



Attique, S., Batool, M., Yaqub, M., Gregory, D., Wilson, C., Goerke, O. and Shah, A. T. (2020) Synthesis and catalytic performance of cesium and potassium salts of aluminum substituted tungstoborate for pyrolysis of polyethylene waste to petrochemical feedstock. *Materials Chemistry and Physics*, 246, 122781.

There may be differences between this version and the published version. You are advised to consult the publisher's version if you wish to cite from it.

<http://eprints.gla.ac.uk/209687/>

Deposited on: 7 February 2020

Enlighten – Research publications by members of the University of Glasgow
<http://eprints.gla.ac.uk>

Synthesis and catalytic performance of cesium and potassium salts of aluminum substituted tungstoborate for pyrolysis of low-density polyethylene to petrochemical feedstock

Saira Attique^{a,b}, Madeeha Batool^a, Mustansara Yaqub^c, Duncan H. Gregory^b, Claire Wilson^b,
Oliver Goerke^c, Asma Tufail Shah^{c,d*}

^aInstitute of Chemistry, University of the Punjab, New Campus, Lahore-54000, Pakistan

^bWestCHEM, School of Chemistry, Joseph Black Building, University of Glasgow, Glasgow, United Kingdom

^cInterdisciplinary Research Centre in Biomedical Materials, COMSATS University Islamabad, Lahore Campus, Lahore-54600, Pakistan

^dFachgebiet Keramische Werkstoffe / Chair of Advanced Ceramic Materials, Institut für Werkstoffwissenschaften und -technologien, Technische Universität Berlin, Hardenbergstr, Berlin, Germany

Corresponding Author:

1. Asma Tufail Shah

PhD, Postdoc (UK), Postdoc (Germany, Alexander von Humboldt fellow)

Contact # +49 (0) 15175185565

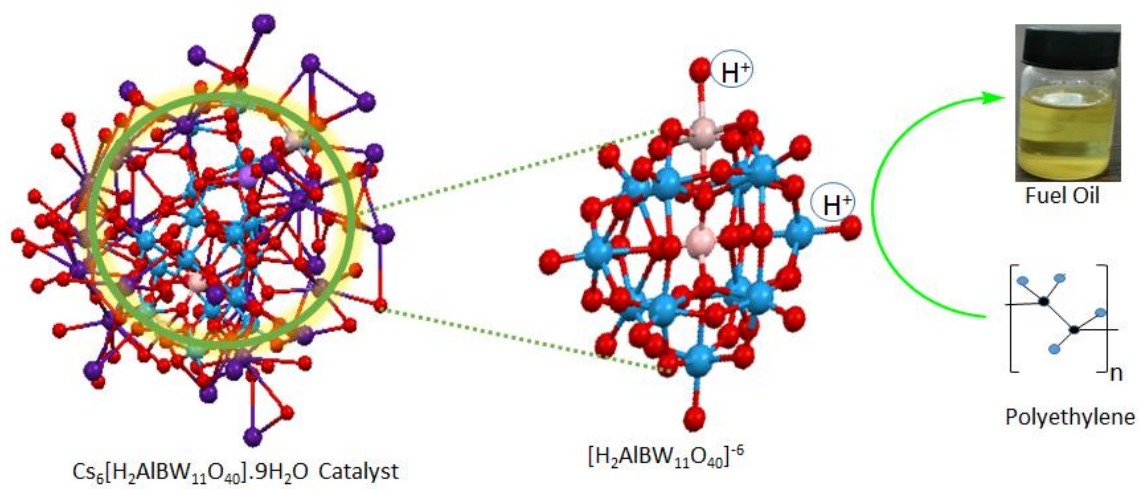
Fax: +49 (0)30 314-28534

E-mail: asma.tufail@campus.tu-berlin.de; drasmashah@cuilahore.edu.pk

2. Dr. Madeeha Batool

Email: s_madeeha_b@yahoo.com

Graphical Abstract



Highlights

- Synthesis of Cesium & potassium salts of aluminum substituted Keggin tungstoborate
- Catalytic cracking of polyethylene produced 80wt.-% liquid hydrocarbons
- Liquid oil showed very high selectivity to gasoline range hydrocarbons
- Al-substituted tungstoborates are excellent catalyst for acid catalyzed reactions

Synthesis and catalytic performance of cesium and potassium salts of aluminum substituted tungstoborate for pyrolysis of polyethylene waste to petrochemical feedstock

Saira Attique^{a,b}, Madeeha Batool^a, Mustansara Yaqub^c, Duncan H. Gregory^b, Claire Wilson^b,
Oliver Goerke^c, Asma Tufail Shah^{c,d*}

^aInstitute of Chemistry, University of the Punjab, New Campus, Lahore-54000, Pakistan

^bWestCHEM, School of Chemistry, Joseph Black Building, University of Glasgow, Glasgow, United Kingdom

^cInterdisciplinary Research Centre in Biomedical Materials, COMSATS University Islamabad, Lahore Campus, Lahore-54600, Pakistan

^dFachgebiet Keramische Werkstoffe / Chair of Advanced Ceramic Materials, Institut für Werkstoffwissenschaften und -technologien, Technische Universität Berlin, Hardenbergstr, Berlin, Germany

Corresponding Author:

1. Asma Tufail Shah

PhD, Postdoc (UK), Postdoc (Germany, Alexander von Humboldt fellow)

Contact # +49 (0) 15175185565

Fax: +49 (0)30 314-28534

Email: asma.tufail@campus.tu-berlin.de; drasmashah@cuilahore.edu.pk

2. Dr Madeeha Batool

Email: s_madeeha_b@yahoo.com

Abstract

Polyoxometalates have gained considerable attention as a catalyst. Herein, we are reporting tungstoborate based catalysts for the conversion of waste polyethylene to liquid fuel. Novel cesium and potassium salts of aluminum substituted tungstoborate Keggin compounds were synthesized by a simple one-pot method and successfully characterized by FTIR, SEM-EDX, thermal analysis, NMR and single-crystal XRD. Catalytic cracking of waste polyethylene by using our prepared aluminum substituted catalysts (CsAB) showed 97% polymer conversion producing 80 wt.% of liquid hydrocarbons with a negligible amount of solid residue (~3 wt.%), significantly lower compared to thermal cracking where 22 wt.% residue was produced. The oil collected at optimum reaction conditions (0.5 catalyst/polymer ratio and 3h reaction time) was subjected to GC-MS analysis. The results showed that oil produced in catalytic cracking has a high selectivity to gasoline range hydrocarbons while thermal cracking showed selectivity to higher hydrocarbons (C₁₃-C₂₆). Olefin selectivity was also more prominent in catalytic cracking. Hence cesium and potassium salts of aluminum substituted tungstoborate are excellent catalysts for acid-catalyzed polymer cracking reactions to produce value-added petrochemicals.

Keywords: Polyoxometalate; Keggin structure; Pyrolysis; Polyethylene; GC-MS.

1. Introduction

Energy crisis and environmental pollution by waste polymers are current burning issues. These issues have led to propose technologies for energy recovery from waste plastic. Among these technologies, thermal or catalytic degradation of waste plastic to liquid fuel is the most attractive one [1, 2]. Catalytic degradation is preferred over thermal degradation as the use of catalyst not only lowers the reaction temperature[3-5] but also produces lighter oil fractions [6]. Liquid fuel is the most valued product in oil fraction, although gaseous hydrocarbons are also a rich source of energy but surplus gas production is not suitable because of their high transportation cost[7].

Catalysts that are mostly used for plastic pyrolysis include zeolites[8], silica- alumina[9], activated carbon[10], mesoporous silica materials[11] and heteropoly acids (HPAs)[12]. As zeolites have strong acidity for carbon-carbon bond breakage, HY, ZSM-5, Beta and Y zeolite[13-15] are widely reported for plastic degradation. However, due to the small pore size of these catalysts, the contact of bulky molecules to acid sites located inside the pores is hindered. Moreover, carbon deposition deactivates quickly[16]. Therefore, mesoporous silica (MCM-41, SBA-15, SBA-16, etc.) materials with large pore sizes were developed [17] but they do not show appropriate catalytic activity due to unavailability of considerable acidic sites[18, 19]. This limitation has been overcome by the use of polyoxometalates in the field of catalysis. HPAs (also known as polyoxometalates, POMs) have discrete and mobile ionic structures with strong Brønsted acid sites which endows them outstanding catalytic abilities for acid-catalyzed reactions[20]. However, low thermal stability and surface area of HPAs, limit their use as a solid acid catalyst in reactions performed at high temperatures like polymer cracking reactions [11, 21]. Previously, we have reported tungstophosphoric acid and kaolin clay composite with high

thermal stability exhibiting the efficient catalytic cracking of low-density polyethylene [22]. It produced a higher percentage of fuel oil (liquid and gaseous hydrocarbons) with a negligible amount of semisolid wax. Tungstoborates are subclass of HPAs having BO_4 as a central tetrahedral unit that is surrounded by 12 edge- and corner-sharing metal-oxygen octahedra. These compounds have been used as catalysts for oxidation reactions [23] and the degradation of dyes [24] and have exhibited good catalytic activities. However, to the best of our knowledge, the use of tungstoborates as solid acid catalyst in polymer degradation reactions has never been reported.

In the present work, we have synthesized aluminum substituted Keggin tungstoborates and used them for plastic degradation reactions. Aluminum substituted tungstoborate Keggin anion is known to have additional Brønsted acid sites[25]. Aluminum insertion not only reduced the cracking temperature to 320 °C (compared to thermal degradation at 375 °C) but also enhanced the yield of liquid fuel oil to 80% with a negligible amount of residue. Hence, aluminum substitution into tungstoborate Keggin structure greatly enhanced the efficacy of the catalyst. Cs and K salts of HPAs are known to possess high surface area and thermal stability up to the melting point of salt [26, 27]. Therefore we have prepared the Cs and K salts of these aluminum substituted Keggin tungstoborates. We are also working on tungstoborate and kaolin composite to evaluate the synergistic effect of clay on catalytic properties of HPAs.

2. Experimental

2.1. Materials

Sodium tungstate ($\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$, Merck), boric acid (98.5 %, Sigma Aldrich), aluminum nitrate nonahydrate (98%, Sigma Aldrich) and acetic acid (99.5 %, Sigma Aldrich) were used for synthesis. Low-density polyethylene pellets were purchased from the local market

(melting point range 140-150 °C). All chemicals were of analytical grade, commercially available and used without further purification unless otherwise stated.

2.2. Methods

2.2.1. Catalyst preparation

$K_6[H_2AlBW_{11}O_{40}].9H_2O$ and $Cs_6[H_2AlBW_{11}O_{40}].9H_2O$ were synthesized as follows: Sodium tungstate (12.32 mmol) and boric acid (3.23 mmol) were dissolved in hot water and reacted for 1 hour at pH 6.8. Then, the mixture was cooled to 4 °C for 24 h, filtered to remove precipitates of dodecatungstate and again heated at 80 °C. Aluminum nitrate (1.77 mmol) dissolved in 5 mL of water was added into the above-mentioned filtrate. The resultant mixture was boiled for an hour at pH of 6.2 and after cooling to room temperature, salted out as potassium or cesium salt by adding their respective chlorides. For generalization, $K_6[H_2AlBW_{11}O_{40}].9H_2O$ was denoted as KAB and $Cs_6[H_2AlBW_{11}O_{40}].9H_2O$ as CsAB. Unsubstituted Keggin 12-tungstoborate (KB) was synthesized by the method reported in literature [28]. Briefly, sodium tungstate (17.0 mmol) and boric acid (4.04 mmol) were dissolved in boiling water (5 mL). 3 mL of 6 M HCl was added to the above solution and the resultant mixture reacted for one hour while heating. Then the precipitates (paratungstate) were separated through filtration and the filtrate pH was adjusted to 2.0 by 6 M HCl and reacted for half an hour while heating. Potassium chloride (6.04 mmol) was added to the above solution in order to precipitate out $K_5BW_{12}O_{40}$, the product was filtered and washed with ethanol.

2.2.2. Acid-Base titrations

The presence of acidic protons in aluminum substituted Keggin anion was confirmed by acid-base titrations as reported previously[29]. Typically, solid CsAB and KAB (0.25 mmol) were placed in 50 mL of standard NaOH solution (0.1 M) and stirred for 2 hours at room

temperature in a closed vessel. Then the solution was filtered off and the filtrate was back titrated against standard HCl solution (0.1 M). The number of acidic protons of CsAB (0.486 mmol/g) and KAB (0.465 mmol/g) was calculated from the consumed amount of NaOH.

2.2.3. Catalyst Characterization

The synthesized catalysts were characterized by different analytical techniques for structural validation. FTIR was performed using Transform Infra-Red Spectrometer from Agilent technology (model 41630) in ATR mode to identify different functional groups in the synthesized samples. Spectra were obtained at 4 cm^{-1} resolution, accumulating 64 number of scans. ^{27}Al NMR spectra of aluminum substituted tungstoborate was recorded at Bruker 400 MHz instrument using $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ as external reference material for aluminum. The sample solution was prepared in D_2O and NMR tubes used for measurement had 5 mm outer diameter, spectra were recorded by accomplishing 64 numbers of scans. The morphology of samples was studied by using XL30 ESEM Scanning Electron Microscope. Samples were pre-coated using gold targets for 90 seconds using a Polaron SC7640 sputter coater. The EDX detector INCA X-Act by Oxford Instruments Analytical Ltd. (UK) was integrated with the microscope system, operating at 20 kV voltage and was used for elemental analysis. Thermal analysis was performed on Netzsch STA 409 instrument. For TGA analysis, approximately 20 mg samples were taken in alumina pans and heated to 1000 °C at a heating rate of 10 °C min^{-1} under flow of argon gas. Liquid hydrocarbons were analyzed by GC-MS using GCMS-QP2010S system with ZB-5 MS column ($30\text{ m} \times 0.32\text{ mm} \times 0.25\text{ }\mu\text{m}$).

2.2.3.1. X-ray Crystallography

The crystalline structure was studied by collecting data on a Bruker D8 VENTURE diffractometer with microfocus sealed tube, INCOATEC Ims 3.0, using Mo $K\alpha$ radiation ($\lambda =$

0.71073 Å), $2\theta = 2.4\text{--}28.3^\circ$. Oxford CryoSystems n-helix low-temperature device was used to cool crystals upto 100 K. The crystal structure was solved by the direct method using *SHELXT* program [30] and structural refinements were made through the full-matrix-least squares method on F^2 using *SHELXL*[31]. Crystal structure was visualized by OLEX 2[32]. Details of data collection and refinements are given in table S2-S4 (supplementary information). Crystallographic data for the reported compound is deposited in the Cambridge Crystallographic Data Center (CCDC No. 1846238)

2.3. Thermal and Catalytic Cracking of Polyethylene

A pyrex glass batch reactor (280 mm x 50 mm) was used for cracking experiments. Polyethylene pellets (15 g) mixed with prepared tungstoborate catalyst (5 wt.%) and were loaded into the reactor. After setting up the reaction assembly, the reactor was heated to 120 °C (2 °C/min) under the flow of nitrogen gas and temperature maintained at 120 °C for 1 hour to remove adsorbed water. Then nitrogen supply was cut off and the temperature was raised to cracking temperature (5 °C/min). Details of the experimental setup could be found in the literature [22]. Cracking products in vapor form was passed through a condenser and collected in a flask. The experiment was allowed to run for three hours. PE cracking products were classified into three groups: (i) gaseous hydrocarbons, (ii) low molecular weight hydrocarbons and (iii) solid residue (carbonaceous and waxy compounds left behind in the reactor after completion of reaction). The weight percentage of gaseous products was determined by subtracting the weight of liquid products and residues from the polyethylene sample feed. Liquid products were analyzed by GC-MS using GCMS-QP2010S system. Total polymer conversion was calculated by the following formula;

$$\text{Total \% conversion} = \frac{\text{wt. of PE} - \text{wt. of residue}}{\text{wt. of PE}} \times 100$$

3. Results and Discussion

3.1. Catalyst Characterization

The synthesized material was characterized by various spectroscopic and surface-based techniques. FTIR spectrum revealed Keggin structure of both unsubstituted 12-tungstoborate (KB)[33, 34] and aluminum substituted tungstoborate (KAB and CsAB) [35, 36]. Both CsAB and KAB showed $W-O_d$, $W-O_b-W$ and $W-O_c-W$ vibrations at positions similar to that of KB i.e. at 950, 890, 810 and 740 cm^{-1} respectively [33, 37, 38] but $B-O_a$ vibrations in aluminum substituted samples were shifted from 910 cm^{-1} to 890 cm^{-1} as shown in figure 1. This shift was attributed to the incorporation of Al into Keggin anion that changed the environment around central BO_4 tetrahedron due to the exchange of one W^{+6} with Al^{+3} [39, 40]. The observed shift in $B-O_a$ stretching frequency is 26 cm^{-1} that is consistent with earlier reports for transition metal substituted Keggin polyoxometalates [39, 40]. Vibrational bands at 710 cm^{-1} are ascribed to very strong asymmetric vibrations of $W-O-Al$ bonds respectively[33, 37, 38, 41]. Water molecules showed vibrations at 1610 cm^{-1} .

Raman spectra of both cesium and potassium salts of Al substituted tungstoborate showed Raman shift at 968 cm^{-1} (vs), 890 cm^{-1} (m), 525 cm^{-1} (m), 230 cm^{-1} (s) and 212 cm^{-1} (s) [34] as shown in figure 2. Prominent vibration at 968 cm^{-1} was corresponded to symmetric stretching of $W-O_d$, while $B-O_a$ vibrations at 910 cm^{-1} were shifted to 890 cm^{-1} due to lowered symmetry by the exchange of one tungsten with aluminum [33, 40]. All other vibration bands are located at approximately the same wavenumbers as that of unsubstituted 12-tungstoborate (KB), although there are some differences in relative intensities that might ensue from the influence of

large cation on the tertiary structure of Keggin polyanion [42]. However, the rest of the vibration bands were located at similar positions.

SEM and EDX analysis were performed to determine the morphology and elemental composition of both Al substituted and unsubstituted tungstoborate salts. These materials showed a regular crystalline morphology (figure 3) that is consistent with the previous reports where the regular crystal structure of parent acid $\text{H}_3\text{PW}_{12}\text{O}_{40}\cdot 6\text{H}_2\text{O}$ was maintained with cations located at $\text{H}^+(\text{H}_2\text{O})_2$ sites[43]. Atomic percentages obtained from the EDX analysis explained that all major elements were present in close agreement to the theoretical values as shown in table S1 (supplementary information). Mono-aluminum substitution into Keggin polyanion was also confirmed by EDX analysis. W/Al atomic ratio was found to be 11:1 for both Cs and K salt of aluminum substituted Keggin tungstoborate.

The aluminum substitution was further confirmed by ^{27}Al NMR spectroscopy. The ^{27}Al NMR spectrum of CsAB and KAB solutions showed a sharp resonance peak at 7.6 ppm (figure 4) corresponding to AlO_6 octahedral environment [44]. This peak was located at slightly greater chemical shift values from 0 ppm due to the bridging of AlO_6 octahedron with neighboring WO_6 octahedra and central BO_4 tetrahedron. D. Müller *et al.* have also reported a variation of ^{27}Al chemical shift depending on the type of neighbouring tetrahedra XO_4 ($\text{X} = \text{P}, \text{Si}$) and MO_6 octahedra [45].

Thermal analysis of both aluminum substituted and unsubstituted Keggin tungstoborate showed weight loss in a single step from 70 to 300 °C (figure 5) corresponded to water molecules of crystallization (9 .0 for CsAB and KAB, 12.0 for KB). For CsAB and KAB, a small mass loss of ~0.4% between 400 and 500°C was also seen that was ascribed to the dehydration of a water molecule formed from free protons and oxygen atoms from Keggin anion. This

dehydration step may be used for measurement of the H^+ content in the Keggin polyoxometalate that is considered very important for acid-catalyzed reactions[21, 42]. After this step, there is no weight loss observed upto 1000°C. These results confirmed that the incorporation of heavy alkali metal ions potassium or cesium cations, stabilize the Keggin structure. This enhanced thermal stability is considered as a primary requisite for catalytic reactions performed at high temperatures [21].

CsAB crystals were studied through single-crystal XRD. It was shown that an asymmetric unit in CsAB crystals contains a Keggin anion and counter cesium cations (figure 6). BO_4 tetrahedral unit is present in the center of heteropoly Keggin anion $[H_2AlBW_{11}O_{40}]^{-6}$ that is surrounded by one AlO_6 and eleven WO_6 octahedra [46]. B–O bond lengths range from 1.51(2) – 1.56(3)Å show a slight distortion of BO_4 tetrahedron. A similar distortion of central SiO_4 tetrahedron has been reported for Keggin tungstosilicate polyanion [47]. Likewise, an outward displacement of tungsten atoms in each WO_6 octahedron was observed as reflected by W–O distances ranging from 1.761(19)–2.341(16)Å, consistent with earlier reports for $[SiW_{12}O_{40}]^{-4}$ and $[PW_{12}O_{40}]^{-3}$ polyanions [47, 48]. This elongation of WO_6 octahedron was also revealed by bond angles at W atoms that range from 92.2(7)° to 73.9(6)°, deviating from 90° (selected geometric parameters are provided in Table S5 (supplementary information)).

In contrast to earlier reports where the aluminum substituted site could not be identified in tungstophosphate polyanion because of almost twelve-fold disorder overall positions in the substituted site[49], the present study reports the identification of mono-aluminum substituted site in tungstoborate Keggin polyanion with full occupancy. In the present study, unambiguous identification of aluminum substituted could be ascribed to the large size of cesium cations[50]. It is reported that the disorder of substituted metal site in the polyanion can be eliminated by

bulky counter cations [51]. AlO_6 octahedron is also slightly distorted as inferred by Al–O bond lengths ranging from 1.832 (19)–2.023 (16) Å. Overall bond lengths of tungstoborate Keggin polyanion were greatly influenced by aluminum substitution. B–O bond lengths in the central BO_4 tetrahedron are longer (1.51(2)–1.56 (3)Å) than estimated for unsubstituted 12-tungstoborate Keggin anion (1.43–1.55)[52] whereas, the bridging oxygen atoms between WO_6 and AlO_6 octahedra have shorter bond lengths than expected for 12-tungstoborate that is consistent with the previous literature for $[\text{PAIW}_{11}\text{O}_{40}]^{-3}$ polyanion[49].

Water molecules of crystallization were estimated by thermogravimetric analysis that confirmed the presence of 9 water molecules per Keggin unit (weight loss $\leq 300^\circ\text{C}$: calcd. 4.40%, observed 4.21%) (figure 5) that is consistent with the crystallographic data. Another significant feature of heteropoly Keggin anion is that it should be protonated for charge balancing. Although no proton sites could be observed by XRD, as expected for lighter atoms (hydrogen) in the presence of heavier ones (tungsten, cesium), that is a common limitation for heteropoly anions [29]. However, the presence of two protons per Keggin unit was confirmed by acid-base titrations. On the basis of X-ray crystallography combined with elemental analysis, TGA and titrations, the proposed chemical formula of CsAB is thus $\text{Cs}_6[\text{H}_2\text{AlBW}_{11}\text{O}_{40}]\cdot 9\text{H}_2\text{O}$.

3.2. Catalytic cracking of polyethylene

Non-catalytic cracking of polyethylene took place at a much higher temperature (375 °C), as compared to pyrolysis in the presence of aluminum substituted catalyst (CsAB and KAB) i.e. 320 °C, furthermore the liquid hydrocarbons yield was also increased. Polyethylene cracking temperature is dependent on the type of catalyst and more specifically, the availability of acidic sites[53-55]. Acidic catalysts are known to decrease the cracking temperature and enhance the yield of liquid hydrocarbons[54, 55].

3.2.1. Percentage yield of cracking products

The percentage yield of different products obtained by catalytic and non-catalytic cracking of polyethylene are summarized in figure 7 and table S6 (supporting information). Thermal pyrolysis produced only 68 wt.% oil with 22 wt.% solid residue. The catalyst without aluminum also showed a similar yield. The percentage yield of liquid and gaseous products in case of catalytic cracking with Aluminum substituted HPA was higher (almost 80 wt.% with a residue of about 3 wt.%) compared to the non-catalytic and unsubstituted HPA based cracking. The better catalytic efficiency of aluminum substituted HPA could be attributed to the additional Brönsted acid sites created by aluminum incorporation in tungstoborate framework. Increasing the catalyst acidity reduces the cracking temperature and leads to the degradation of heavier hydrocarbons into lighter ones [56].

The percentage yield of gaseous hydrocarbons (C_1 - C_4) was also higher for all catalysts compared to the non-catalytic cracking of polyethylene that is also consistent to earlier reports [56]. Both oil and gas fractions obtained by catalytic cracking are useful fuel products. Thus use of our prepared catalysts not only lowered the PE decomposition temperature but also improved the percentage yield of useful fuel products.

3.2.2. Liquid Products

The oil obtained by thermal and catalytic degradation was analyzed by GC-MS. Every peak in gas chromatogram relates to a specific compound present in oil samples (identified by comparing with NIST/EPA/NIH Mass spectral library). The relative abundance of each compound was calculated in terms of mol.%. About 50 major peaks were selected and quantified. Carbon number distribution and the relative abundance of each compound in oil samples

obtained by both catalytic and non-catalytic PE cracking are given in figure(8 a). It can be observed that non-catalytic cracking produced 65 mol.% of heavier hydrocarbons (C_{13} – C_{26}) and only 35 mol.% gasoline hydrocarbons (C_6 – C_{12}) while in the presence of aluminum substituted catalysts, percentage contribution of gasoline hydrocarbons (C_5 – C_{12}) was increased to 60 mol.% and heavier hydrocarbons (C_{13} – C_{21}) were formed in much lesser amount. In case of CsAB and KAB catalytic oil, C_5 showed a large relative abundance which was totally absent in non-catalytic oil. Moreover, C_6 and C_7 hydrocarbons selectivity was very high in oil produced by catalytic cracking as compared to non-catalytic cracking (Figure8b). By contrast, C_{22} and C_{23} , produced in significant amount during thermal pyrolysis, were not found in catalytic pyrolysis. However, product distribution in the case of unsubstituted HPA (KB) based cracking was similar to that of thermal pyrolysis owing to the absence of acidic sites in KB.

The catalytic efficiency of HPAs depend on availability of acidic sites, structure and composition of Keggin anion, and nature of countercations [57]. The substituent metals having strong Lewis acidity, such as Al and Ti, have been reported to enhance Brönsted acidity of the tungstophosphates [58]. Ayedemir *et al.* have reported the aluminum substituted mesoporous material for efficient cracking of polyethylene [56]. Furthermore, BO_4 unit coordinated to AlO_6 octahedron could also have a synergistic effect on Brönsted acidic sites of tungstoborate based catalyst. Sato *et al.* have reported that introduction of BO_4 unit in alumina-boria catalyst creates Brönsted acid sites on alumina surface that considerably enhanced 1-Butene isomerization [59]. Another factor responsible for catalyst acidity is presence of residual protons which are always present in Keggin structure for charge balancing of molecule (even though salt is synthesized in stoichiometric amounts). Acid-Base titration also confirmed the presence of acidic protons in aluminum substituted tungstoborate. These acidic protons could further enhance the catalytic

efficiency of the prepared catalyst [60]. Increasing the catalyst acidity by all these factors is expected to enhance the degradation of heavier hydrocarbons into lighter ones due to PE degradation reaction proceeding over Brønsted acidic sites, which is consistent with earlier reports [56]. Due to the above-mentioned reasons, both CsAB and KAB showed good oil selectivity. However, CsAB showed slightly higher oil selectivity (80 wt.%) than KAB (78.6 wt.%) which could be attributed to the large size of cesium cations. Jan *et al.*, have also reported that the use of BaCO₃ as a catalyst for HDPE cracking exhibited higher oil selectivity (36.36%) compared to CaCO₃ (35.58%). They proposed that moving down a group in the periodic table could enhance the oil selectivity of metal cation [61].

GC-MS analysis showed that the majority of hydrocarbons present in oil produced by both catalytic and non-catalytic cracking were aliphatic in nature (mainly paraffin and olefins). Oil formed by non-catalytic cracking contained paraffin and olefins in almost equal amounts (figure 9). Moreover, the olefins formed by thermal cracking were mainly 1-alkenes, no dienes or alkynes were observed. In contrast, the formation of dienes and a small amount of alkynes in addition to 1-alkenes was favored by catalytic cracking that indicated the enhanced protonation of hydrocarbon chains at protonic acidic sites, forming carbonium ions that eventually undergoes β -scission reactions[62]. The augmented β -scission and rearrangement reactions significantly increased the weight percentage of lower hydrocarbons that were reflected in CsAB and KAB catalytic oil as light olefins and branched-chain alkenes. Sui *et al.* have also reported that polyethylene cracking by aluminum substituted SBA-16 catalyst produced the highest amount of olefins due to an increased number of acid sites by aluminum insertion into mesoporous silica material [63]. However, the catalysts minimized the residence time leading to the elimination of the secondary reactions that produce aromatic compounds[64]. Subsequently, the yield of

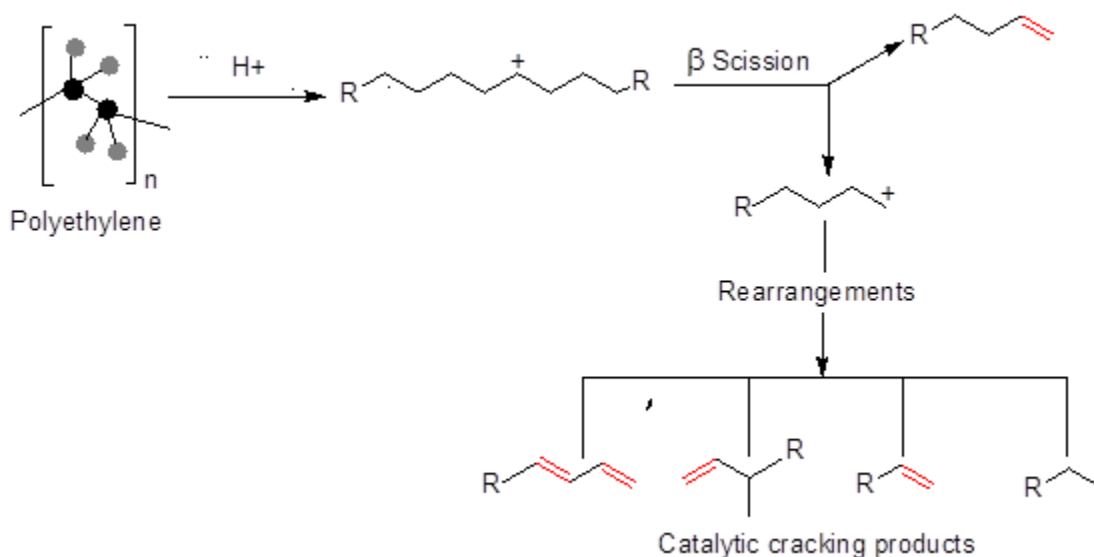
aromatic compounds is negligible, which is highly significant for obtaining the C₅–C₁₂ gasoline fraction and also important from an environmental point of view.

4. Catalyst Recycling

At the end of the experiment, the reusability of the catalyst was tested for a couple of cycles. CsAB catalyst was easily separated from residue through n-hexane washing, dried in an oven at 100 °C and FT-IR spectra for recycled and fresh catalysts were compared in order to investigate the structural integrity of recycled CsAB catalyst. It was found that the spectrum of recycled catalyst is quite analogous to that of fresh catalyst (figure 10). Thus, the maintenance of Keggin structure in the recycled catalyst was confirmed. The regenerated catalyst was also employed for polyethylene cracking and its cracking efficiency was compared with the fresh one and it was observed that the regenerated catalyst cracked polyethylene without considerable activity loss. (Table S5, supplementary information).

5. Mechanism of polyethylene cracking

Catalytic cracking of polyethylene using solid catalysts occurs through carbonium ion mechanism[62]. According to Buekens and Haung, polymer chains are protonated at acid sites of catalyst forming carbonium ions, which undergo β -scission reactions at the end of the polymer chain to produce light olefins and carbonium ion intermediate [65]. Carbonium intermediates also undergo hydrogen or carbon rearrangements to form branched-chain hydrocarbons as shown in Scheme 1. Large amounts of branched-chain hydrocarbons observed in oil obtained by PE catalytic cracking are consistent to above-mentioned consequences. However, no aromatic hydrocarbons were produced that could be attributed to the short reaction time, which increases the positive environmental credentials of the aluminum substituted catalytic cracking process.



Scheme 1: Proposed mechanism of PE degradation that occurs at aluminum substituted catalyst (CsAB and KAB).

6. Conclusion

Synthesis of novel cesium and potassium salts of mono-aluminum substituted Keggin tungstoborate and their application in polyethylene cracking is reported in this study. Aluminum substituted tungstoborate based catalysts degraded polyethylene with a high fuel oil selectivity. GC-MS analysis showed that in the presence of CsAB and KAB catalysts, larger fractions of lower hydrocarbons were obtained. Significantly enhanced catalytic efficacy of these catalysts was a consequence of aluminum incorporation into tungstoborate framework that creates additional Brønsted acid sites that have a synergistic effect on PE cracking reactions. 80 wt.% of fuel oil was obtained by catalytic cracking with high selectivity for $\text{C}_5\text{-C}_{12}$ range hydrocarbons. Thus value-added petrochemicals could be recovered from waste polyethylene using aluminum

substituted tungstoborate based catalyst. We believe these complexes and others similarly designed, will expose new horizons in the field of catalysis.

Supplementary Information: X-ray data collection, refinement details, bond lengths and bond angles, EDX analysis, GC-MS graphs, and peak identification are provided in the supplementary information.

Note

The authors declare no competing financial interest.

Acknowledgement

International Foundation of Science (IFS) is acknowledged for fully funding this project for performing the experiments by a grant (F/5375-1). We are also grateful to the Higher Education Commission of Pakistan for providing Indigenous Ph.D. Scholarship and IRSIP scholarship to conduct part of this collaborative research at the University of Glasgow, UK. We are also thankful to Mr. Gangi Reddy Ubbara for help in GC-MS analysis.

7. References

- [1] Y. Sakata, M.A. Uddin, A. Muto, Degradation of polyethylene and polypropylene into fuel oil by using solid acid and non-acid catalysts, *Journal of Analytical and Applied Pyrolysis*, 51 (1999) 135–155.
- [2] A.K. Panda, R. Singh, Experimental Optimization of Process for the Thermo-catalytic Degradation of Waste Polypropylene to Liquid Fuel, *Advances in Energy Engineering (AEE)*, 1 (2013) 74-84.
- [3] B. Aydemir, N.A. Sezgi, T. Dog̃u, , Synthesis of TPA impregnated SBA-15 catalysts and their performance in polyethylene degradation reaction,, *AIChE*, (2011).

- [4] N.S. Akpanudoh, K. Gobin, G. Manos, Catalytic degradation of plastic waste to liquid fuel over commercial cracking catalysts, Effect of polymer to catalyst ratio/acidity content, *J. Mol. Catal. A – Chem*, 235 (2005) 67–73.
- [5] Y.-H. Lin, M.-H. Yang, T.-F. Yeh, M.-D. Ger, 121–128., Catalytic degradation of high density polyethylene over mesoporous and microporous catalysts in a fluidised bed reactor, *Polym. Degrad. Stab*, 86 (2004) 121-128.
- [6] M. Sarker, et al., , A new technology proposed to recycle waste plastics into hydrocarbon fuel in USA, *International Journal of Energy & Environment*, 5 (2012) 749-760.
- [7] K. Gobin, G. Manos, Polymer degradation to fuels over microporous catalysts as a novel tertiary plastic recycling method, *Polym. Degrad. Stab*, 83 (2004) 267-279.
- [8] W. Kaminsky, I.-J.N. Zorriquetta, Catalytical and thermal pyrolysis of polyolefins, *J. Anal. Appl. Pyrolysis*, 79 (2007) 368-374.
- [9] J. Aguado, J.L. Sotelo, D.P. Serrano, J.M.E. J.A. Calles, Catalytic conversion of polyolefins into liquid fuels over MCM-41: comparison with ZSM-5 and amorphous SiO₂–Al₂O₃, *Energy Fuels*, 11 (1997) 1225-1231.
- [10] Y. Uemichi, Y. Makino, T. Kanazuka, Degradation of polypropylene to aromatic hydrocarbons over Pt- and Fe-containing activated carbon catalysts, *J. Anal. Appl. Pyrolysis*, 16 (1989) 229-238.
- [11] A. Ghanbari-Siahkali, A. Philippou, A. Garforth, C.S. Cundy, M.W. Anderson, J. Dwyer, A comparison of direct synthesis and vapour phase alumination of MCM-41, *Journal of Materials Chemistry*, 11 (2001) 569-577.

- [12] A. Thomas, C. Dablemont, J.-M. Basset, F. Lefebvre, Comparison of H₃PW₁₂O₄₀ and H₄SiW₁₂O₄₀ heteropolyacids supported on silica by ¹H MAS NMR, *Comptes Rendus Chimie*, 8 (2005) 1969-1974.
- [13] J. Aguado, D. Serrano, G. San Miguel, J. Escola, J. Rodríguez, Catalytic activity of zeolitic and mesostructured catalysts in the cracking of pure and waste polyolefins, *Journal of analytical and applied pyrolysis*, 78 (2007) 153-161.
- [14] S. Chaianansutcharit, R. Katsutath, A. Chaisuwan, T. Bhaskar, A. Nigo, A. Muto, Y. Sakata, Catalytic degradation of polyolefins over hexagonal mesoporous silica: Effect of aluminum addition, *Journal of Analytical and Applied Pyrolysis*, 80 (2007) 360-368.
- [15] R. Van Grieken, D. Serrano, J. Aguado, R. Garcia, C. Rojo, Thermal and catalytic cracking of polyethylene under mild conditions, *Journal of Analytical and Applied Pyrolysis*, 58 (2001) 127-142.
- [16] A. Marcilla, A. Gomez-Siurana, D. Berenguer, Study of the influence of the characteristics of different acid solids in the catalytic pyrolysis of different polymers, *Appl. Catal. A – General*, 301 (2006) 222-231.
- [17] C. Kresge, M. Leonowicz, W. Roth, J. Vartuli, J. Beck, Ordered mesoporous molecular sieves synthesized by a liquid-crystal template mechanism, *nature*, 359 (1992) 710-712.
- [18] O. Z, NA, Sezgi, & T, Dogu Performance of acidic MCM-Like aluminosilicate catalysts in pyrolysis of polypropylene. , *Chem Eng Commun*, 196, (2009) 116-130.
- [19] P. A.Jalil, Investigations on polyethylene degradation into fuel oil over tungstophosphoric acid supported on MCM-41 mesoporous silica, *Journal of Analytical and Applied Pyrolysis*, 65 (2002) 185-195.

- [20] I.V. Kozhevnikov, Sustainable heterogeneous acid catalysis by heteropoly acids, *Journal of Molecular Catalysis A: Chemical*, 262 (2007) 86-92.
- [21] A.K. Aboul-Gheit, A.-H.M. Summan, Acid sites strength distribution in heteropoly acids by differential scanning calorimetry, *Thermochimica Acta*, 140 (1989) 21-29.
- [22] S. Attique, M. Batool, M.I. Jalees, K. Shehzad, U. Farooq, Z. Khan, F. Ashraf, A.T. Shah, Highly efficient catalytic degradation of low-density polyethylene Using a novel tungstophosphoric acid/kaolin clay composite catalyst, *Turkish Journal of Chemistry*, 42 (2018) 684-693.
- [23] I.C.M.S. Santos, M.M.Q. Simões, M.M.M.S. Pereira, R.R.L. Martins, M.G.P.M.S. Neves, J.A.S. Cavaleiro, A.M.V. Cavaleiro, Oxidation of monoterpenes with hydrogen peroxide catalysed by Keggin-type tungstoborates, *Journal of Molecular Catalysis A: Chemical*, 195 (2003) 253-262.
- [24] W.Y.-b. GAO Li-hua, BAI Li-jie, Synthesis, Spectroscopy and Photocatalytic Activity of IIIB Elements Substituted Tungstoborate Heteropoly Complexes, *SPECTROSCOPY AND SPECTRAL ANALYSIS*, 31 (2011) 2191-2194.
- [25] Z. Obalt, N.A. Sezgi, T. Doğu, Catalytic degradation of polypropylene over alumina loaded mesoporous catalysts, *Chemical engineering journal*, 207 (2012) 421-425.
- [26] K. Na, T. Okuhara, M. Misono, Skeletal isomerization of n-butane catalyzed by an acidic cesium salt of 12-tungstophosphoric acid, *Chemistry letters*, 22 (1993) 1141-1144.
- [27] A. Corma, A. Martínez, C. Martínez, Acidic Cs^+ , NH_4^+ , and K^+ Salts of 12-Tungstophosphoric Acid as Solid Catalysts for Isobutane/2-butene Alkylation, *Journal of Catalysis*, 164 (1996) 422-432.

- [28] C. Rocchiccioli-Deltcheff, M. Fournier, R. Franck, R. Thouvenot, Vibrational investigations of polyoxometalates. 2. Evidence for anion-anion interactions in molybdenum (VI) and tungsten (VI) compounds related to the Keggin structure, *Inorganic Chemistry*, 22 (1983) 207-216.
- [29] C.-Y. Sun, S.-X. Liu, D.-D. Liang, K.-Z. Shao, Y.-H. Ren, Z.-M. Su, Highly Stable Crystalline Catalysts Based on a Microporous Metal–Organic Framework and Polyoxometalates, *Journal of the American Chemical Society*, 131 (2009) 1883-1888.
- [30] G.M. Sheldrick, SHELXT - Integrated space-group and crystal-structure determination, *Acta Cryst. A*, 71 (2015) 3–8.
- [31] G.M. Sheldrick, Crystal structure refinement with SHELXL, *Acta Crystallographica Section C*, 71 (2015) Pages 3-8.
- [32] L.J.B. O. V. Dolomanov, R. J. Gildea, J. A. K. Howard and H. Puschmann, OLEX2: a complete structure solution, refinement and analysis program *J. Appl. Cryst.* (2009) 339-341.
- [33] C.F. Rocchiccioli-Deltcheff, M.; Franck, R.; Thouvenot, R. , Vibrational investigations of polyoxometalates. 2. Evidence for anion-anion interactions in molybdenum (VI) and tungsten (VI) compounds related to the Keggin structure., *Inorg. Chem.* , 22 (1983) 207.
- [34] A.C. Estrada, I.C. Santos, M.M. Simões, M.G.P. Neves, J.A. Cavaleiro, A.M. Cavaleiro, Silica supported transition metal substituted polyoxotungstates: Novel heterogeneous catalysts in oxidative transformations with hydrogen peroxide, *Applied Catalysis A: General*, 392 (2011) 28-35.
- [35] Q. Chang, J. Li, D. Gu, P. Yin, H. Jiang, L. Shen, Preparation, Characterization, and Conductivity of Polyaniline Doped with 12-Tungstoboric Acid, *Journal of Macromolecular Science, Part B*, 54 (2015) 381-392.

- [36] J.K. Kim, J.H. Choi, J.H. Song, J. Yi, I.K. Song, Etherification of n-butanol to di-n-butyl ether over HnXW12O40 (XCo²⁺, B³⁺, Si⁴⁺, and P⁵⁺) Keggin heteropolyacid catalysts, *Catalysis Communications*, 27 (2012) 5-8.
- [37] J.A.F. Gamelas, M.R. Soares, A. Ferreira, A.M.V. Cavaleiro, Polymorphism in tetra-butylammonium salts of Keggin-type polyoxotungstates, *Inorganica Chimica Acta*, 342 (2003) 16-22.
- [38] W.Y.-b. GAO Li-hua, BAI Li-jie, Synthesis, Spectroscopy and Photocatalytic Activity of IIB Elements Substituted Tungstoborate Heteropoly Complexes, *SPECTROSCOPY AND SPECTRAL ANALYSIS*, 31 (2011) 2191-2194.
- [39] P.A. Shringarpure, A. Patel, Cobalt Substituted Keggin-Type Phosphotungstate, an Efficient Epoxidation Catalyst: Study on Kinetic Behavior as Well as Reaction Mechanism, *Synthesis and Reactivity in Inorganic, Metal-Organic, and Nano-Metal Chemistry*, 45 (2015) 397-406.
- [40] K. Nowińska, A. Waclaw, W. Masierak, A. Gutsze, Manganese (II) Modified Heteropoly Compounds Studied by ESR, *Catalysis Letters*, 92 (2004) 157-162.
- [41] P. Tarte, Infra-red spectra of inorganic aluminates and characteristic vibrational frequencies of AlO₄ tetrahedra and AlO₆ octahedra, *Spectrochimica Acta Part A: Molecular Spectroscopy*, 23 (1967) 2127-2143.
- [42] I. Holclajtner-Antunović, U.B. Mioč, M. Todorović, Z. Jovanović, M. Davidović, D. Bajuk-Bogdanović, Z. Laušević, Characterization of potassium salts of 12-tungstophosphoric acid, *Materials Research Bulletin*, 45 (2010) 1679-1684.
- [43] G.M.N.-S. Brown, M. R.; Busing, W. R.; Levy, H. A., *Acta Crystallogr., Ser.*, 33 (1977) 1038

- [44] J. Akitt, A. Farthing, Aluminium-27 nuclear magnetic resonance studies of heteropolyanions containing aluminium as heteroatom, *Journal of the Chemical Society, Dalton Transactions*, (1981) 1615-1616.
- [45] W.G. D. Müller, A. Samoson, E. Lippmaa and G. Scheler, . Solid-state Aluminium-27 Nuclear Magnetic Resonance Chemical Shift and Quadrupole Coupling Data for Condensed AIO, *Tetrahedra, J. Chem. Soc., Dalton Trans*, 0 (1986,) 1277-1281.
- [46] M.B. Maurin, R.D. Vickery, W. Bryant III, M.A. Hussain, Physicochemical Properties of the Novel Heteropolyanion Antiviral Hexapotassium- α -vanado-11-tungstoborate (DuP 925), *Pharmaceutical research*, 9 (1992) 570-574.
- [47] K.Y. Matsumoto, A. Kobayashi, Y. Sasaki, The crystal structure of β -K₄SiW₁₂O₄₀· 9H₂O containing an isomer of the Keggin ion, *Bulletin of the Chemical Society of Japan*, 48 (1975) 3146-3151.
- [48] J.F. Keggin, The structure and formula of 12-phosphotungstic acid, *proc. Roy, Soc.*, 114 (1934) 75.
- [49] C.N. Kato, Y. Makino, M. Yamasaki, Y. Kataoka, Y. Kitagawa, M. Okumura, Synthesis and X-ray crystal structure of α -Keggin-type aluminum-substituted polyoxotungstate, in: *Advances in Crystallization Processes*, InTech, 2012.
- [50] J. Gamelas, M. R. Soares, A. Ferreira, A. Cavaleiro, Polymorphism in tetra-butylammonium salts of Keggin-type polyoxotungstates, 2003.
- [51] M.T. Pope, Heteropoly and Isopoly Oxomaterials, *Inorganic Chemistry Concept*, 8 (1983).
- [52] H. Fletcher, C.C. Allen, R.C. Burns, D.C. Craig, Pentapotassium dodecatungsto-borate(III) hexadecahydrate, *Acta Crystallographica Section C*, 57 (2001) 505-507.

- [53] P. Gaca, M. Drzewiecka, W. Kaleta, H. Kozubek, K. Nowińska, Catalytic Degradation of Polyethylene over Mesoporous Molecular Sieve MCM-41 Modified with Heteropoly Compounds, *Polish Journal of Environmental Studies*, 17 (2008).
- [54] S.R. Chandrasekaran, B. Kunwar, B.R. Moser, N. Rajagopalan, B.K. Sharma, Catalytic Thermal Cracking of Postconsumer Waste Plastics to Fuels. 1. Kinetics and Optimization, *Energy & Fuels*, 29 (2015) 6068-6077.
- [55] M. Azhar Uddin, Y. Sakata, A. Muto, Y. Shiraga, K. Koizumi, Y. Kanada, K. Murata, Catalytic degradation of polyethylene and polypropylene into liquid hydrocarbons with mesoporous silica, *Microporous and Mesoporous Materials*, 21 (1998) 557-564.
- [56] B. Aydemir, N.A. Sezgi, Alumina and Tungstophosphoric Acid Loaded Mesoporous Catalysts for the Polyethylene Degradation Reaction, *Industrial & Engineering Chemistry Research*, 52 (2013) 15366-15371.
- [57] N. Mizuno, M. Misono, Heterogeneous Catalysis, *Chemical Reviews*, 98 (1998) 199-218.
- [58] M. Tao, L. Xue, Z. Sun, S. Wang, X. Wang, J. Shi, Tailoring the Synergistic Bronsted-Lewis acidic effects in Heteropolyacid catalysts: Applied in Esterification and Transesterification Reactions, *Scientific Reports*, 5 (2015) 13764.
- [59] S. Sato, M. Kuroki, T. Sodesawa, F. Nozaki, G.E. Maciel, Surface structure and acidity of alumina-boria catalysts, *Journal of Molecular Catalysis A: Chemical*, 104 (1995) 171-177.
- [60] J. Moffat, Implicit and explicit microporosity in heteropoly oxometalates, *Journal of molecular catalysis*, 52 (1989) 169-191.
- [61] M.R. Jan, J. Shah, H. Gulab, Catalytic degradation of waste high-density polyethylene into fuel products using BaCO₃ as a catalyst, *Fuel Processing Technology*, 91 (2010) 1428-1437.

- [62] A. Corma, Inorganic Solid Acids and Their Use in Acid-Catalyzed Hydrocarbon Reactions, *Chemical Reviews*, 95 (1995) 559-614.
- [63] S.J. Choi, Y.-K. Park, K.-E. Jeong, T.-W. Kim, H.-J. Chae, S.H. Park, J.-K. Jeon, S.-S. Kim, Catalytic degradation of polyethylene over SBA-16, *Korean Journal of Chemical Engineering*, 27 (2010) 1446-1451.
- [64] M. Artetxe, G. Lopez, M. Amutio, G. Elordi, J. Bilbao, M. Olazar, Light olefins from HDPE cracking in a two-step thermal and catalytic process, *Chemical engineering journal*, 207 (2012) 27-34.
- [65] A.G. Buekens, H. Huang, Catalytic plastics cracking for recovery of gasoline-range hydrocarbons from municipal plastic wastes, *Resources, Conservation and Recycling*, 23 (1998) 163-181.

Figure Captions

Figure 1: FTIR spectra of (a) KB, (b) CsAB and (c) KAB.

Figure 2: Raman spectra of (a) CsAB, (b) KAB and (c) KB.

Figure 3: SEM micrographs of CsAB (a), KAB (b) and KB (c).

Figure 4: ^{27}Al NMR spectra for (a) CsAB and (b) KAB.

Figure 5: Thermogravimetric analysis of (a) CsAB, (b) KAB and (c) KB.

Figure 6: Aluminum substituted tungstoborate Keggin polyanion $[\text{H}_2\text{AlBW}_{11}\text{O}_{40}]^{-6}$ structure visualized by OLEX 2. B, W, Al and atoms are represented by yellow, blue, green and red ellipsoids respectively at 50% probability.

Figure 7: PXRD patterns for (a) KAB and (b) CsAB.

Figure 8: Product distribution in catalytic and non-catalytic cracking reactions.

Figure 9: (a) Carbon number distribution and (b) carbon number selectivity in oil produced by catalytic and thermal cracking.

Figure 10: Comparison between alkenes (a) and alkanes (b) obtained by catalytic and thermal degradation of PE.

Figure 11: FTIR spectra of (a) fresh and (b) regenerated CsAB catalyst.

Figures

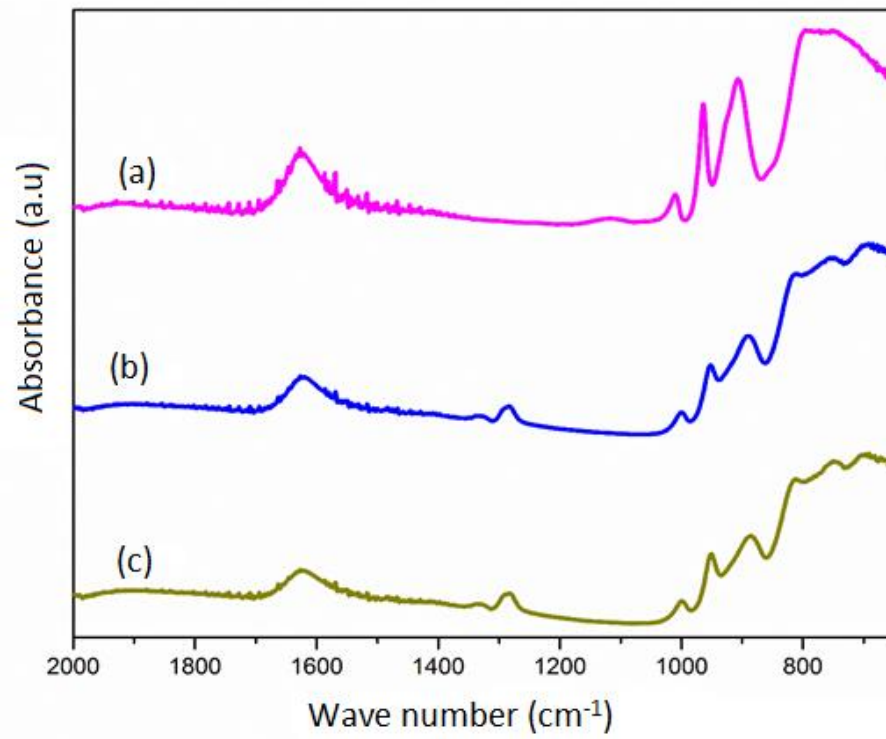


Figure 1

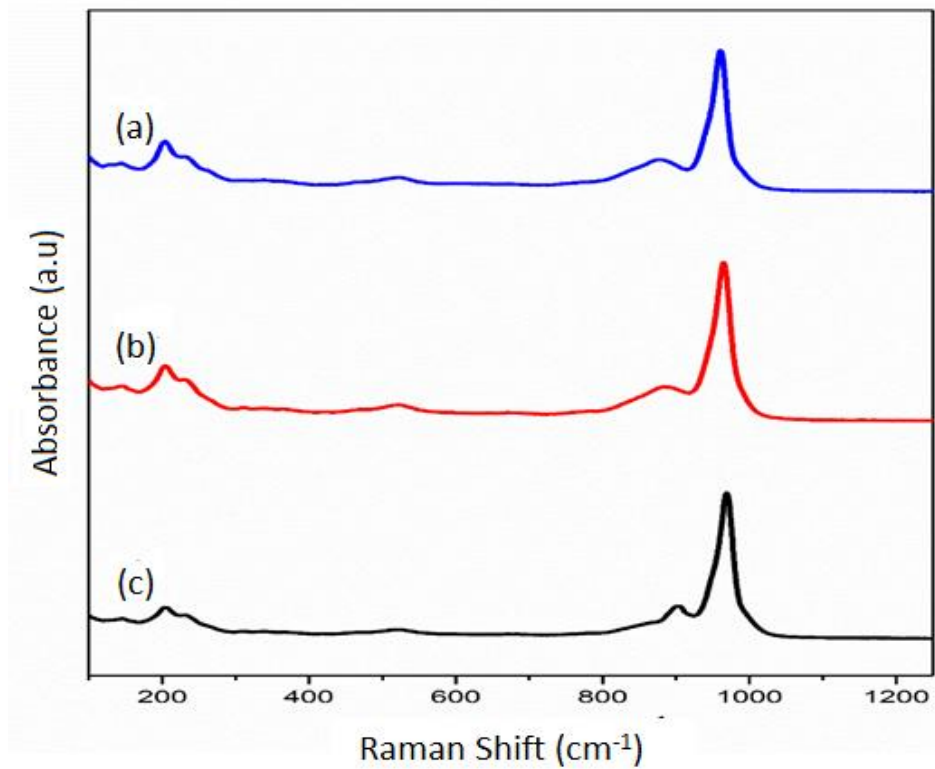


Figure 2

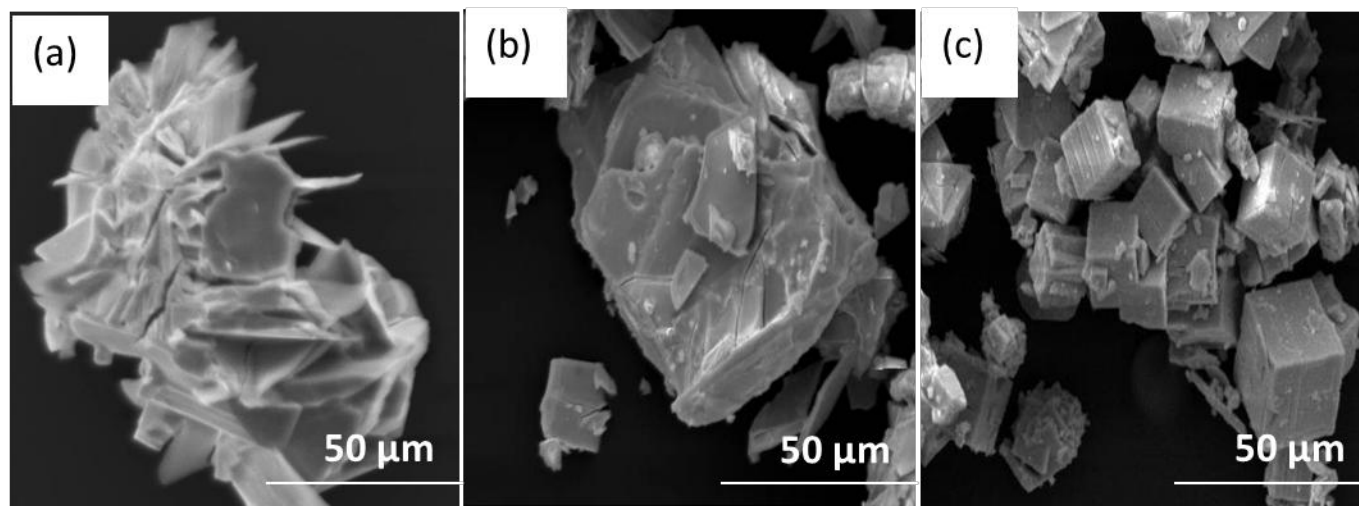


Figure 3

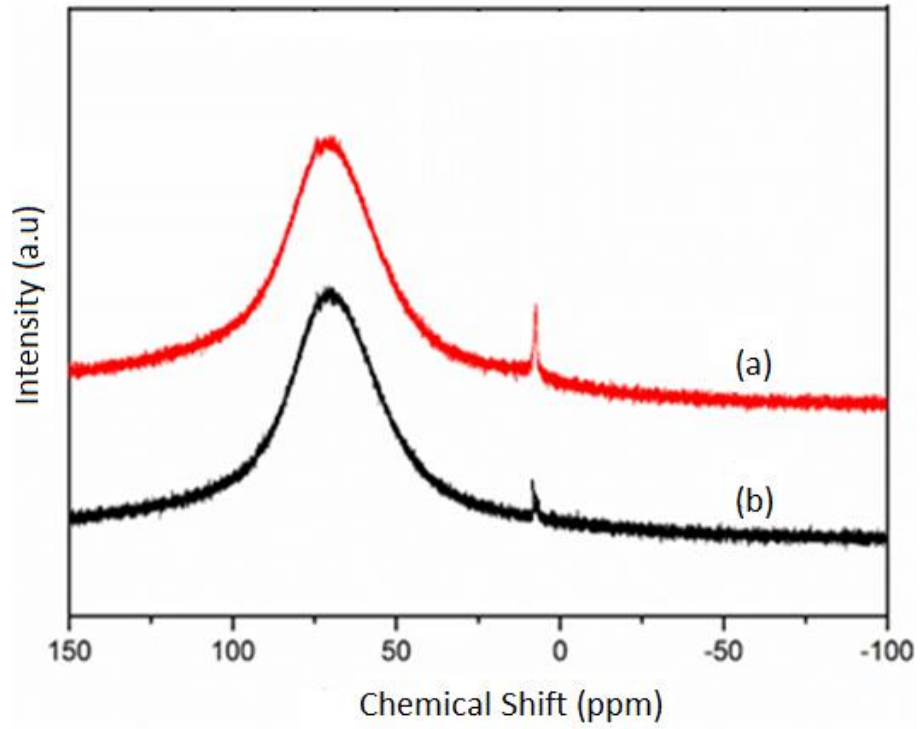


Figure 4

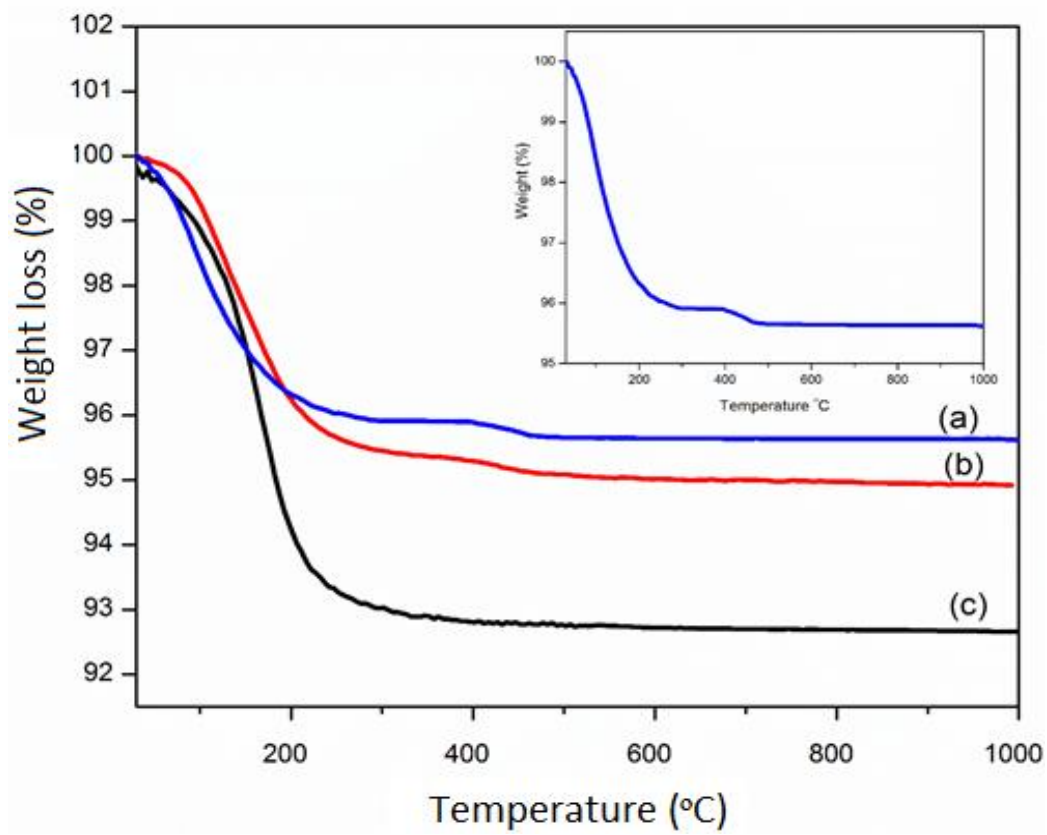


Figure 5

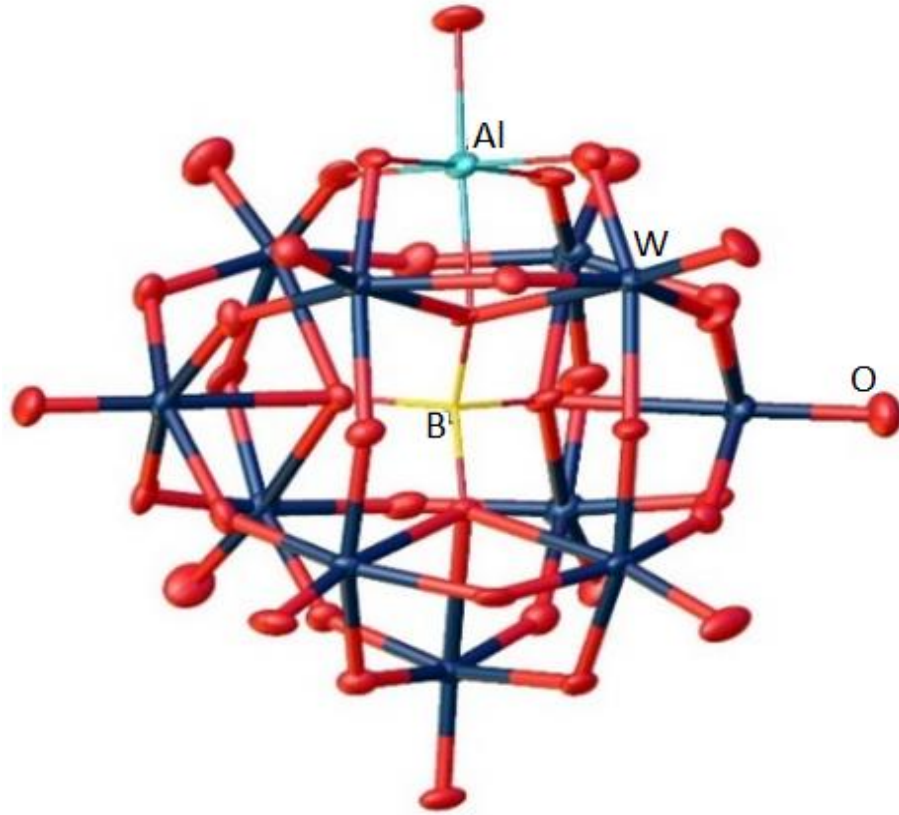


Figure 6

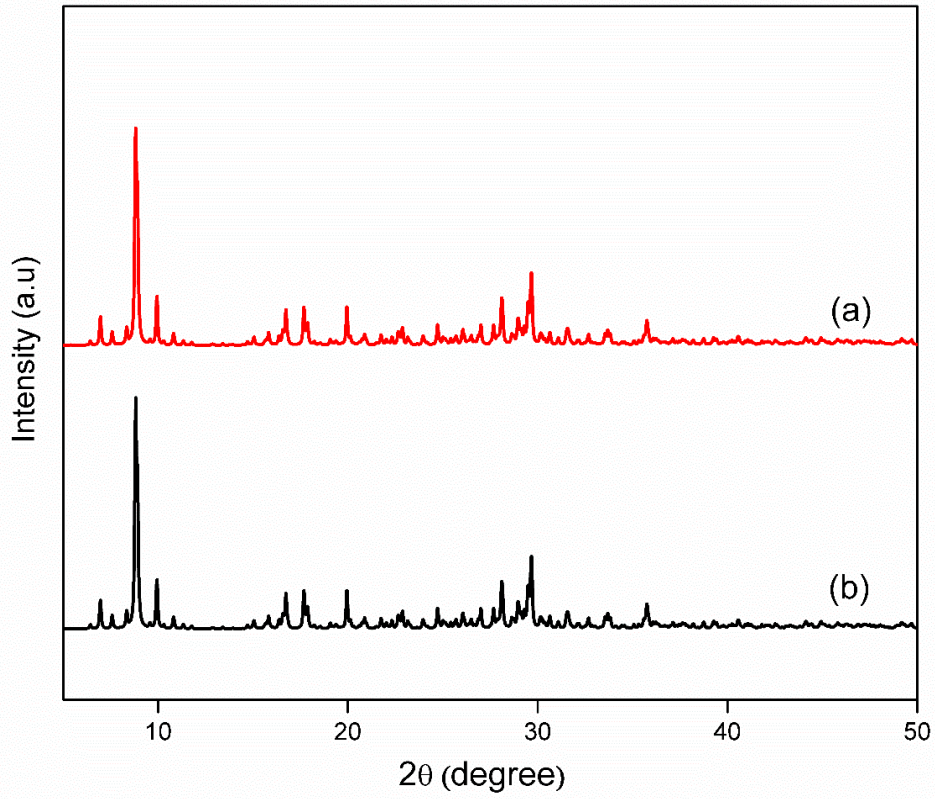


Figure 7

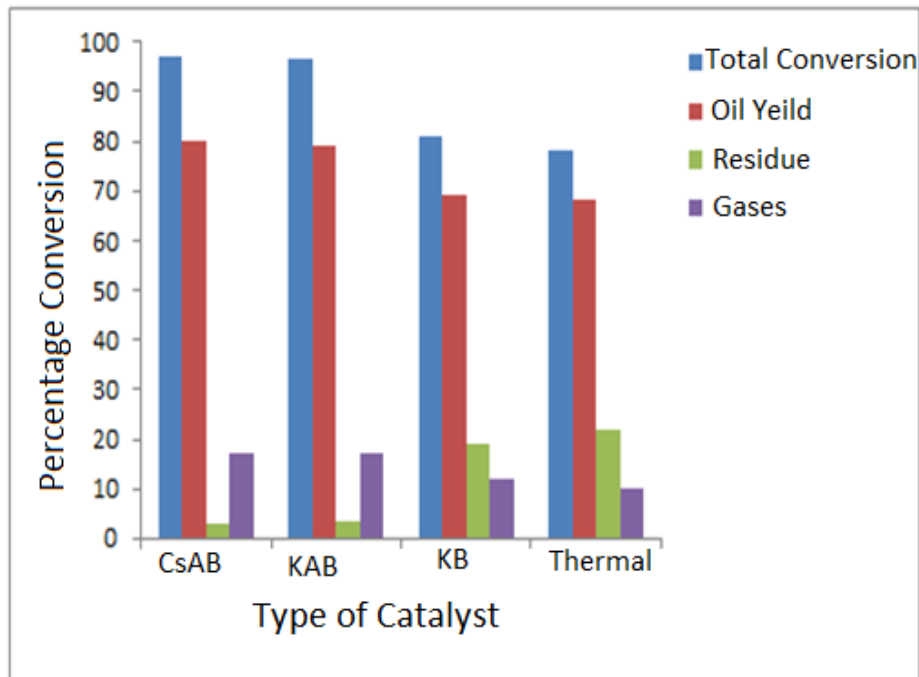


Figure 8

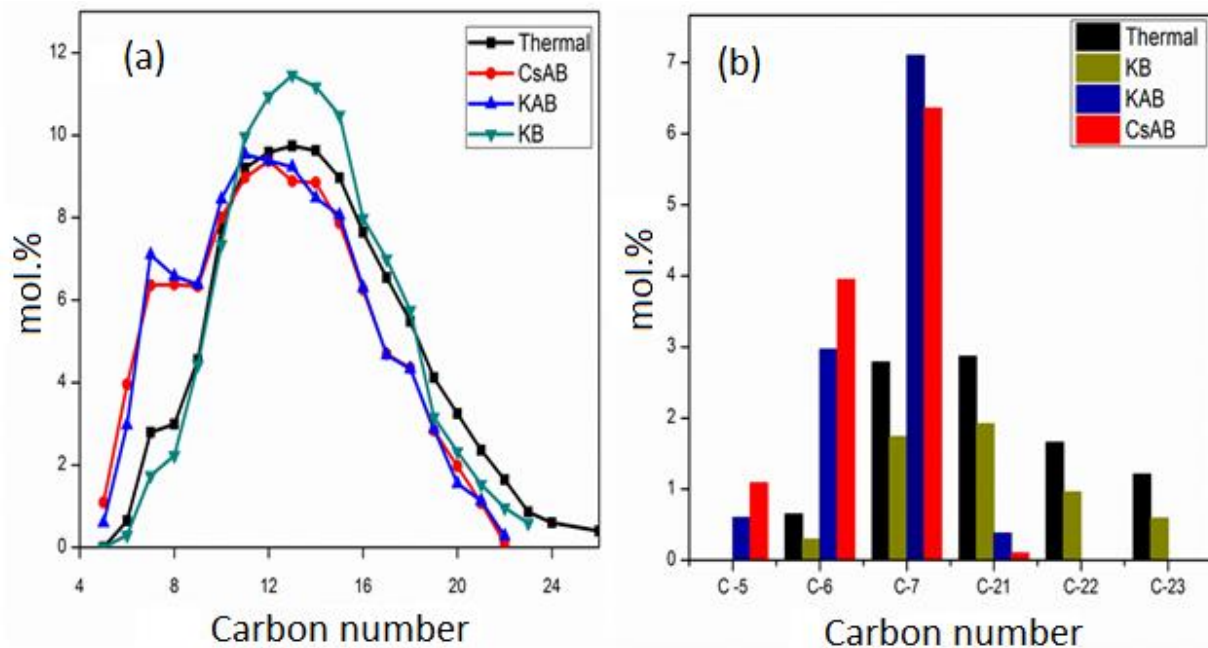
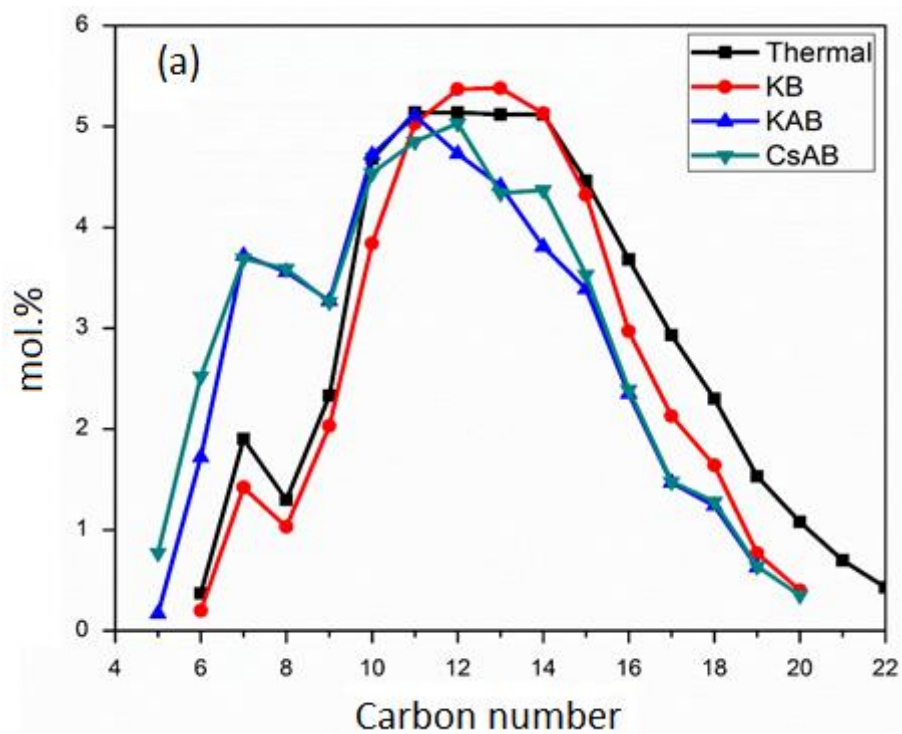


Figure 9



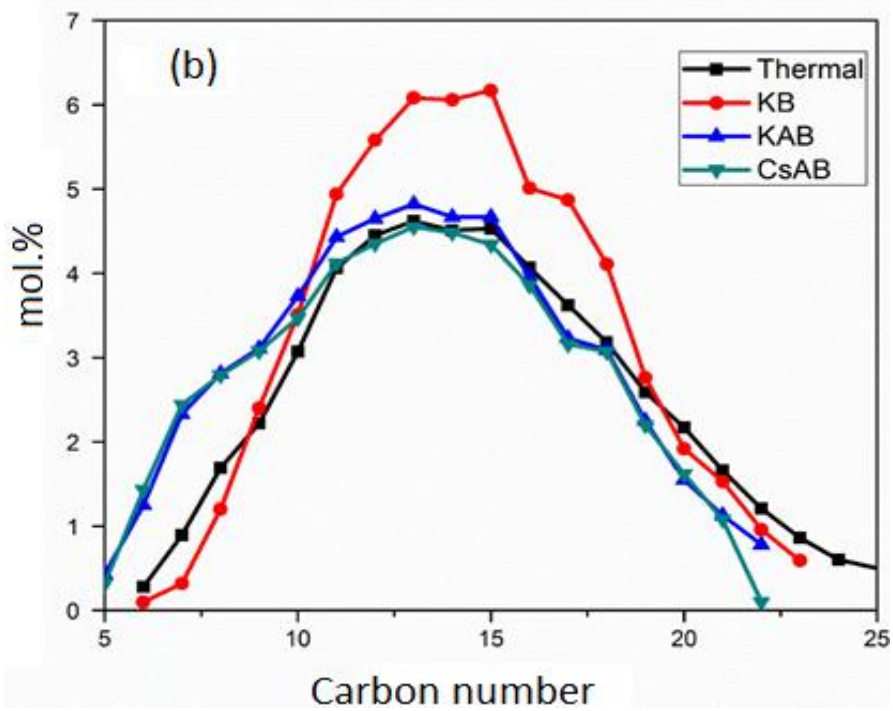


Figure 10

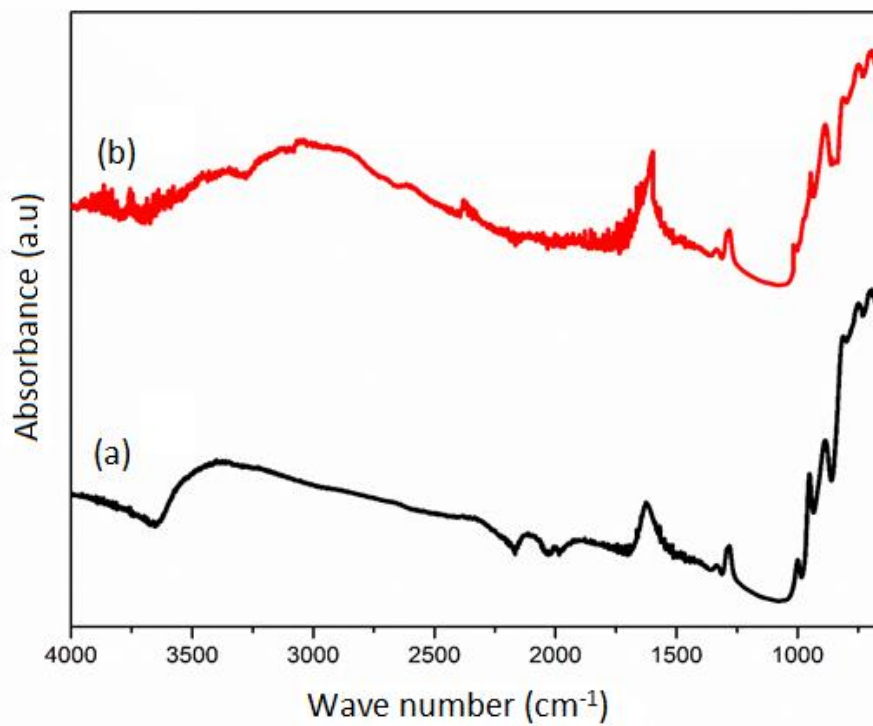


Figure 11