Highly efficient catalytic pyrolysis of polyethylene waste to derive fuel products by novel polyoxometalate/kaolin composites

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Abstract

We report here alumina-substituted Keggin tungstoborate/kaolin clay composite materials (KAB/kaolin) as polyethylene cracking catalysts. KAB/kaolin composites with varying concentrations of KAB (10–50 wt.%) were synthesized by the wet impregnation method and successfully characterized by Fourier-transform infrared spectroscopy, powder X-ray diffraction, thermo-gravimetric analysis and scanning electron microscopy with energy dispersive X-ray spectroscopy analytical techniques. Use of KAB loaded kaolin composites as the catalyst for low-density polyethylene (LDPE) cracking exhibited a higher percentage of polymer conversion (99%), producing 84 wt.% of fuel oil and negligible amount ($^<$ 1 wt.%) of solid residue while thermal cracking produced ~22 wt.% residue. Furthermore, gas chromatography–mass spectrometry analysis of oil obtained by non-catalytic cracking exhibited a high selectivity to high molecular weight hydrocarbons (C_{13}–C_{23}) compared to the catalytic cracking where 70 mol.% of gasoline range hydrocarbons (C_5–C_{12}) were produced. We propose that higher cracking ability of our prepared catalysts might ensue from both Brønsted and Lewis acid sites (from KAB and kaolin respectively), which enhanced the yield of liquid fuel products and reduced the cracking temperature of LDPE. These findings suggest that the prepared composites were cost-effective and excellent cracking catalysts that could be recommended for highly efficient conversion of waste plastic materials to petrochemicals at an industrial scale.

Introduction

Conversion of waste plastic to valuable chemicals such as fuel products is an area of great research interest (Uddin et al., 1997). Thermal and catalytic cracking of waste polymers to fuel oil has been investigated by many researchers (Akpanudoh et al., 2005; Lin et al., 2004; Predel and Kaminsky, 1998; Uddin et al., 1997). However, catalytic cracking is more effective compared to thermal cracking as the application of catalyst decreases the reaction temperature (Aydemir et al., 2012) and increases the yield of lighter hydrocarbons (Sarker et al., 2012).

Zeolite Socony Mobil–5 (Aguado et al., 2007), β zeolite (Chaianansutcharit et al., 2007) and Y-zeolite (Van Grieken et al., 2001) are widely reported for plastic degradation. Zeolites show excellent catalytic properties for degradation of polymers due to strong Lewis acidity that facilitates carbon–carbon bond breakage. However, the small pore size of zeolite hinders the contact of bulky polymer chains to acid sites located inside the pores and is deactivated quickly by carbon deposition (Marcilla et al., 2006). To overcome this problem, mesoporous materials possessing large pore sizes have been developed (Kresge et al., 1992) but in pure silica form – they have low acidity compared to zeolites that limit their use as cracking catalysts (Marcilla et al., 2006). The catalytic activity of these materials was reported to be enhanced by incorporation of some metal ions (Al^{3+} and Fe^{3+}) (Obali et al., 2008) and heteropoly acids (HPAs) into a silica framework (Jalil, 2002).

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The HPAs possess a discrete and mobile ionic structure that endows them with high redox potential, uniform surface charge distribution and proton transferability (Shah et al., 2012). Owing to these exclusive physiochemical properties, HPAs are widely applied as homogeneous as well as heterogeneous catalysts for a number of chemical reactions (Timofeeva, 2003; Zhang et al., 2010). HPAs also possess strong Brønsted acid sites that make them excellent acidic catalysts (Kozhevnikov, 2007). However, due to the small surface area ($\leqslant$ 10 m^2g^{-1}) and low thermal stability of HPAs, their application as a polymer cracking catalyst is limited (Ghanbari-Siahkali et al., 2001). Both of the above challenges have been overcome by dispersing HPAs on a suitable silica support. Tungstophosphoric acid (TPA) loaded on mesoporous silica (MCM-41 and SBA-15) has been reported for the polyethylene (PE) cracking (Aydemir et al., 2012; Jalil, 2002). Compared to thermal cracking, TPA/MCM-41 composite material decreased the activation energy to the half value (Jalil, 2002). Use of TPA/SBA-15 composite for PE degradation produced a higher amount of gas but liquid yeild was only 42% at 460ºC (Aydemir and Sezgi, 2013). In our previous studies, TPA/kaolin composites was used for PE cracking and the oil yeild was 81% (Attique et al., 2018).

Among the series of HPAs, tungstophospates are mostly used for PE cracking (Jalil, 2002). However, tungstoborates have never been applied for cracking reactions. Recently we have used cesium and potassium salts of alumina-substituted Keggin tungstoborates (KAB) for PE degradation (Attique et al., in press). Aluminum substitution is reported to create extra Brønsted acid sites (Marcilla et al., 2006; Obalı et al., 2012), so it helped to decrease the cracking temperature down to 320ºC.

The present study describes the impregnation of KAB (K-salt) on kaolin (a clay material) and the use of composite materials for PE cracking reactions. Although kaolin is a low-cost material and possesses some Lewis acidity and extraordinary thermal stability, it has been reported that its application for polypropylene cracking reactions require very high temperature (~500ºC) (Panda and Singh, 2013). Having an aim of achieving a cost-effective and highly active cracking catalyst, we report here KAB/kaolin composite materials which combine the characteristic properties of both substances towards low PE cracking temperature (295ºC) and extraordinary catalytic performance (high fuel oil percentage $\geqslant$ 84% with majority of branched chain and olefinic hydrocarbons and low residue) that is a considerable achievement in the field of waste management to reduce environmental pollution by effective utilization of the waste polymeric materials.

Experimental

Materials

Sodium tungstate dihydrate ($Na_2WO_4 \cdot 2H_2O$, 98%; Merk), disodium hydrogen phosphate ($Na_2HPO_4 \cdot 12H_2O$), 98%; Sigma Aldrich), boric acid (H_3BO_3, 98.5%, Sigma Aldrich), aluminum nitrate nonahydrate ($Al(NO_3)_3 \cdot 9 H_2O$, 98%, Sigma Aldrich), potassium chloride (KCl, 99%; Merk) and acetic acid (CH_3COOH, 99.5 %, Sigma Aldrich) were used for synthesis of KAB. All chemicals were of analytical grade, commercially available and used as received from the supplier without further purification. Kaolin clay was purchased from M&B Laboratory Chemicals. Low-density polyethylene (LDPE) pellets (20 μm thickness, melting point range 140–150ºC) were provided by the Qatar Chemical and Petrochemical Marketing and Distribution Company.

Methods

Synthesis of $K_6[H_2AlBW_{11}O_{40}] \cdot 9H_2O$. The $K_6[H_2AlBW_{11}O_{40}] \cdot 9H_2O$ was synthesized by a simple method. Briefly, sodium tungstate (3.62 g) and boric acid (0.2 g) were dissolved in boiling water (8 mL), pH adjusted at 6–7 by glacial acetic acid and stirred for an hour while heating. The resultant solution was placed at 4ºC for a day, then filtered off to remove any precipitates. Aluminum nitrate solution (0.378 g/5mL) was added to the above filtrate (dropwise) and the resultant mixture was stirred again for 1 hour at pH 6.2, while heating (80–90ºC). The solution was cooled to room temperature and potassium chloride (6 mmol) was added in the solution while stirring. The solid product was separated by addition of three volumes of ethanol and washed three to five times with ethanol. The product, $K_6[H_2AlBW_{11}O_{40}] \cdot 9H_2O$ was abbreviated as KAB for simplification.

Preparation of KAB/kaolin composites (KABK). 1 g of kaolin clay was added in 50 mL of water and stirred vigorously for 4 hours to obtain a stable dispersion. Then, the solution of aluminum substituted tungstoborate (K-salt), having a specific concentration (10–50 wt.%) was added dropwise to kaolin dispersion for preparation of 10%, 30% and 50% KAB/kaolin composites. The resulting mixture was stirred again for 12 hours at 25ºC, then heated at 60ºC on a water bath in order to evaporate the solvent. The solid mass obtained was dried in an oven for 10 hours at 100ºC. The synthesized composites were denoted as KABK-1, KABK-3 and KABK-5 corresponding to 10, 30 and 50 wt.% of KAB dispersed on the kaolin surface.

PE cracking experiment. The PE cracking experiment was performed in a pyrex glass reactor (280 mm × 50 mm) by the batch operation. 15g PE pellets and 0.75g catalyst (5 wt.%) were mixed well and introduced into the reactor for cracking reactions. The reactor was placed in a specially designed furnace (equipped with an external temperature controller) and heated slowly (2ºC/minute) to 120ºC under nitrogen flow to make the reaction environment inert. After maintaining this temperature for an hour, N_2 supply was terminated and reactor temperature raised slowly to reach cracking temperature. When the first drop of liquid oil comes out, the reactor temperature was then kept fixed until the completion of the reaction. Details

of experimental setup can be found elsewhere (Attique et al., 2018). After completion of the reaction, cracking products were divided into three categories: (1) gases (products which could not condense at water cooling temperature); (2) liquid hydrocarbons; and (3) residues (wax and coke left behind after reaction completion). The amount of gaseous fraction was assessed by the subtraction of the weight of liquid oil and residue from the total weight of the plastic sample. Gas chromatography–mass spectrometry (GC/MS) analysis of liquid products was performed on a GCMS-QP2010S system. Degree of polymer conversion was calculated by the formula given in the following equation:

$$DC\% = \frac{m_{PE} - m_{residue}}{m_{PE}} x100$$

where m_{PE} and $m_{residue}$ represent the mass of PE feed and residue respectively.

Characterization techniques. Synthesized catalysts were characterized by Fourier-transform infrared spectroscopy (FT-IR), powder X-ray diffraction (p-XRD), scanning electron microscopy with energy dispersive X-ray spectroscopy (SEM-EDX) and thermogravimetric analysis (TGA). Functional groups were determined by FT-IR spectrum recorded on FT-IR Spectrometer (Agilent technology; model 41630) accumulating 256 number of scans within mid-IR range (4000–400 cm^{-1}) at 4cm^{-1} resolution (operating in attenuated total reflection mode). Morphology of composite materials was studied with the help of an XL30 environmental scanning electron microscope operating at 20 kV. Samples were mounted on a carbon tape and pre-coated by gold targets with the help of Polaron SC7640 sputter coater. EDX spectra were recorded on INCA X-Act EDX detector (Oxford Instruments Analytical Ltd. UK) with a working distance of 10 mm. p-XRD data for the prepared composites were collected on a PANalytical XPERT-PRO instrument, operating at 40kV using a Cu Kα radiation source in a 2θ range of 5º ⩽ 2θ ⩽ 85º with 0.02º step size and 80 seconds were spent per step. TGA was accomplished by a Netzsch STA 409 system – approximately 20 mg of these samples was inserted in alumina pans and temperature was raised to 1000ºC at 10ºC/minute under argon flow. The GC/MS analysis of liquid products was performed on a GCMS-QP2010S instrument equipped with a ZB-5 MS column (30 m × 0.32 mm × 0.25 μm) under flow of helium. The temperature of the GC oven was held at 40ºC for 1 minute, then raised to 310ºC (3ºC/minute) and kept constant for 30 minutes. Injector and detector temperatures were kept at 280ºC and 310ºC, respectively. Mass to charge ratio (m/z) was recorded from 30 to 500 using electron ionization as the ionization mode at 70 eV. Temperature of the ion source and interface was maintained at 180ºC and 250ºC, respectively. Mass spectra were compared with standard spectra from the NIST/EPA/NIH Mass Spectral Library.
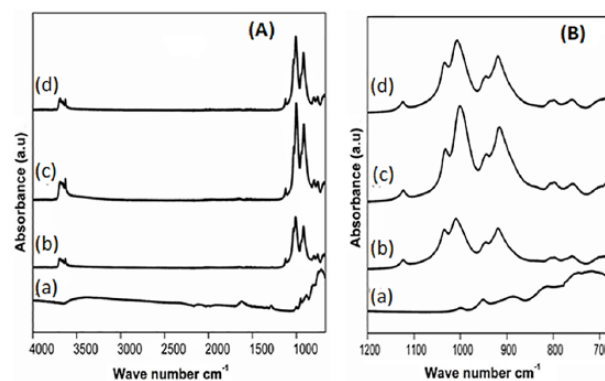
Figure 1. Fourier-transform infrared spectroscopy (FT-IR) spectra of: (a) alumina-substituted Keggin tungstoborate (KAB); (b) KABK-5; (c) KABK-3; and (d) KABK-1 (A). Expansion of FT-IR spectra in the 700–1200 cm^{-1} region (B).

Results and discussion

Catalyst characterization

The prepared catalysts were characterized by several techniques such as FT-IR, p-XRD, SEM-EDX, and TGA in order to check the final structure and morphology of KAB/kaolin composites. FT-IR spectrum of KAB exhibited characteristic asymmetric vibrations for W–O$_d$, W–B–O$_a$, W–O$_b$–W, W–O$_c$–W and W–O–Al at 950, 890, 822, 740 and 710 cm^{-1}, respectively, that confirmed the formation of Keggin structure (Li-hua et al., 2011; Tarte, 1967) (Figure 1). FT-IR spectrum of kaolin presented vibrations of Si–O–Al bond at 761 cm^{-1} and 795 cm^{-1}, while OH bending vibrations were seen at 914 cm^{-1}. Si–O–Si in-plane bending and stretching vibrations were recorded at 1007 cm^{-1} and 1123 cm^{-1}, respectively (Kuang et al., 2003). All the characteristic bands of kaolin were shown in the FT-IR spectra of KAB loaded kaolin samples with different wt.% of KAB while only two vibration bands of KAB could be seen at 950 and 890 cm^{-1} corresponding to W–O$_d$ and W–O$_b$–W vibrations, respectively. The vibration bands of KAB located at 740 and 710 cm^{-1} were overlapped with the strong Si–O–Si bands of the kaolin support (Basir et al., 2015).
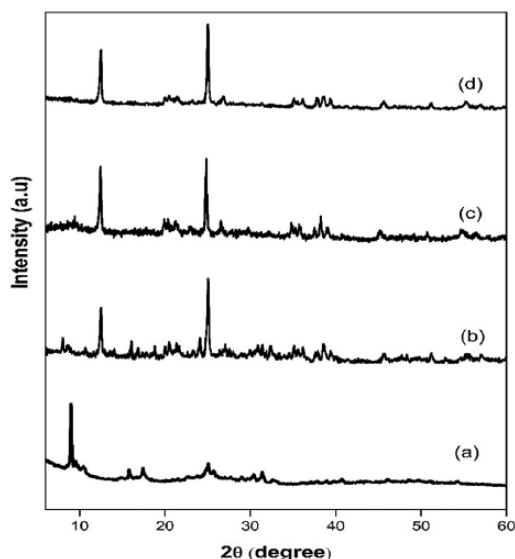
The XRD results illustrated the crystalline structure of bulk KAB presenting all the diffraction peaks, characteristic for tungstoborate Keggin structure at 2θ values of 8.3, 18.7, 29.1, 33.7 and 34º (Li-hua, 2011) (as shown in Figure 2). XRD patterns of kaolin also shows a highly crystalline structure having an intense and narrow diffraction peak d001 at 2θ value of 12.32º (Basir et al., 2015). KAB/kaolin composites exhibited reduced crystallinity compared to kaolin and did not exhibit all diffraction peaks, characteristic for tungstoborate Keggin structure. At 10 wt.% KAB loading, the typical diffraction peak of KAB at 2θ = 8.3º was extremely small and the intensity of this peak was enhanced with the increasing amount of KAB loaded (Aydemir et al., 2012). However, even for the KABK-5 sample, all the diffraction peaks, characteristic of KAB crystalline phase could not be seen,

representing the fine distribution of KAB on the surface of kaolin (Dong et al., 2013).

The SEM images showed a regular crystalline shape of KAB particles (Figure 3a). Polyoxometalate salts of bulky counter-cations such as Cs and NH_4 have also been reported to maintain the ordered crystal structure of parent acid ($H_3PW_{12}O_{40}.6H_2O$) in which cations are positioned at $H^+(H_2O)_2$ sites (Brown et al., 1977). The average crystal size of these KAB particles was 4

Figure 2. Powder X-ray diffraction patterns of: (a) alumina-substituted Keggin tungstoborate (KAB); (b) synthesized composites of KABK-5; (c) KABK-3; and (d) KABK-1 samples.

μm. Kaolin also has a crystalline structure but all KAB loaded kaolin composites did not exhibit this crystalline morphology that revealed the fine dispersion of KAB particles on the surface of clay (Figure 3 b–d). EDX analysis of KAB crystals revealed the mono-aluminum substitution into tungstoborate Keggin anion. Atomic percentages of other major elements such as K, O, and W were also found in close approximation to the theoretically calculated values (online Supplemental Table S1). Moreover, the atomic ratio of tungsten increased through the KABK-1 to KABK-5 samples indicating the increase in amount of tungstoborate loading on the kaolin surface. It was also observed that with the increase of KAB amount being loaded on kaolin, the Al/Si ratio was also increased. The increase in Al/Si ratio is considered as an important factor for acid-catalyzed reactions (Obali et al., 2008).

The TGA curve of KAB exhibited a mass loss of ~4.54% in a single step (70°C to 280°C) that corresponded to removal of water molecules of crystallization. After this step, no obvious mass loss was observed that indicated the stability of KAB up to 1000°C (Figure 4). Only 0.9% mass loss was observed in the TGA curve of kaolin during the first step, that is, ≥ 100°C due to removal of adsorbed water molecules. During a second step (450–700°C), 9.4% mass loss was observed that could be ascribed to dehydroxylation of kaolinite sheets and development of metakaolinite (Kakali et al., 2001). KAB loaded kaolin composites were also thermally decomposed in two steps. For instance, 50% KAB/kaolin sample (KABK-5) exhibited 3% mass loss during the first step, corresponding to the removal of adsorbed and crystallized water molecules. This mass loss percentage is in-between the mass loss
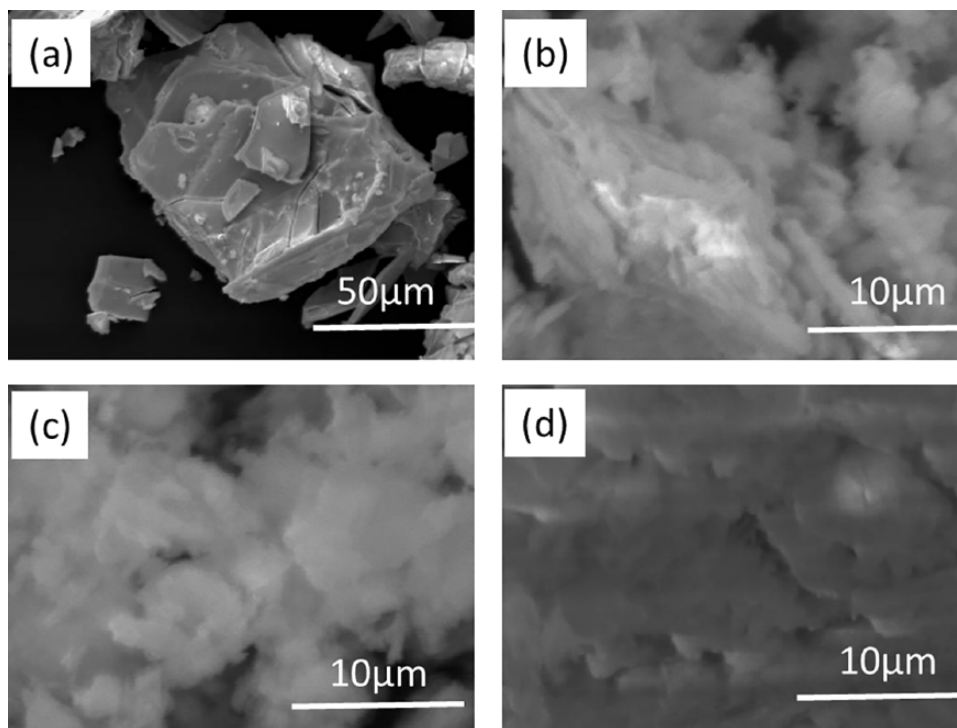
Figure 3. Scanning electron microscope micrographs of: (a) alumina-substituted Keggin tungstoborate (KAB); synthesized composites of (b) KABK-1; (c) KABK-3; and (d) KABK-5 samples.
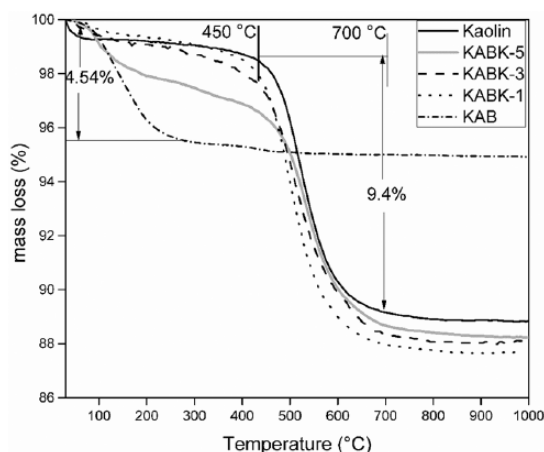
Figure 4. Thermo-gravimetric analysis curves of alumina-substituted Keggin tungstoborate (KAB) and KAB/kaolin composites.
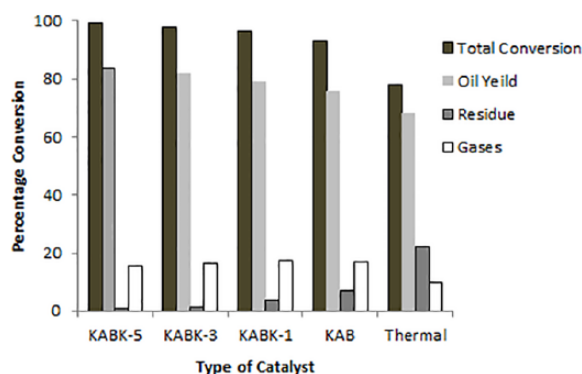

Figure 5. Effect of catalyst on product distribution during low-density polyethylene cracking with different types of catalysts.

exhibited by pure tungstoborate and kaolin samples during the first step. In the second step, a mass loss of 7.6% was observed that is less than the mass loss exhibited by kaolin. Thermal behavior of KABK-1 and KABK-3 samples was quite analogous to kaolin that indicated the presence of large portions of kaolin in 10% and 30% KAB loaded kaolin composites compared to 50% loaded sample.
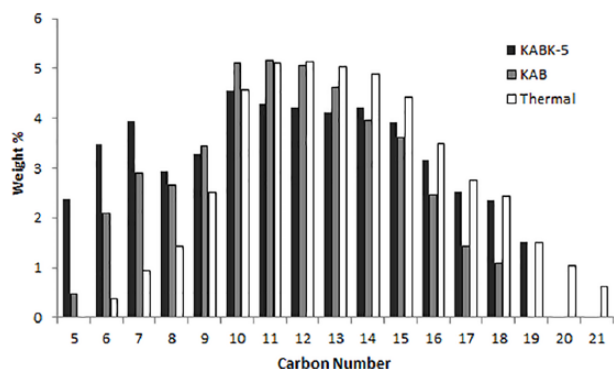
Catalytic cracking of PE

The PE cracking performed in the absence of catalyst took place at 375ºC while the use of KAB/kaolin composites as cracking catalysts lowered the degradation temperature to a considerable extent and especially the KABK-3 and KABK-5 samples that degraded LDPE at 295ºC. The use of catalysts also enhanced the percentage yield of valuable fuel products. Total percentage conversion of polymer and the percentage yield of various cracking products (liquid oil, residue, and gas) obtained by the non-catalytic and catalytic cracking of LDPE are shown in Figure 5. Percentage conversion of LDPE was very high in the case of cracking reactions using KAB/kaolin composites
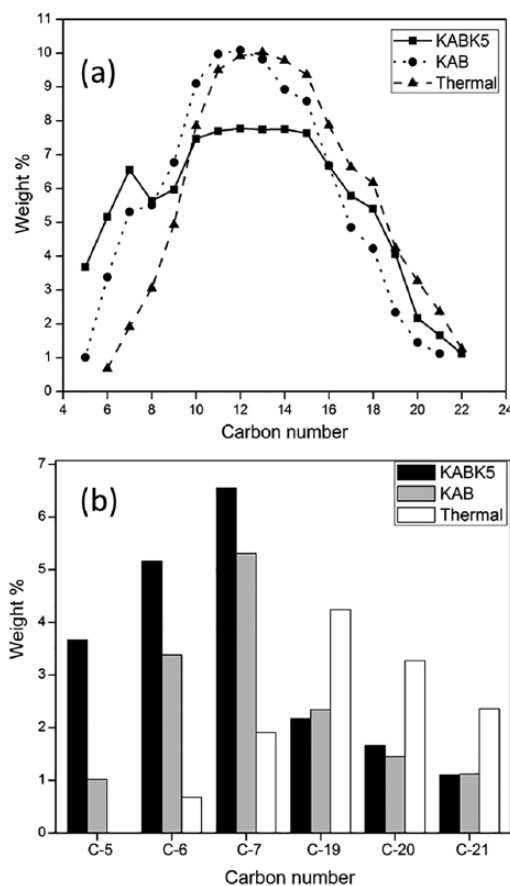
Figure 6. (a) Carbon number distribution in oil produced by thermal and catalytic cracking; and (b) carbon number selectivity for thermal and catalytic cracking.

(99.2%) while thermal cracking showed only 78% total conversion. Moreover, the comparative yield of liquid and gaseous hydrocarbons in the oil produced by LDPE cracking over KAB/kaolin samples was also high compared to non-catalytic cracking. Both oil and gas fractions obtained by catalytic cracking are valuable fuel products (Aydemir and Sezgi, 2013; Jalil, 2002). Liquid hydrocarbon yield was enhanced with an increase of KAB amount loaded and reached to the highest value (84 wt.%) with KABK-5. Similarly, the quantity of residue was decreased by increasing KAB loading and was negligible in the case of KABK-5 catalyst. On the contrary, only 68 wt.% of liquid oil and 22% residue was produced by thermal cracking. The increase in oil yield by catalytic cracking could be ascribed to the mutual effect of Lewis and Brønsted acid sites (from kaolin and KAB, respectively) (Basir et al., 2015). Similarly, Gaca et al. (2008) have explored that the use of tungstophosphoric acid impregnated on MCM-41 for PE cracking, produced an explicitly higher quantity of liquid hydrocarbons. Furthermore, comparatively higher percentage yield of gaseous hydrocarbons (C_1–C_4) was observed for all KAB/kaolin catalysts. Thus, the application of KAB/kaolin-based catalysts lowered the cracking temperature (~295ºC) as well as enhancing the yield of valuable fuel products (C_5–C_{21}) that is consistent with the previous studies (Jalil, 2002). Details of reactions' conditions and

Figure 7. Alkenes distribution in oil produced by non-catalytic and catalytic cracking of low-density polyethylene.

percentage yield of different cracking products are given in the online Supplemental Table S2.

Composition of liquid products. The liquid oil received by non-catalytic and catalytic cracking of LDPE was analyzed by GC/MS and presented in online Supplemental Figure S1. Every peak in the chromatogram belongs to a specific compound present in oil samples. The mass spectrum of every compound was interpreted by comparison with standard spectra of corresponding compounds with the help of a GC/MS library (NIST/EPA/NIH Mass spectral Library). About 35 major peaks were selected and quantified. The similarity index for identification of compounds was kept > 90. The identification of all compounds with respect to their relative abundance are provided in the online Table S3 and it was seen that the major components of the oil were paraffins and olefins (C_5–C_{26}). A broad range of hydrocarbons (C_6–C_{26}) was present in the oil produced by non-catalytic cracking and it was observed that the majority of oil fractions consisted of higher molecular weight hydrocarbons. Oil produced by catalytic cracking of LDPE using KAB and KAB/kaolin catalysts exhibited larger amounts of lighter hydrocarbons, especially gasoline range (C_5–C_{12}) hydrocarbons. Detailed analysis showed that oil produced by KAB presented only a small quantity of C_5 but KAB impregnated kaolin catalysts showed significantly larger quantities of C_5. Likewise, the amount of C_7 was increased to a greater extent by the use of KAB/ kaolin samples as shown in Figure 6. This might ensue from KAB loading on kaolin that could create additional Brønsted acid sites in the composite materials, posing a synergistic effect on the catalyst performance for LDPE cracking. The increase in total amount of acidity (Brønsted and Lewis) could initiate LDPE degradation reactions at Brønsted acidic sites and in this way speed up the breakdown of heavier hydrocarbons to lighter ones as reported earlier (Aydemir and Sezgi, 2013).

Liquid oil obtained by LDPE cracking exhibited both paraffins and olefins. As presented in the online Supplemental Table S3, the maximum percentage of olefins was observed in oil obtained by KABK-5 catalyst and the contribution of branched olefinic compounds was also substantially high (Figure 7). On the contrary, non-catalytic LDPE cracking showed high selectivity for paraffins, while olefins were produced in a comparatively lower amount and branched-chain hydrocarbons were negligible. The lower weight percentage of olefins compared to paraffins in non-catalytic oil might be from higher cracking temperature that favors the production of paraffins (Rahimi and Karimzadeh, 2011). The Haag–Dessau mechanism also explains the formation of olefinic hydrocarbons during thermal and catalytic cracking of PE (Kotrel et al., 2000). The increase in olefins produced by KABK–5 could be ascribed to protonic acid sites and increased Al/Si ratio in the catalyst. Many researchers have described the effect of Al/Si ratio on production of alkenes (Han et al., 2004; Wei et al., 2005). The enhanced protonation of hydrocarbons at Brønsted acidified sites forms carbonium ions that eventually undergo β-scission reactions (Corma, 1995). The increased β-scission and rearrangement reactions significantly enhanced the percentage of lighter hydrocarbons that was reflected in catalytic oil as low molecular weight and branched-chain olefins. However, KAB/kaolin-based catalysts also decreased the reaction time, thus minimizing the secondary reactions that lead to the production of aromatic compounds (Artetxe et al., 2012). Consequently, the yield of aromatic compounds is negligible, which is highly significant for blending the C_5–C_{12} fraction in the gasoline pool and also important from an environmental point of view. Moreover, the increased thermal stability of catalysts enabled the recycling and reuse for cracking reactions without considerable activity loss (online Supplemental Table S2). The recycled catalyst was further characterized by p-XRD to check its structural integrity and it was observed that the chemical structure of KAB/ kaolin composite was preserved after completion of reaction (online Supplemental Figure S2).

Conclusion

Novel KAB/kaolin composites have been synthesized and successfully characterized by different analytical techniques. The synthesized tungstoborate loaded kaolin composites exhibited great catalytic performance for PE conversion to lighter hydrocarbons, hence they considerably increased the yield of fuel products. Increasing the amount of KAB loading, enhanced the liquid oil yield and among the tested catalysts, highest oil yield was obtained by the KABK-5 sample (50% KAB loaded sample). The yield of olefinic and branched hydrocarbons was also higher in KAB/kaolin samples which shows good quality of fuel oil. Use of KAB/ kaolin composites also reduced the PE cracking temperature, hence it lowered the overall cost of the pyrolysis process by saving energy. The recovery of valuable fuel products from waste plastic using our synthesized catalysts, proposes the application of these catalysts for energy production from polymer waste at an industrial scale and effective pollution control of the environment.

Declaration of conflicting interests

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Supplemental material

Supplemental material for this article is available online.

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