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Highly Efficient Catalytic Pyrolysis of Polyethylene Waste to Derive Fuel Products by Novel Polyoxometalate/Kaolin Composites

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1 Abstract

We report here potassium salt of Al-substituted Keggin tungstoborate (KAB)/kaolin clay 2 composite materials as polyethylene cracking catalysts. KAB/kaolin composites with varying 3 concentrations of KAB (10-50 wt.%) were synthesized by wet impregnation method and 4 5 successfully characterized by FTIR, powder XRD, TGA and SEM-EDX analytical techniques. Use of KAB loaded kaolin composites as the catalyst for low-density polyethylene (LDPE) 6 7 cracking, exhibited a higher percentage of polymer conversion (99%), producing 84 wt.% of fuel oil and solid residue in negligible amount (<1 wt.%), while thermal cracking produced ~22 wt.% 8 9 residue. Furthermore, GC/MS analysis of oil obtained by non-catalytic cracking exhibited a high 10 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 11 12 cracking ability of our prepared catalysts might ensue from both Brönsted and Lewis acid sites (from KAB and kaolin respectively), which enhanced the yield of liquid fuel products and reduced 13 the cracking temperature of LDPE. These findings suggest that the prepared composites were cost-14 effective and excellent cracking catalysts that could be recommended for highly efficient 15 conversion of waste plastic materials to petrochemicals at industrial scale. 16



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- 20

1 **1. Introduction**

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

8 ZSM-5 (Aguado et al. 2007), ß zeolite (Chaianansutcharit et al. 2007) and Y- zeolite (Van Grieken et al. 2001) are widely reported for plastic degradation. Zeolites show excellent catalytic 9 properties for degradation of polymers due to strong Lewis acidity that facilitates carbon-carbon 10 11 bond breakage. However, the small pore size of zeolite hinders the contact of bulky polymer chains to acid sites located inside the pores and deactivate quickly by carbon deposition (Marcilla et al. 12 2006). To overcome this problem, mesoporous materials possessing large pore sizes have been 13 developed (Kresge et al. 1992) but in pure silica form, they have low acidity compared to zeolites 14 that limit their use as cracking catalysts (Marcilla et al. 2006). The catalytic activity of these 15 materials can be enhanced by incorporation of some metal ions (Al^{3+}, Fe^{3+}) (Obali et al. 2008) and 16 heteropoly acids into silica framework (Jalil 2002). 17

Heteropoly acids (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 Brönsted acid sites that make them excellent

acidic catalysts (Kozhevnikov 2007). However, due to the small surface area ($\leq 10m^2g^{-1}$) and low 1 thermal stability of HPAs, their application as polymer cracking catalyst is limited (Siahkali et al. 2 2001). Both of the above challenges are being overcome by dispersing HPAs on a suitable silica 3 support. Tungstophosphoric acid (TPA) loaded on mesoporous silica (MCM-41 and SBA-15) has 4 been reported for the polyethylene (PE) cracking (Jalil 2002, Aydemir et al. 2012). Compared to 5 6 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 higher amount of 7 gas but liquid yeild was only 42% at 460 °C (Aydemir et al. 2013). We have also studied 8 9 TPA/kaolin composites for PE cracking and 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 Al-substituted Keggin tungstoborates for PE degradation for the first time (Attique et al. 2019). Aluminum substitution is reported to create extra Brönsted acid sites (Marcilla et al. 2006, Obalı et al. 2012), so it helped to decrease the cracking temperature down to 320 °C.

The present study describes the impregnation of Al-substituted Keggin tungstoborate (K-salt) 16 17 on the surface of 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 18 19 extraordinary thermal stability but it has been reported that its application for polypropylene 20 cracking reactions required very high temperature (~500 °C) (Panda and Singh 2013). Having as an aim achieving a cost-effective and highly active cracking catalyst, we report here KAB/kaolin 21 22 composite materials that combine the characteristic properties of both substances towards low 23 polyethylene cracking temperature (295 °C) and extraordinary catalytic performance (high fuel oil percentage ≥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.

4 2. Experimental

5 2.1. Materials

6 Sodium tungstate dihydrate (Na₂WO₄·2H₂O, 98%; Merk), disodium hydrogen phosphate (Na₂HPO₄.12H₂O), 98%; Sigma Aldrich), boric acid (H₃BO₃, 98.5 %, Sigma Aldrich), aluminum 7 nitrate nonahydrate (Al(NO₃)₃.9 H₂O, 98%, Sigma Aldrich), potassium chloride (KCl, 99%; 8 Merk) and acetic acid (CH₃COOH, 99.5 %, Sigma Aldrich) were used for synthesis of KAB. All 9 10 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-11 density polyethylene pellets (20 µm thickness, melting point range 140-150 °C) were provided by 12 Qatar chemical and petrochemical distribution company. 13

14 **2.2. Methods**

15 **2.2.1. Synthesis of K₆[H₂AlBW₁₁O₄₀]·9H₂O**

K₆[H₂AlBW₁₁O₄₀]·9H₂O 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 4 °C 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 1h at pH 6.2,
while heating (80-90 °C). 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 3 to 5 times with ethanol. The product,
 K₆[H₂AlBW₁₁O₄₀]·9H₂O was abbreviated as KAB for simplification.

3 2.2.2. Preparation of KAB/Kaolin composites (KABK)

1 g of kaolin clay was added in 50 mL of water and stirred vigorously for 4 h to obtain a 4 stable dispersion. Then, the solution of aluminum substituted tungstoborate (K-salt), having a 5 specific concentration (10-50 wt.%) was added dropwise to kaolin dispersion for preparation of 6 10%, 30% and 50% KAB/kaolin composites. The resulting mixture was stirred again for 12 h at 7 8 25 °C, then heated at 60 °C on a water bath in order to evaporate the solvent. The solid mass 9 obtained was dried in oven for 10 h at 100 °C. The synthesized composites were denoted as KABK-1, KABK-3 and KABK-5 corresponding to 10, 30 and 50 wt.% of KAB dispersed on kaolin 10 11 surface.

12

2 2.2.3. Polyethylene cracking Experiment

Polyethylene cracking experiment was performed in a pyrex glass reactor (280 mm x 50 13 mm) by the batch operation. 15 g PE pellets and 0.75g catalyst (5 wt.%) were mixed well and 14 introduced into reactor for cracking reactions. The reactor was placed in a specially designed 15 furnace (equipped with an external temperature controller) and heated slowly (2 °C/min) to 120 °C 16 under nitrogen flow to make reaction environment inert. After maintaining this temperature for 17 an hour, N₂ supply was terminated and reactor temperature raised slowly to reach cracking 18 temperature. When first drop of liquid oil comes out, the reactor temperature was then kept fixed 19 until the completion of reaction. The cracking reaction was considered complete when no oil drop 20 21 is observed coming out of reactor for at least 15 minutes. Details of experimental setup could be found elsewhere (Attique et al. 2018). After completion of reaction, cracking products were 22

divided into three categories: (i) gases (products which could not condense at water cooling
temperature), (ii) liquid hydrocarbons and (iii) 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 total weight of plastic sample. 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;

$$DC\% = \frac{m_{PE} - m_{residue}}{m_{PE}} x \ 100$$

8 Where m_{PE} and m_{residue} represent the mass of polyethylene feed and residue respectively.

9 2.2.4. Characterization Techniques

10 Synthesized catalysts were characterized by FTIR, PXRD, SEM-EDX and thermogravimetric analysis. Functional groups were determined by FTIR spectrum being recorded on FTIR 11 Spectrometer (Agilent technology; model 41630) accumulating 256 number of scans within mid-12 IR range (4000 – 400 cm⁻¹) at 4 cm⁻¹ resolution (operating in ATR mode). Morphology of 13 composite materials was studied with the help of an XL30 ESEM instrument operating at 20 kV. 14 Samples were mounted on a carbon tape and pre-coated by gold targets with the help of Polaron 15 SC7640 sputter coater. EDX spectra were recorded on INCA X-Act EDX detector (Oxford 16 Instruments Analytical Ltd. UK) with a working distance of 10 mm. Powder XRD data for the 17 prepared composites were collected on a PANalytical XPERT-PRO instrument, operating at 40kV 18 19 using a Cu K α radiation source in a 2 θ range of 5 \leq 2 θ \leq 85 with 0.02° step size and 80 seconds were spent per step. Thermogravimetric analysis was accomplished by a Netzsch STA 409 system, 20 21 approximately 20 mg of these samples was inserted in alumina pans and temperature raised to 1000 °C at 10 °C /min under argon flow. The GC/MS analysis of liquid products was performed 22 on a GCMS-QP2010S instrument equipped with a ZB-5 MS column ($30 \text{ m} \times 0.32 \text{ mm} \times 0.25 \text{ \mu m}$) 23

under flow of helium. The temperature of GC oven was held at 40 °C for 1 minute, then raised to
310 °C (3 °C/min) and kept constant for 30 minutes. Injector and detector temperatures were kept
at 280 °C and 310 °C respectively. Mass m/z was recorded from 30 to 500 using EI as ionization
mode at 70 eV. Temperature of the ion source and interface was maintained at 180 °C and 250 °C
respectively. Mass spectra were compared with standard spectra from NIST/EPA/NIH Mass
Spectral Library.

7 **3. Results and Discussion**

8 **3.1.** Catalyst Characterization

The prepared catalysts were characterized by several techniques like FTIR, powder X-ray 9 diffraction, SEM-EDX, and thermogravimetric analysis in order to check the final structure and 10 morphology of KAB/kaolin composites. FTIR spectrum of aluminum substituted Keggin 11 tungstoborate exhibited characteristic asymmetric vibrations for W-O_d, W-B-O_a, W-O_b-W, W-12 O_c-W and W-O-Al at 950, 890, 822, 740 and 710 cm⁻¹ respectively that confirmed the formation 13 of Keggin structure (Li-hua 2011, Tarte 1967) (Figure 1). FTIR spectrum of kaolin presented 14 vibrations of Si–O–Al bond at 761 cm⁻¹ and 795 cm⁻¹, while OH bending vibrations were seen at 15 914 cm⁻¹. Si–O–Si in-plane bending and stretching vibrations were recorded at 1007 cm⁻¹ and 1123 16 cm⁻¹ respectively (Kuang et al., 2003). All the characteristic bands of kaolin were shown in the 17 FTIR spectra of KAB loaded kaolin samples with different wt.% of KAB while only two vibration 18 bands of KAB could be seen at 950 and 890 cm⁻¹ corresponding to W–O_d and W–O_b–W vibrations 19 respectively. The vibration bands of KAB located at 740 and 710 cm⁻¹ were overlapped with the 20 strong Si–O–Si bands of the kaolin support (Basir et al., 2015). 21



Figure 1: (A) FTIR spectra of (a) KAB, (b) KABK-5, (c) KABK-3 and (d) KABK-1 samples
and (B) expansion of FTIR spectra in the 1200-700 cm⁻¹ region.

XRD results illustrated the crystalline structure of bulk KAB presenting all the diffraction 4 peaks, characteristic for tungstoborate Keggin structure at 20 values of 8.3°, 18.7°, 29.1°, 33.7° and 5 34° (Li-hua 2011) (as shown in figure 2). XRD patterns of kaolin also represent a highly crystalline 6 structure having an intense and narrow diffraction peak d001 at 20 value of 12.32° (Basir et al., 7 8 2015). KAB/kaolin composites exhibited a reduced crystallinity compared to kaolin and did not exhibit all diffraction peaks, characteristic for tungstoborate Keggin structure. At 10 wt.% KAB 9 loading, the typical diffraction peak of KAB at $2\theta = 8.3^{\circ}$ was extremely small and the intensity of 10 11 this peak was enhanced with the increasing amount of KAB being loaded (Aydemir et al., 2012). However, even for KABK-5 sample, all the diffraction peaks, characteristic of KAB crystalline 12 phase could not be seen, representing the fine distribution of KAB on the surface of kaolin (Dong 13 et al., 2013). 14





Figure 2: (a) KAB, (b) KABK-5, (c) KABK-3 and (d) KABK-1 samples.

SEM images represented a regular crystalline shape of KAB particles (Figure 3a). 3 4 Polyoxometalate salts of bulky counter-cations like Cs and NH₄ have also been reported to 5 maintain the ordered crystal structure of parent acid (H₃PW₁₂O₄₀.6H₂O) in which cations are 6 positioned at $H^+(H_2O)_2$ sites (Brown 1977). The average crystal size of these KAB particles was 4 7 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 8 9 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 like K, O, and W were 10 also found in close approximation to the theoretically calculated values (Table 1). Moreover, 11 12 atomic ratio of tungsten increased through KABK-1 to KABK-5 sample indicating the increase in amount of tungstoborate loading on kaolin surface. It was also observed that with the increase of 13

1 KAB amount being loaded on kaolin, Al/Si ratio was also increased. The increase in Al/Si ratio is



2 considered as an important factor for acid-catalyzed reactions (Obali et al. 2008).

4 **Figure 3:** SEM micrographs of (a) KAB, (b) KABK-1, (c) KABK-3 and (d) KABK-5 samples.

3

TGA curve of KAB exhibited a mass loss of ~4.54% in a single step (70 to 280 °C) that 5 6 corresponded to removal of water molecules of crystallization. After this step, no obvious massloss 7 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 first step i.e. ≥100 °C due to removal of adsorbed 8 water molecules. During a second step (450–700 °C), 9.4% mass loss was observed that could be 9 ascribed to dehydroxylation of kaolinite sheets and development of metakaolinite (Kakali et al. 10 2001). KAB loaded kaolin composites were also thermally decomposed in two steps. For instance, 11 50% KAB/kaolin sample (KABK-5) exhibited 3% massloss during the first step, corresponding to 12 13 the removal of adsorbed and crystallized water molecules. This mass loss percentage is in-between the mass loss exhibited by pure tungstoborate and kaolin samples during the first step. In the 14 15 second step, a mass loss of 7.6% was observed that is less than the massloss 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.

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5

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Figure 4: TGA curves of KAB and KAB/kaolin composites.

7 **3.2.** Catalytic cracking of polyethylene

8 Polyethylene cracking performed in the absence of catalyst took place at 375 °C while the 9 use of KAB/kaolin composites as cracking catalysts lowered the degradation temperature to a 10 considerable extent and especially the KABK-3 and KABK-5 samples that degraded LDPE at 295 11 °C. The use of catalysts also enhanced the percentage yield of valuable fuel products. Total 12 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 1 Figure 5. Percentage conversion of LDPE was very high in case of cracking reactions using 2 KAB/kaolin composites (99.2%) while thermal cracking showed only 78% total conversion. 3 Moreover, the comparative yield of liquid and gaseous hydrocarbons in the oil produced by LDPE 4 cracking over KAB/kaolin samples was also high compared to non-catalytic cracking. Both oil 5 6 and gas fractions obtained by catalytic cracking are valuable fuel products (Jalil 2002, Aydemir and Sezgi 2013). Liquid hydrocarbon yield was enhanced with an increase of KAB amount being 7 loaded and reached to the highest value (84 wt.%) with KABK-5. Similarly, the quantity of residue 8 9 was decreased by increasing KAB loading and was negligible in case of KABK-5 catalyst. On the contrary, only 68 wt.% of liquid oil and 22% residue was produced by thermal cracking. The 10 increase in oil yield by catalytic cracking could be ascribed to the mutual effect of Lewis and 11 Brönsted acid sites (from kaolin and KAB respectively) (Basir et al., 2015). Similarly, Gaca et al. 12 (2008) have explored that the use of tungstophosphoric acid impregnated on MCM-41 for PE 13 cracking, produced an explicitly higher quantity of liquid hydrocarbons. Furthermore, 14 comparatively higher percentage yield of gaseous hydrocarbons (C1-C4) was observed for all 15 KAB/kaolin catalysts. Thus, the application of KAB/kaolin based catalysts lowered the cracking 16 17 temperature (~295 °C) as well as enhanced the yield of valuable fuel products (C_5 - C_{21}) that is consistent with the previous studies (Jalil 2002). Details of reactions conditions and percentage 18 19 yield of different cracking products are given in Table S2 (supplementary information).



Figure 5: Effect of Catalyst on product distribution during LDPE cracking with different types of catalysts.

3

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4 **3.2.1.** Composition of Liquid Products

The liquid oil received by non-catalytic and catalytic cracking of LDPE was analyzed by 5 GC/MS. Every peak in the chromatogram belongs to a specific compound present in oil samples. 6 7 Mass spectrum of every compound was interpreted by comparison with standard spectra of corresponding compounds with the help of GC/MS library (NIST/EPA/NIH Mass spectral 8 Library). About 35 major peaks were selected and quantified. The similarity index for 9 identification of compounds was kept >90. The identification of all compounds with respect to 10 their relative abundance are provided in Table S3.It was seen that the major components of the oil 11 were paraffins and olefins (C_5 - C_{26}). A broad range of hydrocarbons (C_6 - C_{26}) was present in the 12 oil produced by non-catalytic cracking and it was observed that majority of oil fractions consisted 13 of higher molecular weight hydrocarbons. While the oil produced by catalytic cracking of LDPE 14 15 using KAB and KAB/kaolin catalysts exhibited larger amounts of lighter hydrocarbons especially

gasoline range (C₅-C₁₂) hydrocarbons. Detailed analysis showed that oil produced by KAB 1 presented only a small quantity of C₅ but KAB impregnated kaolin catalysts showed significantly 2 larger quantities of C₅. Likewise, the amount of C₇ was increased to a greater extent by the use of 3 KAB/ kaolin samples as shown in figure 5. This might ensue from KAB loading on kaolin that 4 could create additional Bronsted acid sites in the composite materials, posing a synergistic effect 5 on the catalyst performance for LDPE cracking. The increase in total amount of acidity (Bronsted 6 and Lewis) could initiate LDPE degradation reactions at Bronsted acidic sites and in this way 7 speed up the breakdown of heavier hydrocarbons to lighter ones as reported earlier (Aydemir and 8 9 Sezgi 2013).



Figure 6: (a) Carbon number distribution in oil produced by thermal and catalytic cracking, (b)
carbon number selectivity for thermal and catalytic cracking.

Liquid oil obtained by LDPE cracking exhibited both paraffins and olefins. As presented
in 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 1 were produced in comparatively lower amount and branched-chain hydrocarbons were negligible. 2 The lower weight percentage of olefins compared to paraffins in non-catalytic oil might ensue 3 from higher cracking temperature that favors the production of paraffins (Rahimi and Karimzadeh 4 2011). Haag-Dessau mechanism also explains the formation of olefinic hydrocarbons during 5 6 thermal and catalytic cracking of PE (Kotrel et al. 2000). The increased amount of olefins produced by KABK-5 could be ascribed to protonic acid sites and increased Al/Si ratio in the catalyst. Many 7 researchers have described the effect of Al/Si ratio on production of alkenes (Wei et al. 2005, Han 8 9 et al. 2004). The enhanced protonation of hydrocarbons at Bronsted acidified sites forms carbonium ions that eventually undergo β -scission reactions (Corma 1995). The increased β -10 scission and rearrangement reactions significantly enhanced the percentage of lighter 11 hydrocarbons that was reflected in catalytic oil as low molecular weight and branched-chain 12 olefins. However, KAB/kaolin based catalysts also decreased the reaction time, thus minimizing 13 14 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 15 blending the C_5-C_{12} fraction in the gasoline pool and also important from an environmental point 16 17 of view. Moreover, the increased thermal stability of catalysts enabled the recycling and reuse for cracking reactions without considerable activity loss. (Table S2, supplementary information). The 18 19 recycled catalyst was further characterized by powder XRD to check its structural integrity and it 20 was observed that the chemical structure of KAB/ kaolin composite was preserved after completion of reaction (Figure S2, supplementary information). 21





2 **Figure 7**: Alkenes distribution in oil produced by non-catalytic and catalytic cracking of LDPE.

3 4. Conclusion

Novel aluminum substituted Keggin tungstoborate/kaolin composites have been 4 synthesized and successfully characterized by different analytical techniques. The synthesized 5 6 tungstoborate loaded kaolin composites exhibited great catalytic performance for polyethylene conversion to lighter hydrocarbons, hence considerably increased the yield of fuel products. 7 Increasing the amount of KAB loading, enhanced the liquid oil yield and among the tested 8 9 catalysts, highest oil yield was obtained by KABK-5 sample (50% KAB loaded sample). The yield of olefinic and branched hydrocarbons was also higher in KAB/kaolin samples that shows good 10 quality of fuel oil. Use of KAB/ kaolin composites also reduced the PE cracking temperature, 11 hence lowered the overall cost of pyrolysis process by saving energy. The recovery of valuable 12 fuel products from waste plastic using our synthesized catalysts, propose the application of these 13 14 catalysts for energy production from polymer waste at industrial scale and effective pollution control of the environment. 15

4. Supplementary Information

2 EDX elemental analysis, percentage yield of cracking products, Gas chromatograms and peak

3 identification for GC/MS are provided in Supplementary Information file.

4 **5. Disclosure**

5 The authors declare no competing financial interest.

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