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Published in:
Environmental science and pollution research international

Link to article, DOI:
[10.1007/s11356-019-04878-9](https://doi.org/10.1007/s11356-019-04878-9)

Publication date:
2020

Document Version
Peer reviewed version

[Link back to DTU Orbit](#)

Citation (APA):
Almustapha, M. N., Farooq, M., Mohammed, M. L., Farhan, M., Imran, M., & Andresen, J. M. (2020). Modification of acidic and textural properties of a sulphated zirconia catalyst for efficient conversion of high-density polyethylene into liquid fuel. *Environmental science and pollution research international*, 27, 55–65. <https://doi.org/10.1007/s11356-019-04878-9>

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Modification of Acidic and Textural Properties of a Sulphated Zirconia Catalyst for Efficient Conversion of High-Density Polyethylene into Liquid Fuel

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Abstract

Consumption of plastic has rapid increase of about 8% per annum and reached to 400 million per tonnes approximately, where about 50% plastic was disposed after using only once. Different techniques for treating this increased waste faced number of issues related to cost, environmental and sustainable development. Catalytic conversion has been found as one of the most viable solution to solve this problem. Sulphated zirconia (SZ) catalyst modified with calcium Carbide (CC) was found to improve HDPE conversion into liquids fuel. The liquid content was improved from 39.0wt% to 66.0wt% at 410°C. HDPE was converted 100% by weight using, SZ/CC with 66wt% liquid yield as compared to the conversion of approximately 98wt% with about 40wt% only liquid yield for the pure SZ. The composition of hydrocarbon liquid product was significantly changed from paraffin (16%) and aromatic (58%) to olefin (74%) and naphthenic (23%) compounds. This significant increase in liquid was related to changes in the acidic and textural characteristics of the new hybrid catalyst, SZ/CC where the total ammonia desorption of 337.0 $\mu\text{mNH}_3/\text{g}$ for the SZ was modified to 23.4 $\mu\text{mNH}_3/\text{g}$ for the SZ/CC. Both SZ and SZ/CC catalysts showed characteristics of mesoporous material, where the internal pore volume of SZ had reduced from 0.21mL/g for SZ to 0.04 mL/g for SZ/CC. Furthermore, XRD analysis indicated the presence of a new compound, CaZrO_3 in the SZ/CC, which confirmed a chemical interaction between the SZ and CC through sintering of ZrO_2 and CaO . Therefore, the SZ/CC catalyst improves the liquid yield significantly and the selectivity towards olefinic and naphthenic compounds

Key words— *Catalytic conversion, sulphated zirconia, calcium carbide, HDPE, plastic waste*

1. Introduction

Consumption of plastics, in particular high density polyethylene (HDPE), has increased at-least 8% each year since the 1950s, which is predicted as to reach 322 and 405 million tonnes by the years 2015 and 2018, respectively, where about 50% of plastic is disposed after using only one time as usual practice (Hopewell et al., 2009; Panda et al., 2010; Reddy et al., 2013; Singhabhandhu & Tezuka, 2010). Although various recycling methods have been applied to manage plastic waste, many of these have practical, environmental and economic limitations (Farooq et al., 2018; Huang et al., 2010; Keane, 2009; Lin et al., 1998; Lin & Yen, 2005; Miskolczi et al., 2009; Shah et al., 2010a; Shent et al., 1999; Zadgaonkar, 2004). Chemical recycling has been suggested as a viable option for plastic waste management when using a suitable catalyst to convert plastic waste into valuable hydrocarbon products (Aguado et al., 2008; Al-Salem et al., 2009; Almustapha et al., 2017; Miskolczi et al., 2006; Panda et al., 2010; Singhabhandhu & Tezuka, 2010; Walendziewski & Steininger, 2001; Wei et al., 2010). Unlike the products obtained from thermal conversion, which requires upgrading, the hydrocarbon product using catalytic conversion have the capacity to be used as feedstock or fuel for different industrial processes (Keane, 2009; Lin et al., 1998; López et al., 2011; Shah et al., 2010a; Shah et al., 2010b). Various catalysts, in particular basic and acidic zeolites, have been tested but few have resulted in both high conversions and high liquid yield with selectivity towards desirable hydrocarbon components (Arandes et al., 2007; Gobin & Manos, 2004a; Gobin & Manos, 2004b; Huang et al., 2010; Lin & Yen, 2005; López et al., 2011; Saha et al., 2008; Serrano et al., 2000a; Serrano et al., 2007; Shah et al., 2010a; Tarrío-Saavedra et al., 2011). Recently, it was found that sulphated zirconia showed excellent catalytic activity toward HDPE recycling at temperatures below 400°C where a conversion of over 99wt% with liquid and gas yields of 34wt% and 66wt%, respectively, was reported (Almustapha & Andrésen, 2012). Sulphated zirconia is one of the best catalyst for oil refining techniques, however, it needs wide spread in the literature for plastic conversion (Ahmed et al., 2008; Arata et al., 2003; Clark, 2002; Hino et al., 2006; Yadav & Nair, 1999). One of the best characteristics of SZ catalyst are related to its good acidity, chemical as well as thermal stability. However, sulphated zirconia was found to promote aromatic compounds similar to that widely reported for zeolites (Almustapha & Andrésen, 2012; Saha et al., 2008; Serrano et al., 2000b). This study has focused on achieving this by modifying the textural as well as acidic characteristics

of the SZ with the mixing of CC to promote liquid yield as high and impede secondary reactions leading to aromatics as demonstrated in the work reported Shah et al. (2010a). The saturated and aromatic compounds have previously worked well with zeolites and are proposed for the first time here with the sulphated zirconia (Elordi et al., 2009; López et al., 2011; Marcilla et al., 2009; Serrano et al., 2007; Sharratt et al., 1997).

2. Experimental

2.1 Materials and Catalyst Preparation

High density poly-ethylene (HDPE) in pellet form (about 3mm, and melt index of 42 grams) was used. The HDPE particle size was reduced to 0.25 - 0.05mm using a SM2000 Retch Mill. Different characteristics includes proximate and elemental compositions of the HDPE sample are listed in Table 1. A commercial sulphated zirconia catalyst (XZO 1248, $\approx 7\text{mol}\%$ SO_3) with the size of the particle range of 100-150 μm . The hybrid catalyst SZ/CC was prepared by mechanically mixing the sulphated zirconia and calcium carbide at a ratio of 1:1. The mixture was calcined in air at 550°C for four hours using a Type 1500 Thermo Scientific Barnstead /Thermolyne Compact Benchtop Muffle Furnace.

Table 1. Proximate and Elemental Composition of the High-Density Polyethylene

Proximate composition* %			Elemental analysis (%)				
Fixed carbon	Ash content	Volatile matter	Carbon	Hydrogen	Nitrogen	Oxygen	Sulphur
3.2	0.0	96.8	85.7	14.3	0.0	0.0	0.0

* dry basis

2.2 Catalyst characterisations

SEM (Scanning Electron Microscopy-FEI 600F version 2.4) was used for the surface morphology of the SZ catalyst. Elemental and oxide analysis were conducted to find the elemental composition of particles. The XRD powder patterns were received with the help of a Hilton-brooks DG which was operated at 20mA with 40Kv Philips PW 1000 goniometer approx. Scanning speed of 2 degree (2θ) per minute was conducted with a range about 5-60 degree and a step size of 0.05°. The textural characteristics of the SZ catalyst including the surface area and porosity were determined using the Micrometrics Gemini-VII. A Quanta-chrome Chem-BET TPR/TPD instrument was fitted for data analysis to carry out the NH_3 temperature programmed desorption (TPD) for measurement of acidic strength of the catalyst.

2.3 HDPE conversion procedure

Figure 1 explains the fixed bed system of stainless-steel tube (2.2cm ID, 45cm L) installed for the catalyst conversion of HDPE. A programmable temperature controller furnace was used to provide a uniform heat and mass transfer along the reactor. The run was conducted with equal amount (roughly 5g each) of HDPE and catalyst placed into an alumina crucible and inserted into the stainless-steel tube reactor. The N₂ was purged in the tube with 30cl/min for about half hour prior to heating and during heating at 20°C per minute from ambient to 410°C, where the system was held for 30 min before it was cooled to the room standard temperature. The product yields were calculated using Equation 1 according to previous published methods (Aguado et al., 2007; Lin & Yen, 2005; Miskolczi et al., 2009).

$$Yield\ (wt\%) = \frac{W_p}{W_r} \times 100$$

Where, W_p is the weight of products (liquid and gas) and W_r is the weight of reactants

Figure 1. Fixed-bed reactor for the catalytic conversion into liquid fuel

2.4 Product analysis

Hydrocarbon composition of the liquid yield was analysed with 70 eV ionising energy at 280°C. A column of silica capillary was used for the separation which was coated with BPX5 phase. Helium gas with a 2 min hold at 50°C was used as carrier gas, which was then increased to 300°C with 5°C min⁻¹ and kept for about half hour. The analyses of gaseous yields with a flame ionization detector were conducted with an initial hold for 13 min at 60°C and further increased to 160°C with 10°C min⁻¹ and kept for about 15 minutes.

3. Results and discussion

3.1 Catalyst analysis for HDPE conversion

Table 2 compares the HDPE conversion of the SZ with that of the new hybrid catalyst SZ/CC. Calcium carbide on its own did not show any conversion and was not included. The liquid yield for the new hybrid catalyst SZ/CC was 66wt% indicating a significant improvement compared to 39wt% in the presence of the pure SZ. Also, the gas and unconverted residue have all reduced significantly to <0.1 and 34wt% compared to 2wt% and 59wt%, respectively. The liquid obtained using the hybrid catalyst SZ/CC had a composition of 74wt% olefin, 23wt% naphthens, 3wt% paraffins and <0.1wt% aromatics. However, there is a significant change from the pure SZ, where the liquid composed of highest proportion of aromatic (58wt%). This indicates by adding CC, the catalytic activity of the pure SZ has modified to support high liquid output. Figure 2 compares the hydrogen and hydrocarbon compositions of the gas fractions obtained in the presence of the pure SZ and the hybrid catalyst SZ/CC. The gaseous fraction obtained in the presence of SZ contained more saturated hydrocarbons and low hydrogen compared to that of the hybrid catalyst SZ/CC, which promoted mainly olefins particularly C5, C4 and C3. This composition is same and in-lined with the liquid obtained using these catalysts. The results indicate that SZ promoted the formation of aromatics and perhaps generates a surplus of hydrogen, which could have been used to form more saturated hydrocarbon compounds in the gas phase. However, this was not the case for the hybrid catalyst SZ/CC, where an unzipping of the structure took place leaving olefinic compounds both in the gas and liquid phases.

Table 2. Comparison of conversion, liquid and gas yields

	Sulphated zirconia (SZ)	Calcium carbide modified SZ
Total conversion (%)	98.0	100
Residue (wt%)	2.0	0
Total liquid yield (wt%)	39.0	66.0
Olefins (%)	21.0	74.0
Naphthens (%)	5.0	23.0
Paraffins (%)	16.0	3.0
Aromatics (%)	58.0	<0.1
Total Gas yield (wt%)	59.0	34.0

Figure 2. Hydrogen and Hydrocarbon compositions of the gaseous fraction

3.2 Catalyst Characterisation

Table 3 summarised and compared the acidic strength and total ammonia desorption of the pure SZ, the calcined CC and the hybrid catalyst SZ/CC obtained from NH₃-Temperature-Programmed Desorption (TPD) spectra. The NH₃-TPD spectra were classified into three temperature regions, as, 200-350°C (a), 350-550°C (b) and above 550°C (c). Since the desorption was owing to physisorption, so it was discontinued before 200°C (Elordi et al., 2009; Katada et al., 1997; López et al., 2011; Shi & Li, 2013; Zhao et al., 2008). Pure SZ had three acid sites at temperatures of maximum desorption of 230°C, 365°C and 640°C. The hybrid

catalyst SZ/CC and the calcined CC had only two desorption peaks at 294°C and 541°C for the SZ/CC and 371°C and 542°C for calcined CC, respectively. This shows that acidic strengths are normal, strong as well as very strong for the SZ, which co-inside with the published literature (Barthos et al., 2001; Oh et al., 2011; Zhao et al., 2008). But, the peak above 550°C, which indicates very strong acidic strength was completely absent in both the hybrid catalysts SZ/CC and calcined CC. The SZ seems to have the highest ammonia desorption of 337.0 $\mu\text{molNH}_3/\text{g}$ but reduced to 23.4.0 $\mu\text{molNH}_3/\text{g}$ for hybrid catalyst SZ/CC. The calcined CC on its own had ammonia desorption of 45.923.4 $\mu\text{mmolNH}_3/\text{g}$. The increased ammonia desorption observed in calcined CC at 350-550°C is attributed largely to ammonia adsorbed by CaO (Yang et al., 2012). Overall, the high acidic strength and total ammonia desorption could be responsible for the cracking ability of the catalyst. In the presence of the hybrid catalyst SZ/CC with the total ammonia desorption of only 23.4.0 $\mu\text{molNH}_3/\text{g}$ of only strong acidity, the liquid yield increased to 66.0wt% compared to only 39.0w% for the SZ, which has high total ammonia desorption of 337.0 $\mu\text{molNH}_3/\text{g}$ with both strong and very strong acidities. This is expected since catalysts with high acidic strength generally give excessive cracking that leads to high gas yields (Angyal et al., 2009; López et al., 2011; Miskolczi et al., 2004). Calcined calcium carbide on its own with 44.4 $\mu\text{molNH}_3/\text{g}$ did not affect the HDPE conversion even though with about twofold ammonia desorption than the hybrid catalyst SZ/CC. This because the ammonia desorption by the calcined CC was due ammonia adsorbed by CaO not by acid sites of the catalyst, thus, provided very little HDPE cracking.

Table 3 Analysis of the NH₃ desorbed with acidic strength for SZ, hybrid catalyst SZ/CC and the calcined CC from curve-fitted NH₃-TPD spectra

Catalysts	NH ₃ desorbed ($\mu\text{molNH}_3/\text{g}$)			
	200-300	300-550	>550	Total NH ₃ desorbed
SZ	142.0	158.5	37.1	337.6
SZ/CC	2.8	20.6	nd	23.4
CC	1.4	44.4	nd	45.8

nd: not detected

3.3 Comparison of SEM micrograph and EDX spectrum of the pure SZ

Figure 3 compares the SEM micrographs and EDX spectra of the SZ, the hybrid catalyst SZ/CC and the calcined CC. The SEM images showed that the SZ, the calcined CC and the hybrid

catalyst SZ/CC have same particle size (100nm to 200nm). The SZ particles appeared less clustered and contained many open pores as illustrated by circles A while the CC particles appeared highly clustered as indicated by circles C. However, the particles of hybrid catalyst SZ/CC appear clustered but with few open pores as indicated by circles B. The SEM image of SZ/CC indicated that the open pore structure in the SZ was blocked by the particle of calcium carbide. The pore volume and surface area of the hybrid catalyst could get reduced as outlined in Table 4, which shows that the hybrid catalyst SZ/CC had 0.04cm³/g, 23.1m²/g and 22.2m²/g as pore volume, BET and external surface areas, respectively. These characteristics are much lower than those of pure SZ, which had 0.21cm³/g, 116.0m²/g and 112.0m²/g as pore volume, BET and external surface areas, respectively. This reveals that by adding CC has significantly reduced the pore volume, BET and external surface areas of the new catalyst as suggested by SEM results. The reduction in pore volume also lead to the reduction of internal porosity in the hybrid catalyst, where the micropore area is reduced from 3.9m²/g to < 0.1m²/g. The pore size has also significantly reduced from 10.8nm for SZ to 8.2 and 5.0 for the hybrid catalyst and calcined CC, respectively. The EDX spectra showed that in SZ there are peaks indicating the zirconium predominance and large portion of oxygen while in CC carbon predominates with substantial amount of oxygen. However, in SZ/CC calcium appeared predominant with large portion of zirconium and substantial amount of oxygen. This show that mixing sulphated zirconia with calcium carbide has led to significantly change in the textural and physicochemical properties of the new SZ/CC catalyst.

Table 4 Comparison of characteristics of the SZ, the calcined CC and the hybrid catalyst SZ/CC.

Characteristics	SZ	SZ/CC	CC
BET total surface area (m ² /g)	116.0	23.1	10.2
External surface area (m ² /g)	112.0	22.2	8.7
Micropore volume (cm ³ g ⁻¹)	0.0013	nd	nd
Micropore area (m ² /g)	3.90	< 0.1	< 0.1
pore volume (cm ³ g ⁻¹)	0.21	0.04	0.012
Average pore size (nm)	10.8	8.2	5.0

Figure 3 Comparison of SEM micrograph and EDX spectrum of the pure SZ, the hybrid catalyst SZ/CC and the CC calcium carbide after calcination at 550°C.

3.4 Comparison of nitrogen adsorption isotherms

Figure 4 compares the N₂ adsorption isotherms of the pure SZ, hybrid catalyst SZ/CC and the calcined CC. The shape of the adsorption isotherms of all the three catalysts resemble that of Type IV isotherm (Donohue & Aranovich, 1999). However, the nitrogen absorption was more prominent in the SZ than SZ/CC and calcined CC. The SZ had the highest nitrogen adsorption of about 1.10mmol/g at low relative pressure ($P/P^0 < 0.1$) than the hybrid catalyst SZ/CC and calcined CC with 0.22 and 0.10mmol/g, respectively. This indicated some level of micropores in SZ, which reduced in the hybrid catalyst SZ/CC and virtually none in the calcined CC as evidenced by the nitrogen adsorbed at low relative pressure ($p/p^0 < 0.01$) (Serrano et al., 2007).

This indicates that the overall porosity of sulphated zirconia has significantly reduced in hybrid catalyst SZ/CC after addition of calcium carbide. This again corroborated with SEM and BET results, which showed overall reduction of porosity and surface area after CC addition.

Figure 4 Comparison of N₂ isotherms of the SZ, the hybrid catalyst SZ/CC and the calcined CC.

3.5 Pore size distribution using BJH method

Figure 5 shows the distribution of the pores with respect to size for the SZ catalyst, the calcined CC and hybrid catalysts SZ/CC. It has been revealed from the results as presented in the figure that all the samples with size from 1.5 to 12 nm has broad distribution of pores. This depicts the mesoporous structure of the particles, since these falls mostly from 2nm to 12nm. This behaviour validate the presence of mesoporous particles in all samples as described in the N₂ isotherm in Figure 5 (Mishra et al., 2003; Rezaei et al., 2006).

Figure 5 Pore size distributions of the SZ, the CC and the hybrid catalysts SZ4CC1 to SZ1CC4 using BJH method

Table 5 compares bulk elemental and oxide compositions of the catalysts obtained from EDX. The hybrid catalyst SZ/CC indicated the increase of CaO (27.7 Mol%) and CaCO₃ (44.4 Mol%) against < 0.1 Mol % each in pure SZ. However, the SO₃ (2.4 Mol%) and ZrO₂ (25.5 Mol%) in the hybrid catalyst SZ/CC were considerably low compared to 6.6 Mol% and 93.36 Mol% for sulphated zirconia and < 0.1 Mol% but higher than that of the calcined CC. This particularly for SO₃, is in line with 1 total ammonia desorption of 23.4 μmolNH₃/g for the hybrid catalyst SZ/CC indicating a significant reduction compared to the SZ with 337.0 μmolNH₃/g. This further confirmed that addition of calcium carbide has significantly modified the acidic strength of the hybrid catalyst, which significantly enhanced the conversion and liquid yield.

Table 5 Bulk compositions of the SZ, the calcined CC and hybrid catalyst SZ/CC.

Surface compositions	Sulphated zirconia (SZ)	Hybrid catalyst (SZ/CC)	Calcium carbide (CC)
SO ₃ (Mol%) ^e	6.6	2.4	< 0.1
ZrO ₂ (Mol%) ^e	93.36	25.5	< 0.1
CaO (Mol%) ^e	<0.1	27.7	53.1
CaCO ₃ (Mol%) ^f	<0.1	44.4	46.9

^eEDX

^fEDX (by difference)

3.6 Comparison of the powder XRD diffraction pattern

Figure 6 shows the powder XRD patterns of the pure SZ, the calcined CC and the hybrid catalyst SZ/CC. The SZ appeared to have four major peaks (●) contained tetragonal ZrO_2 (JCPD no. 50-1089) observed at $2\theta = 30.41$ (relative intensity is 100) as well as 35.25 (20), 50.71(52) and 60.28 (31). These set of peaks were still observed from the hybrid catalyst SZ/CC with only additional phase of compound indexed CaZrO_3 (JCPD no. 48-0904). The new particles of the new complex compound (CaZrO_3) formed probably blocked the open pores observed in pure SZ. This again reaffirmed the suggestion that addition of the CC could affect the selectivity of the catalyst by reducing accessibility to internal acid site which allows secondary reaction leading to aromatic formation.

Figure 6. Comparison of the powder XRD diffraction pattern of the sulphated zirconia (SZ) and hybrid version (SZ/CC).

3.7 Summary of the characteristics of pure SZ and hybrid catalyst, SZ/CC and their catalytic activities towards HDPE conversion.

Figure 7 highlighted the summary characteristics of the pure SZ and the new hybrid catalyst SZ/CC and results outcome of their performance towards HDPE conversion. Pure SZ showed low liquid yield, which contains large aromatic compounds, while the new hybrid catalyst gave high liquid yield that contains high proportion of olefinic and naphthenic hydrocarbon compounds. The changes in the liquid yield and selectivity shown by the new hybrid catalyst were linked with the changes in the physicochemical compositions, acidic strength and textural properties of the new hybrid catalyst SZ/CC. As catalysts with strong acidity are mainly in gaseous state and hence very low liquid yields (Akpanudoh et al., 2005; Angyal et al., 2009; Hernandez et al., 2006; Liu & Smith, 2008; López et al., 2011; Miskolczi et al., 2004; Saha et al., 2008). Also catalysts with large surface area and porosity give easy accessibility to the internal acid site due to less diffusional coorce and promote secondary reactions such as aromatisation and yield aromatic compounds as seen in pure SZ (Aguado et al., 2009; Marcilla et al., 2009; Serrano et al., 2007; Sharratt et al., 1997).

Figure 7. Summary of the properties of pure SZ and hybrid catalyst, SZ/CC and their catalytic activities towards HDPE conversion.

4. Conclusion

A commercial sulphated zirconia catalyst was modified with calcium carbide and the resulting hybrid catalyst, SZ/CC showed improved catalytic activity and selectivity for HDPE conversion into low-aromatic liquids. Catalytic conversion of HDPE using the new hybrid catalyst revealed a significant increase in liquid yield of 66.0wt% compared to only 39.0wt% of the pure SZ. The unconverted residue and gaseous product decreases from 2.0wt% and 59.0wt% for the pure SZ to <0.1wt% and 34.0wt%, respectively. Various catalysts characterisation techniques revealed that the physicochemical, textural and acidic properties of the catalyst have changed significantly after addition of calcium carbide. The BET and external surface area as well as pore volume have reduced significantly 116, 1120m²/g, 0.2cm³ for the SZ to 24.0m²/g, 23.0m²/g and 0.04cm³, respectively. Acidic strength has also been modified from very strong for pure the SZ to strong for the new hybrid catalyst SZ/CC. The liquid and gaseous product compositions have also changed significantly in the presence of the hybrid catalyst SZ/CC. The hydrocarbon composition of liquid fraction in particular was changed from 58vol% aromatic and 16vol% paraffin dominated to 74% olefin and 23% naphthenic hydrocarbon compounds dominated. Hence, the efficient performance of new hybrid catalyst is strongly linked with the modification of textural properties and moderation of acidic strength due to calcium carbide addition.

5. Acknowledgments

The Authors remain indebted to MEL Chemicals and equally thankful to Petroleum Technology Development Fund for providing sponsorship for the PhD. We are also thankful to Professor Mercedes Maroto-Valer in whose laboratory some of the analyses were conducted.

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