Bridging Plastic Recycling and Clean Energy Production:Hydrogen-

Free Catalytic Pyrolysis of Polyethylene over CuMgAlOx for High-

Yield Diesel Fuel Generation

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Characterization methods of catalysts

Scanning electron microscopy (SEM): The scanning electron microscope used in the experiments was a HITACHI SU8000 field-emission scanning electron microscope (FE-SEM) with an operating voltage of 5.0 kV. Prior to analysis, samples were sputter-coated with gold under vacuum conditions to dissipate accumulated charge during imaging, prevent sample discharge, and enhance conductivity.

Nitrogen adsorption-desorption: The nitrogen adsorption-desorption characterization of the catalysts was performed on a Micromeritics ASAP 2460 automated surface area and porosity analyzer. The test gas was N₂, and the procedure involved degassing the catalysts at 200°C for 4 hours to remove physically adsorbed impurities from the hydrotalcite catalysts. The Brunauer-Emmett-Teller (BET) method was employed to calculate the specific surface area of hydrotalcite catalysts with varying compositions. Total pore volume was determined using the single-point adsorption method at P/P₀ = 0.99. Pore size distribution curves were derived from the desorption branch of the isotherms using the Barrett-Joyner-Halenda (BJH) method.

XRD: Phase analysis of the catalysts was conducted on a Bruker D8 Advanced Xray diffractometer using Cu K α radiation ($\lambda = 0.15418$ nm) with operating parameters of 40 kV and 40 mA. The diffraction patterns were recorded over a 2 θ range of 5–80° at a scan rate of 5°/min, with signals detected by a Vantec detector. The crystal phase structure was analyzed using JADE6 software.

CO₂-TPD: The CO₂ temperature-programmed desorption (CO₂-TPD) of the catalyst was performed on a chemisorption analyzer. The procedure involved loading 50 mg of sample into a reactor tube, followed by a drying pretreatment under a He flow (50 mL/min) by heating from room temperature to 460°C at 10°C/min. After cooling to 50°C, the sample was saturated with a 25% CO₂/He gas mixture (50 mL/min) for 1 h. Subsequently, weakly physisorbed CO₂ was removed by purging with He (50 mL/min) for 1 h. Desorption was then carried out in a He atmosphere by heating to 460°C at

10°C/min, with desorbed gases detected using a thermal conductivity detector (TCD).

液体产物分析

GC-FID: Quantitative analysis of plastic pyrolysis oil products was performed using gas chromatography-flame ionization detection (GC-FID, SHIMADZU GC-2010 Plus) equipped with an SH-1701 capillary column (30 m \times 0.25 mm \times 0.25 μ m). Operational parameters included: injector temperature 280°C, detector temperature 280°C, hydrogen flow rate 40 mL/min, air flow rate 400 mL/min, makeup gas flow rate 30 mL/min, and split ratio 116. The oven temperature program was set to hold at 40°C for 3 min, followed by a 10°C/min ramp to 280°C with a 15 min hold.

GC-MS: The components of the liquid oil were analyzed using gas chromatography-mass spectrometry (GC-MS, PerkinElmer Clarus 690). The temperature program was set as follows: initial temperature 40°C held for 3 min, followed by a ramp to 280°C at 10°C/min and held for 15 min, resulting in a total run time of 42 min. MS detection conditions included a solvent delay time of 0–1.8 min, MS Scan mode, scan time of 1.80–42.00 min, mass-to-charge (m/z) range of 35.00–500.00, and scan speed of 0.30 sec per scan. Components were identified by matching spectra with reference data in the NIST MS library and literature reports on liquid products.

TG: Thermogravimetric analysis (TG, SDT Q600) was performed to determine the boiling point distribution of the pyrolysis oil. Approximately 30 mg of sample was loaded into the thermogravimetric microbalance, heated from ambient temperature to 600° C at a ramp rate of 20°C/min under a N₂ carrier gas purge with a flow rate of 50 mL/min.

GPC: Gel permeation chromatography (GPC, Shimadzu LC-10A VP Plus) was employed to analyze the molecular weight distribution of liquid products. Samples were dissolved in tetrahydrofuran (THF, 5 mg/mL concentration) for analysis. Operational conditions included: column (SHO-F6028010 KF-801, 300 × 8.0 mm, 6 μ m), polystyrene standards, mobile phase (THF), flow rate 0.6 mL/min, column temperature 35°C, and detector (SPD-10Avp Plus). **EA:** Elemental analysis (EA, Vario MACRO cube) was employed to determine the contents of C, H, N, and S in the pyrolysis oil samples. Samples (30–50 mg) were sealed in tin capsules prior to analysis.

Determination of oil physical properties: Density and dynamic viscosity of the oil were measured using an SVM 3001 COLD multi-function oil tester (Anton Paar GmbH). The measurements were conducted at specified temperatures ranging from –40°C to 40°C in accordance with ASTM D4052, with dynamic viscosity calculated based on ASTM D7042. Freezing point was determined using a TP526 freezing point analyzer (Beijing Shidai Xinwei Test and Control Equipment Co., Ltd.) under a nitrogen atmosphere, with heating/cooling cycles between –70°C and 35°C.



Fig. S1 schematic diagram of the experimental setup



Fig. S2 TG curve of experimental material



Fig. S3 components of liquid products from $CuMgAlO_X$ catalytic pyrolysis



Fig. S4 TG curves of catalyst after five cycles



Fig. S5 catalyst CO2-TPD curve



Fig. S6 product distribution of HDPE without catalyst (temperature: 500 °C, Residence Time: 60s).



Fig. S7 product distribution of HDPE without catalyst (temperature: 500 °C, Residence Time: 60s) .



Fig. S8 yield of gaseous products from non-catalytic pyrolysis (temperature: 500 °C, Residence Time: 60s)



Fig. S9 partial non-alpha olefin mass spectrometry



Figure S10. Model fit to alkane, olefin, aromatic yields: a. 450 °C; b. 500 °C; c. 550 °C; d. 600 °C



Figure S11. Fitting of the model to catalytic pyrolysis products with different carbon numbers: a.450 °C; b.500 °C; c.550 °C; d.600 °C $_{\circ}$

Sample		HHV (MJ/kg)				
	С	Н	0	Ν	S	
Pyrolysis oil	85.22	14.39	< 0.5	<0.5	<0.5	49.29

Table S 1 elemental analysis of $CuMgAlO_X$ catalytic pyrolysis oil

Determined by Dulong formula: HHV = $0.3383 \times C + 1.422 \times (H - O/8)$.

Table S2 physical properties of CuMgAlO_X catalysts

1 5	1 1		0 1	5				
催化剂	Cu/(Cu+	Cu ^b	Mg^{b}	Alb	(Cu+Mg)/	$S^a_{\;BET}$	V ^a pore	Da
	Mg) ^b	/wt.%	/wt.%	/wt.%	Alb	$/m^2g^{-1}$	/cm ³ g ⁻¹	/nm
CuMgAlOx	0.19	16.41	26.59	9.01	4.09	183.1	0.88	14.92

a: BET specific surface area, pore volume, and pore size were determined according to N2 adsorption-desorption. b: the contents of Cu, Mg and Al were determined according to ICP-AES.

			Yield(wt.	%)	
		10S	20S	40S	60S
01	Alkanes	21.4(0.7)	22.5(1.0)	24.7(0.1)	26.1(0.4)
composition	Olefins	17.4(2.0)	19.1(1.7)	17.6(0.1)	19.5(2.3)
	Aromantics	5.5(0.6)	5.8(0.9)	6.3(0.2)	7.5(0.9)
Carbon	C1-C5	11.7(1.7)	9.9(0.2)	10.1(0.5)	13.2(0.6)
number distribution	C6-C22	26.6(1.2)	26.3(3.2)	31.5(0.6)	40.3(1.1)
	>C22	51.5(2.5)	51.6(3.4)	50.9(0.3)	42.8(1.5)

Table S3 450°C distribution of catalytic pyrolysis products at different residence times

		Yield(wt.%)				
		10S	208	40S	60S	
Oil composition	Alkanes	19.4(2.1)	18.0(1.0)	18.5(0.8)	23.2(0.7)	
	Olefins	17.3(0.5)	19.2(1.7)	19.5(0.7)	25.2(0.3)	
	Aromantics	7.4(0.2)	7.9(0.9)	7.6(0.1)	10.7(0.2)	
Carbon	C1-C5	14.8(0.6)	13.8(0.6)	13.5(0.5)	12.9(0.3)	
number	C6-C22	38.8(0.8)	37.4(0.4)	37.9(0.5)	53.0(0.8)	
distribution	>C22	33.4(2.1)	36.6(1.3)	42.0(1.7)	32.4(0.6)	

Table S4 500°C distribution of catalytic pyrolysis products at different residence times

			Yield(wt.	%)	
		10S	20S	40S	60S
01	Alkanes	10.3(1.8)	11.3(0.5)	12.2(0.9)	12.4(0.9)
Oll	Olefins	14.9(0.7)	16.5(0.0)	21.5(0.9)	21.4(1.7)
composition	Aromantics	9.2(0.1)	6.9(0.2)	9.1(0.3)	9.7(0.2)
Carbon	C1-C5	18.2(1.2)	22.9(1.5)	23.7(0.7)	28.7(1.1)
number distribution	C6-C22	24.5(1.1)	32.3(1.2)	40.7(1.6)	42.2(0.9)
	>C22	33.2(2.7)	21.9(3.2)	29.9(0.6)	21.9(0.4)

Table S5 550°C distribution of catalytic pyrolysis products at different residence times

		Yield(wt.%)				
		10S	20S	40S	60S	
Oil composition	Alkanes	7.5(0.0)	7.3(1.6)	6.6(0.4)	5.2(0.5)	
	Olefins	8.9(0.8)	11.5(1.2)	12.2(1.2)	11.1(1.4)	
	Aromantics	5.6(0.4)	5.9(1.6)	7.3(0.3)	6.6(0.5)	
Carbon	C1-C5	34.4(0.2)	40.5(3.6)	48.7(0.2)	56.1(1.7)	
number distribution	C6-C22	21.0(1.2)	24.2(4.3)	25.2(1.8)	21.9(1.9)	
	>C22	20.6(0.0)	11.8(0.8)	15.9(1.5)	13.4(1.8)	

Table S6 600°C distribution of catalytic pyrolysis products at different residence times

Entory	Catalyst	Ingredie	Temp.	Deseter	Liquid yield(Gas yield	Ref.
Entey	Cataryst	nts	°C	Reactor	%)	(%)	
1	HZSM-5	HDPE	500	Fixed bed	17.3	72.6	[1]
2	HUSY	HDPE	500	Fixed bed	41.0	39.5	[1]
3	Beta	HDPE	600	Fixed bed	30.5	55.6	[2]
4	Zn/HZSM-5+Cu-Fe ₃ O ₄	PE	360	Reaction Kettle	50.8	34.7	[3]
5	H ₃ PO ₄ -Activated Carbon	PE	550	two-staged fixed-bed reactor	41.8	50.5	[4]
6	ZSM-5	PE	700	semi batch reactor	46.36	49.46	[5]
7	MgO	LDPE	500	microwave reactor	30.3	67.0	[6]
8	s-ZSM-5 +Zn/meso-ZSM-5	PE	400	dual-bed reactor	54.9	45.1	[7]
9	15wt%Ni/HZSM-5	HDPE	400	batch autoclave reactor	55	/	[8]
10	Ru/HZSM-5(300)	HDPE	280	Hastelloy slurry reactor	58.0	/	[9]
11	Pt/ZSM-5(38)	PE	500	micropyrolyzer	60.5	32.9	[10]
12	CaO	Mixed P	700	0.1.1.1.1	31	65	[11]
12	CaU	lastics		nuldized bed			
13	Ga/P/ZSM-5	LDPE	500	two-staged fixed-bed reactor	42.1	57.0	[12]
14	MCM - 41	LDPE	550	Fixed bed	66.0	34.0	[13]
15	Pt/Al ₂ O ₃	LDPE	280	Stainless steel mini reactor	56	/	[14]

Table S7 statistics of polyethylene pyrolysis yields over various catalysts

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