred for 1 hour. The resulting white precipitate was filtered under a vacuum, washed with distilled water, and left to dry at room conditions. The resulting raw product (Fig. 1) was recrystallized from 20 mL of hot ethyl acetate solution containing 1 mL of acetylacetone [22].

2.3. Synthesis of $[Zn(p\text{-}H_2NC_6H_4COO)_2]1.5H_2O$ Complex from Stratified Zinc Hydroxide

A solution of 10 mL PABA (3.6 mmol) was titrated with $Zn(NO_3)_2.6H_2O$ solution (3.65 mmol). One molal of NaOH solution was used to adjust the pH of the solution to 7. The mixture was stirred for 1 hour and then filtered. The filtrate was held for several days to form $[Zn(p\text{-}H_2NC_6H_4COO)_2]1.5H_2O$ ($[Zn(PABA)_2]1.5H_2O$) crystals, and the crystals were washed several times with distilled water, filtered and dried (Fig. 2) [23].

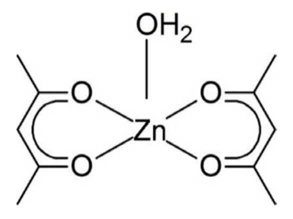

Figure 1. Structure of $[Zn(acac)_2H_2O]$ complex.

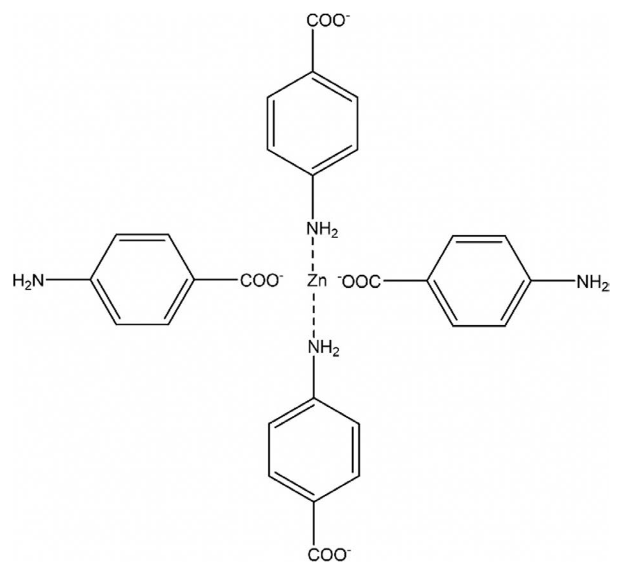

Figure 2. Structure of $[Zn(PABA)_2]1.5H_2O$ complex.

2.4. Preparation of Acid Activated Clay

0.1 M CH_3COOH solution was added to 100 g of natural bentonite and mixed in a magnetic shaker for 6 hours. The mixture was centrifuged, and the intermediate phase was taken from the three phases and washed with ultrapure water many times. The resulting acid-activated clay (HB) was dried at 110 °C for 6 hours, ground at 500 rpm for 15 minutes, and passed through a 70-mesh sieve [24].

2.5. Preparation of Organo-clay

25 g of HB was slowly added to the 250 mL solution of 5 g CTAB. The mixture was stirred for 18 hours at 25 °C, filtered, and washed several times with ultrapure water (controlled with 0.1 M $AgNO_3$ solution) to remove Br- ions. The obtained organo-clay (HB/CTAB) was dried at 110 °C for 6 hours, ground at 500 rpm for 15 minutes, and passed through a 70-mesh sieve [25].

2.6. Transport of Complexes on Modified Clays

0.360 mmol $[Zn(acac)_2H_2O]$ complex was dissolved in 200 mL of chloroform, and 2.4 g of HB was slowly added to this solution. The suspension was refluxed at 300 rpm at 75 °C for 24 hours. The mixture was rested, filtered, and the product was dried at 80 °C, and the transport of $[Zn(acac)_2H_2O]$ complex on HB was achieved (Fig. 3). The resulting complex was named ($[Zn(acac)_2H_2O]$-HB) [26].

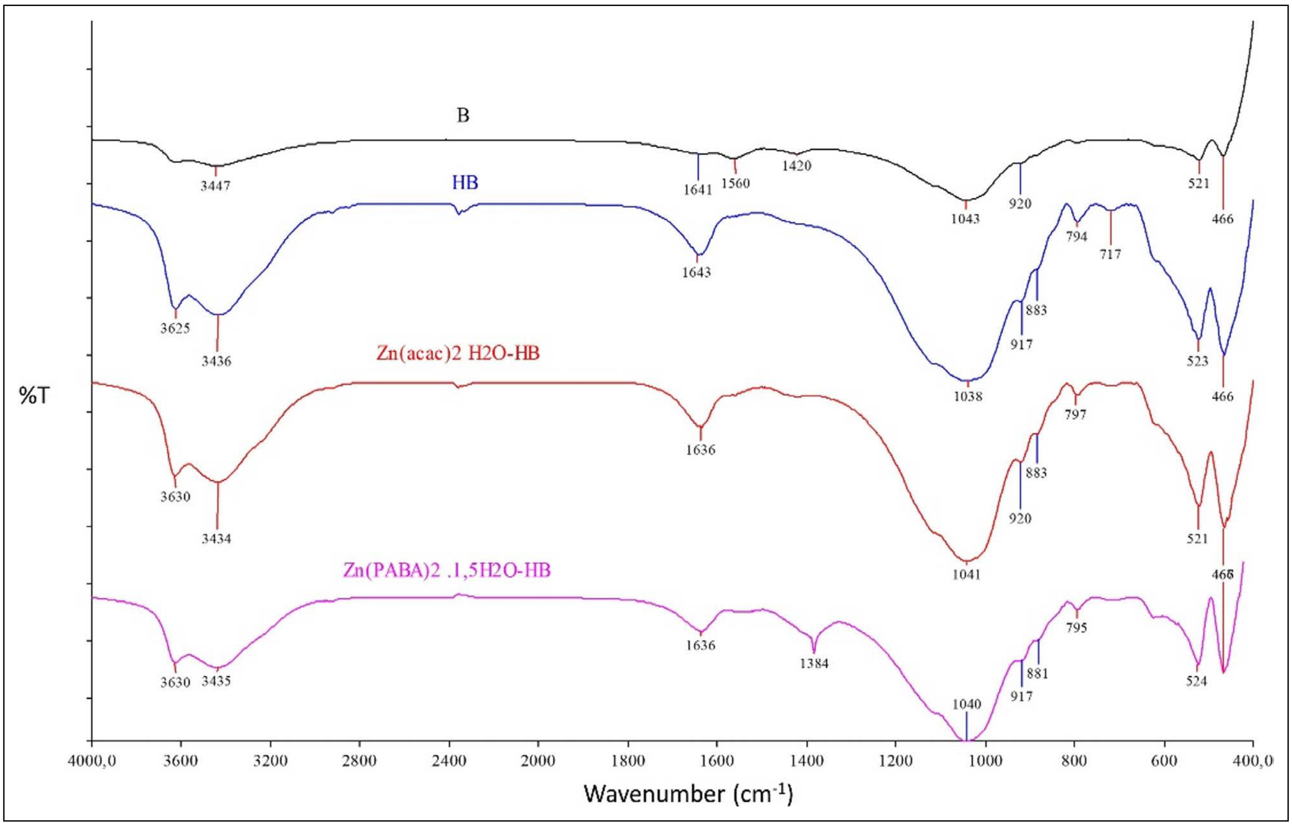

Figure 3. FTIR spectra of HB-based catalysts, including B, HB, and zinc complexes.

In the study, the transport of $[Zn(PABA)_2]1.5H_2O$ complex on HB and the transport of $[Zn(acac)_2H_2O]$ or $[Zn(PABA)_2]1.5H_2O$ complexes on HB/CTAB were also repeated according to the method described above for HB. The prepared catalysts were named as ($[Zn(PABA)_2 1.5H_2O]$-HB), ($[Zn(acac)_2H_2O]$-HB/CTAB), ($[Zn(PABA)_2 1.5H_2O]$-HB/CTAB), respectively.

2.7. Structure Analysis of Complexes

The synthesized catalysts were characterized by using X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), thermogravimetric analysis (TG/DTG), surface scanning electron microscope (SEM), and Brunauer-Emmett-Teller (BET) specific surface analysis methods. XRD analyses were performed with a Rigaku-Rint 2200/PC (Ultima 3) diffractometer using Cu Kα radiation at a scanning speed of 0.4 degrees/minute in the 2θ range of 2–10°. Perkin–Elmer Spectrum BX-II Model FTIR spectrophotometer was used for FTIR analysis. KBr pellets were analyzed with a resolution of 4 cm^{-1} in the range of 4000–400 cm^{-1} as an average of 25 scans. TG/DTG analyses of the complexes were performed with Perkin Elmer Diamond TG/DTG analyzer in porcelain pans at 25–1000 °C at a heating rate of 10 °C/min under a nitrogen atmosphere. SEM analyses were performed with FEI Quanta FEG 250 SEM Scanning Electron Microscope at an acceleration voltage of 5 kV, and before the analysis, the surfaces of the complexes were coated with a gold layer. The specific surface areas of the samples were determined by the Brunauer-Emmett-Teller (BET) method after N_2 adsorption-desorption at 77 K with the Quantachrome Corporation Autosorb-6 device.

Table 1. 2θ/° and d (Å) values of catalysts

Sample	2θ/°	d/Å
B	7.04	12.55
HB	7.12	12.40
$[Zn(acac)_2H_2O]$-HB	7.80	11.32
$[Zn(PABA)_2]1.5H_2O$-HB	8.54	10.34
HB/CTAB	5.22	16.92
$[Zn(acac)_2H_2O]$-HB/CTAB	5.28	16.72
$[Zn(PABA)_2]1.5H_2O$-HB/CTAB	5.72	15.44

3. RESULTS AND DISCUSSION

3.1. XRD Analysis

XRD patterns and results of the complexes are given in Figure 4 and Table 1. With the acid modification (HB), the reflection peak (2θ/°) and basal spacing (d/Å) values of the bentonite's (001) surface slightly changed, and it was observed that the basal spacing value was increased from 12.55 Å to 16.92 Å and the value of 2θ/° shifted from 7.04 Å to 5.22 Å with the organo-clay modification (HB/CTAB). In all synthesized catalysts, it is considered that $[Zn(acac)_2H_2O]$ and $[Zn(PABA)_2]1.5H_2O$ complexes have been placed between the layers of HB and HB/CTAB.

3.2. FTIR Analysis

FTIR spectra of the catalysts are given in Figure 3 and Figure 5. The stretching and bending bands observed in the spectrum of bentonite (Fig. 3) at 3630 cm^{-1} and 883 cm^{-1}, respectively, are Al-Mg-OH vibrations, considered

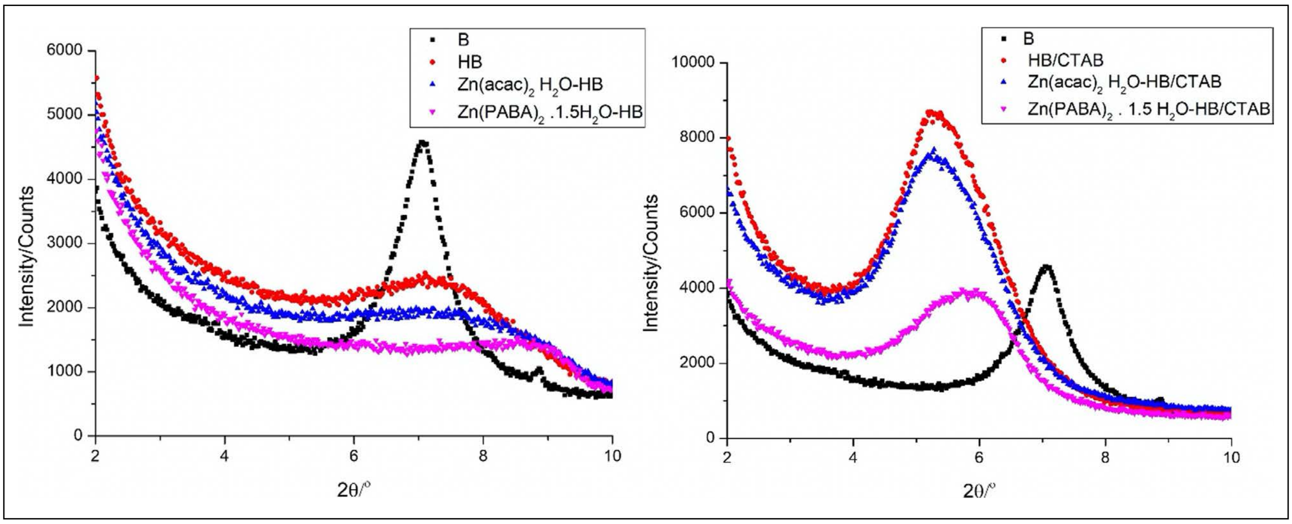

Figure 4. XRD patterns of zinc complex /modified bentonite-based catalysts.

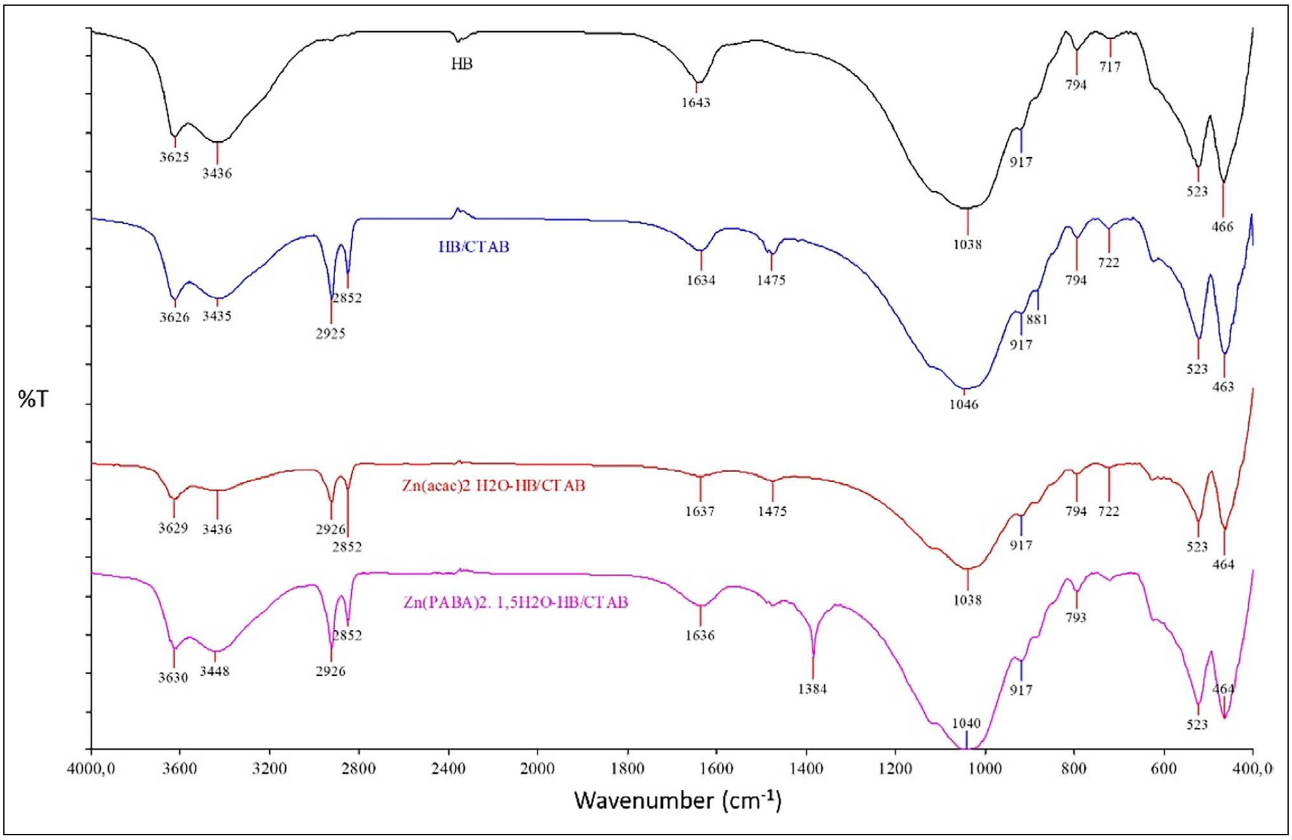

Figure 5. FTIR spectra of HB/CTAB-based catalysts, including HB, HB/CTAB, and zinc complexes.

characteristic bands of smectite minerals containing large amounts of Al in the octahedral layer. The -OH vibrations about water that exist in bentonite were observed at 3448 cm^{-1} and 1621 cm^{-1}, respectively. The bands observed in 1600–1400 cm^{-1} are attributed to Si-O-Si stretching's [27]. The bands observed at 1041 cm^{-1} and 792 cm^{-1} represent the Si-O- in the plane for the layered silicates and Si-O stretching vibrations, indicating the presence of quartz and silica, respectively [28]. The bands belong to Al-Al-OH, octahedral Si-O-Al and Si-O-Si bending vibrations were observed at 920 cm^{-1}, 521 cm^{-1} and 466 cm^{-1}, respectively [29]. When the FTIR spectra of HB and B were compared, it was seen that there were small shifts in the frequencies of the bands, and their intensities increased considerably. The bands in the range of 1600–1400 cm^{-1} observed in the spectrum of bentonite have undergone significant changes in the spectrum of HB, and some bands have not been observed at all.

The bands observed in the HB/CTAB are generally consistent with those observed in the spectrum of B and HB (Fig. 5). The -CH stretching bands of methyl and methylene groups observed at 2926 cm^{-1} and 2852 cm^{-1} in the spectrum of HB/CTAB are characteristic of organo-bentonite. It can be considered that the bands

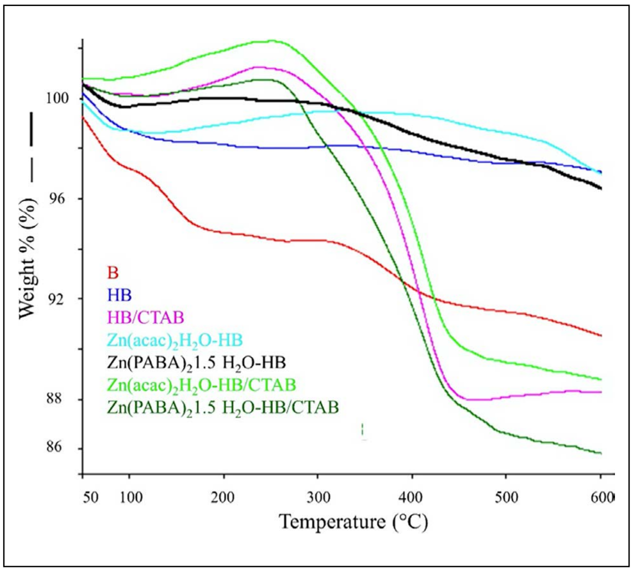

Figure 6. TG/DTG curves of HB/CTAB-based catalysts, including B, HB, HB/CTAB, and zinc complexes.

observed at 1476 cm^{-1} belong to the deformation of the methyl and methylene groups in organo-bentonite or the NH_4^+ bending vibration and that these bands overlap with each other. Moreover, the stretching vibration band of the NH_4^+ group is also considered to be covered by the -OH stretching band of water in bentonite. On the other hand, when the bands in the spectra of raw materials HB and HB/CTAB were compared with the bands in the spectra of HB and HB/CTAB-based catalysts containing [Zn(acac)$_2$H$_2$O] and [Zn(PABA)$_2$]1.5H$_2$O complexes, no significant difference in the intensities of the bands but only small shifts in their frequencies were observed.

3.3. TG/DTG Analysis

The thermal stability of all synthesized catalysts was evaluated by the obtained thermograms (Fig. 6) and thermogravimetric analysis data (Table 2).

Thermograms of HB and HB/CTAB samples agree with each other (Fig. 6). The first step of the two different degradation steps corresponds to the loss of moisture in the structures. In the second decomposition step, while the water molecule in the bentonite structure gives a decomposition of approximately 6.85%, it is seen that the amount of water due to the interlayer ion exchange decreases (0.76%) in the HB structure. The second degradation step in the thermogram of the organo-clay (HB/CTAB) corresponds to the decay of the CTAB molecule (13.17%). When the second step decompositions of [Zn(PABA)$_2$]1.5H$_2$O-HB and [Zn(acac)$_2$H$_2$O]-HB complexes were examined, the loss of 1.5 hydrate water and 1 mole of water molecule bound as a ligand were determined as 4.06% and 3.34%, respectively. In the second step of decomposition of the [Zn(acac)$_2$H$_2$O]-HB/CTAB complex, it can be seen that (Table 2), the CTAB molecule decomposes, and the water molecule remains in the structure. On the other hand, in the [Zn(PABA)$_2$]1.5H$_2$O-HB/CTAB complex, CTAB and 1.5 hydrate water decompose together.

Table 2. TG/DTG analysis data of HB/CTAB-based catalysts, including B, HB, HB/CTAB, and zinc complexes

Sample	**First step Weight loss (%)**	**Second step Weight loss (%)**
B	1.92	6.85
HB	2.28	0.76
HB/CTAB	0.56	13.17
[Zn(acac)$_2$H$_2$O]-HB	1.69	3.34
[Zn(PABA)$_2$]1.5H$_2$O-HB	0.34	4.06
[Zn(acac)$_2$H$_2$O]-HB/CTAB	1.53	13.57
[Zn(PABA)$_2$]1.5H$_2$O-HB/CTAB	0.27	15.13

Table 3. Specific surface areas of catalysts

Sample	**A_{BET} (m^2/g)**
B	65
HB	64
HB/CTAB	25
[Zn(acac)2H2O]-HB	67
[Zn(PABA)2]1.5H2O-HB	31
[Zn(acac)2.H2O]-HB/CTAB	34
[Zn(PABA)2]1.5H2O-HB/CTAB	26

3.4. SEM Analysis

SEM images of the catalysts are shown in Figure 7. When the surfaces of the catalysts are examined for ×5000 magnification, unlike B, HB, HB/CTAB, it has been observed that the particles in the catalysts containing the complexes are in the form of aggregates, and these aggregates are smaller and scattered in the catalysts containing the [Zn(PABA)$_2$]1.5H$_2$O complex compared to the catalysts containing [Zn(acac)$_2$H$_2$O].

3.5. BET Analysis

The results of the BET analysis of the samples are given in Figure 8 and Table 3, respectively. It was observed that the surface area of bentonite (65 m^2/g) did not change so much with the acid activation (64 m^2/g). In the organo-clay modification, the surface area decreased significantly (25 m^2/g), as expected, with the penetration of the "CTAB" molecule between the layers of HB. The surface areas of the synthesized [Zn(PABA)$_2$]1.5H$_2$O-HB and [Zn(PABA)$_2$]1.5H$_2$O-HB/CTAB catalysts decreased due to the large molecular structure of the "PABA" ligand. However, the same manner did not observe in [Zn(acac)$_2$H$_2$O]-HB catalyst due to the smaller molecular structure of the "acac" ligand, while the surface area of [Zn(acac)$_2$.H$_2$O]-HB/CTAB catalyst relatively decreased depending on "CTAB" molecule.

4. CONCLUSIONS

Clays and clay minerals are used directly as catalysts or support solids in many chemical processes. Today, natural and unprocessed clays are only exported

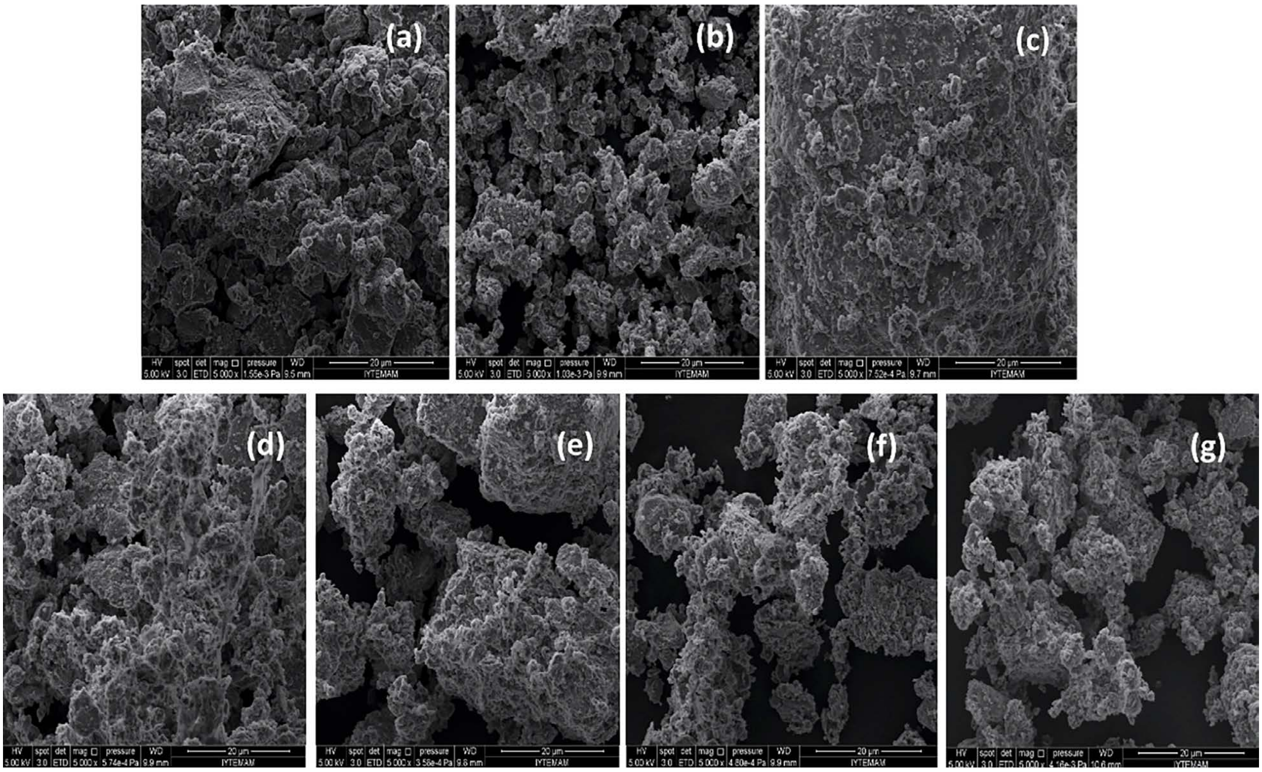

Figure 7. SEM photos of synthesized catalysts at a magnification of ×5000 **(a)** B, **(b)** HB, **(c)** HB/CTAB, **(d)** [Zn(acac)$_2$H$_2$O]-HB, **(e)** [Zn(acac)$_2$H$_2$O]-HB/CTAB, **(f)** [Zn(PABA)$_2$]1.5H$_2$O-HB, **(g)** [Zn(PABA)$_2$]1.5H$_2$O-HB/CTAB.

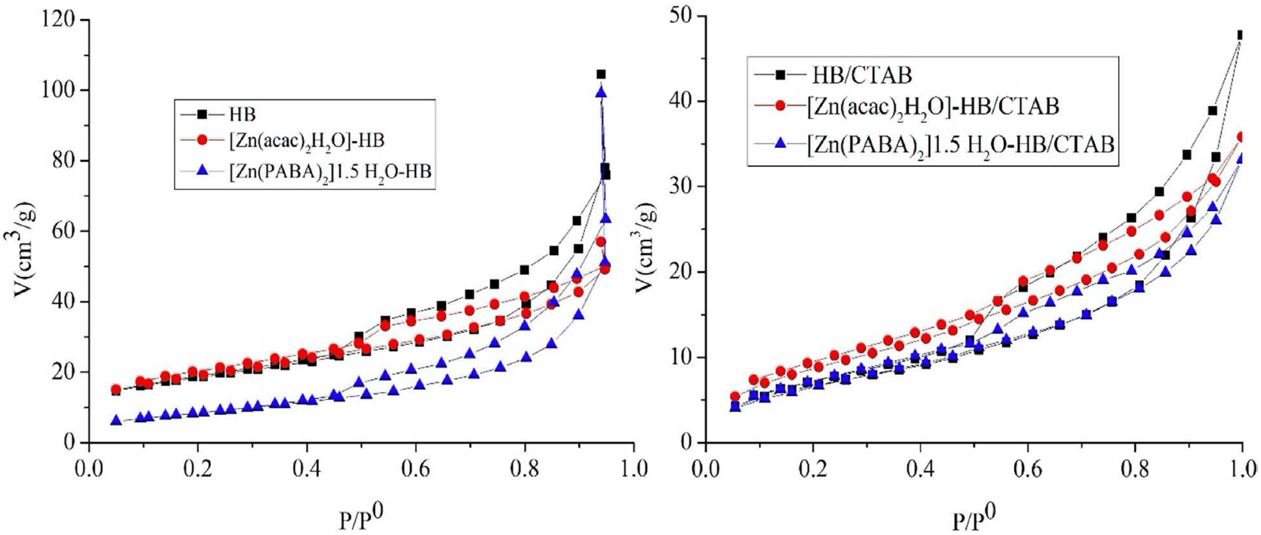

Figure 8. Multi-point BET adsorption-desorption isotherms of HB, HB/CTAB, and synthesized catalysts from N$_2$ gas phase at 77K.

at a very low cost. With this study, an environmentally friendly method has been developed, and a new area of use has been opened for bentonite-type clays, which are abundant and naturally found in our country. According to XRD results, it is considered that [Zn(acac)$_2$H$_2$O] and [Zn(PABA)$_2$]1.5H$_2$O complexes have been placed between the layers of acid-activated and organo-clays. Synthesized catalysts have been observed in aggregates, unlike their raw materials, especially in the catalysts containing the [Zn(PABA)$_2$]1.5H$_2$O complex. These aggregates are smaller and scattered due to the SEM images. The surface area of bentonite did not change so much with the acid activation, while it was significantly decreased in the organo-clay modification with the penetration of the "CTAB" molecule between the layers of acid-activated clay. As a result, the prepared bentonite-based zinc catalysts have the potential to be used as heterogeneous catalysts in various reactions.

ETHICS

There are no ethical issues with the publication of this manuscript.

DATA AVAILABILITY STATEMENT

The authors confirm that the data that supports the findings of this study are available within the article. Raw data that support the finding of this study are available from the corresponding author, upon reasonable request.

CONFLICT OF INTEREST

The authors declare that they have no conflict of interest.

FINANCIAL DISCLOSURE

The authors declared that this study has received no financial support.

PEER-REVIEW

Externally peer-reviewed.

REFERENCES

[1] Parmeggiani, C., Matassini, C., & Cardona, F. (2017). A step forward towards sustainable aerobic alcohol oxidation: new and revised catalysts based on transition metals on solid supports. *Green Chemistry*, 19(9), 2030-2050. [CrossRef]

[2] Xia, Y., Campbell, C. T., Roldan Cuenya, B., & Mavrikakis, M. (2021). Introduction: Advanced materials and methods for catalysis and electrocatalysis by transition metals. *Chemical Reviews*, 121(2), 563-566. [CrossRef]

[3] Zhang, Y., Li, W., Wang, J., Jin, J., Zhang, Y., Cheng, J., & Zhang, Q. (2023). Advancement in utilization of magnetic catalysts for production of sustainable biofuels. *Frontiers in Chemistry*, 10, Article 1106426. [CrossRef]

[4] Miceli, M., Frontera, P., Macario, A., & Malara, A. (2021). Recovery/reuse of heterogeneous supported spent catalysts. *Catalysts*, 11(5), 591. [CrossRef]

[5] Valkenberg, M. H., & Hölderich, W. F. (2002). Preparation and use of hybrid organic–inorganic catalysts. *Catalysis Reviews*, 44(2), 321-374. [CrossRef]

[6] Dioos, B. M., Vankelecom, I. F., & Jacobs, P. A. (2006). Aspects of immobilisation of catalysts on polymeric supports. *Advanced Synthesis & Catalysis*, 348(12-13), 1413-1446. [CrossRef]

[7] Corma, A., & Garcia, H. (2006). Silica-bound homogenous catalysts as recoverable and reusable catalysts in organic synthesis. *Advanced Synthesis & Catalysis*, 348(12-13), 1391-1412. [CrossRef]

[8] De Vos, D. E., Dams, M., Sels, B. F., & Jacobs, P. A. (2002). Ordered mesoporous and microporous molecular sieves functionalized with transition metal complexes as catalysts for selective organic transformations. *Chemical Reviews*, 102(10), 3615-3640. [CrossRef]

[9] Xia, Q. H., Ge, H. Q., Ye, C. P., Liu, Z. M., & Su, K. X. (2005). Advances in homogeneous and heterogeneous catalytic asymmetric epoxidation. *Chemical Reviews*, 105(5), 1603-1662. [CrossRef]

[10] Pereira, C., Silva, A. R., Carvalho, A. P., Pires, J., & Freire, C. (2008). Vanadyl acetylacetonate anchored onto amine-functionalised clays and catalytic activity in the epoxidation of geraniol. *Journal of Molecular Catalysis A: Chemical*, 283(1-2), 5-14. [CrossRef]

[11] Cardona, Y., Korili, S. A., & Gil, A. (2023). Use of clays and pillared clays in the catalytic photodegradation of organic compounds in aqueous solutions. *Catalysis Reviews*, 1-48. [CrossRef]

[12] Kashif, M., Yuan, M., Su, Y., Heynderickx, P. M., & Memon, A. (2023). A review on pillared clay-based catalysts for low-temperature selective catalytic reduction of NOx with hydrocarbons. *Applied Clay Science*, 233, Article 106847. [CrossRef]

[13] Pizarro, A. H., Molina, C. B., Rodriguez, J. J., & Epron, F. (2015). Catalytic reduction of nitrate and nitrite with mono-and bimetallic catalysts supported on pillared clays. *Journal of Environmental Chemical Engineering*, 3(4), 2777-2785. [CrossRef]

[14] B. Velde, (1992). Introduction to clay minerals, chemistry, origins, uses and environmental significance. Chapman & Hall.

[15] Jawad, A. H., Saber, S. E. M., Abdulhameed, A. S., Farhan, A. M., ALOthman, Z. A., & Wilson, L. D. (2023). Characterization and applicability of the natural Iraqi bentonite clay for toxic cationic dye removal: Adsorption kinetic and isotherm study. *Journal of King Saud University-Science*, Article 102630. [CrossRef]

[16] Şahin, Ö., Kaya, M., & Saka, C. (2015). Plasma-surface modification on bentonite clay to improve the performance of adsorption of methylene blue. *Applied Clay Science*, 116, 46-53.

[17] Niu, M., Li, G., Cao, L., Wang, X., & Wang, W. (2020). Preparation of sulphate aluminate cement amended bentonite and its use in heavy metal adsorption. *Journal of Cleaner Production*, 256, Article 120700. [CrossRef]

[18] Grim, R. E. (1968). Clay Mineralogy (2nd ed.) McGraw-Hill.

[19] Ghiaci, M., Sedaghat, M. E., Aghaei, H., & Gil, A. (2009). Synthesis of CdS-and ZnS-modified bentonite nanoparticles and their applications to the degradation of eosin B. *Journal of Chemical Technology & Biotechnology*, 84(12), 1908-1915. [CrossRef]

[20] Farias, A. F. F., Torres, S. M., Longo, E., Jaber, M., Fonseca, M. G., Pontes, L. F. B. L., & Santos, I. M. G. D. (2021). ZnO/bentonite hybrids obtained by a simple method of synthesis and applied as catalyst for biodiesel production. *In Functional Properties of Advanced Engineering Materials and Biomolecules. Springer*, Cham. [CrossRef]

[21] Chakraborty, T., Chakraborty, A., Shukla, M., & Chattopadhyay, T. (2019). ZnO–Bentonite nanocomposite: an efficient catalyst for discharge of dyes, phenol and Cr (VI) from water. *Journal of Coordination Chemistry*, 72(1), 53-68. [CrossRef]

[22] Rudolph, G., Henry, M. C., & Muetterties, E. L. (1967). Bis (2, 4-pentanedionato) Zinc. *Inorganic Syntheses*, 10, 74-77. [CrossRef]

[23] Prondzinski, N., & Merz, K. (2008). Hydrated Zinc p-Aminobenzoate [Zn (p-$H_2NC_6H_4COO)_2(H_2O)$]·H_2O from a Layered Zinc Hydroxide. *Zeitschrift für Anorganische und Allgemeine Chemie*, 634(3), 555-558. [CrossRef]

[24] Mahmoud, S., & Saleh, S. (1999). Effect of acid activation on the de-tert-butylation activity of some Jordanian clays. *Clays and Clay Minerals*, 47, 481-486. [CrossRef]

[25] Akçay, G., & Yurdakoc, M. K. (1999). Nonyl-and dodecylamines intercalated bentonite and illite from Turkey. *Turkish Journal of Chemistry*, 23(1), 105-114.

[26] Pereira, C., Patrício, S., Silva, A. R., Magalhães, A. L., Carvalho, A. P., Pires, J., & Freire, C. (2007). Copper acetylacetonate anchored onto amine-functionalised clays. *Journal of Colloid and Interface Science*, 316(2), 570-579. [CrossRef]

[27] Pramanik, S., Das, G., & Karak, N. (2013). Facile preparation of polyaniline nanofibers modified bentonite nanohybrid for gas sensor application. *RSC Advances*, 3(14), 4574-4581. [CrossRef]

[28] Güngör, N., & Karaoğlan, S. (2001). Interactions of polyacrylamide polymer with bentonite in aqueous systems. *Materials Letters*, 48(3-4), 168-175. [CrossRef]

[29] Coşkun, S., Taşçı, Z., Ulusoy, M., & Yurdakoç, M. (2014). Catalytic conversion of carbon dioxide into cyclic carbonates by Cu (II) and Ni (II) acetylacetonates anchored onto Siral 80. *Turkish Journal of Chemistry*, 38(4), 600-610. [CrossRef]