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Evaluation of PtPd-modified Zeolite Catalysts (ZSM-5, Beta, USY) for Pyrolysis of Jatropha Waste

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Fast pyrolysis with three typical modified zeolite catalysts was evaluated to produce bio-oil from Jatropha waste. Jatropha waste was pyrolyzed in a stainless-steel reactor at 600 °C under N₂ gas flow. The aromatic hydrocarbon selectivity in the bio-oil was in the order: PtPd/ZSM(30) (73.7 %) > PtPd/Beta(22.5) (68.6 %) > PtPd/USY(20) (48.7 %), where the weight ratio of Jatropha/catalyst was 1. In addition, catalyst regeneration was carried out to study the catalyst efficiency. The analysis of fresh and regenerated catalysts by XRD, NH₃-TPD, and TG/DTG, as well as product selectivity and surface properties showed that coke deposition and removal were associated with the zeolite structure and surface acid property. Due to pore size regulation, H-ZSM-5 with 10-membered ring (10 MR) could promote the pyrolysis reaction on the outside surface rather than in the inside channels. In USY zeolite with 12 MR, the reaction could occur inside the channels, but the moderate acid nature resulted in only slightly developed coke formation, which could be removed, at least partly, after regeneration. In beta zeolite with 12 MR, the total amount of surface acidity was more than twice that of USY, which undergoes more condensed coke formation, and was more difficult to remove by regeneration than the coke over USY. Thus, under these pyrolysis conditions, PtPd/ZSM(30) seems to be a better candidate for pyrolysis of Jatropha waste compared to PtPd/Beta(22.5) and PtPd/USY(20).

Keywords

Fast pyrolysis, Jatropha waste, Modified zeolite catalyst, Aromatic hydrocarbon, Catalyst regeneration, Surface acid property

1. Introduction

Renewable and sustainable production of biofuels has become increasingly important because of greater demand, concerns over global warming and finite fossil fuel reserves, and the quality of crude oil^{1)–3)}. Biomass is expected to provide an alternative energy source because biomass utilization results in low emissions of NO_x and SO_x⁴⁾ and is CO₂ neutral. One of the most viable renewable energy sources is biomass from agricultural residues⁵⁾, because it is cheap, plentiful, and does not require significant effort to collect. *Jatropha curcas* L., commonly known as the physic nut or purging nut, has gained popularity as potential biomass source for non-edible oil because it can grow in arid, semiarid, and waste areas. This species has well

developed drought tolerance and adaptation capacity to long, severely dry seasons, so that established plants have been reported to grow even if rain has not fallen for 2–3 years⁶⁾. On the other hand, Jatropha also appears to tolerate humid conditions equally well, showing good growth with high rainfall, can survive on infertile soils, and is not browsed by cattle. Moreover, Jatropha has a high-seed yield and high oil content⁷⁾.

Consequently, conversion of such biomass residues to liquid fuels and chemicals should be beneficial for solving energy and environmental problems. Technology to convert solid biomass to liquid fuels uses many approaches, which may involve with multiple steps or low yield, thus greatly increasing the cost of biomass conversion. For example, gasification needs very high temperatures of 900–1000 °C and subsequent liquefaction processes of biogas such as the Fischer-Tropsch reaction and methanol synthesis are required to obtain liquid fuel⁸⁾. Fermentation proceeds under mild conditions, but production is slow, and pretreatment of

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biomass and fermentation waste products are still problems to be solved.

Pyrolysis of biomass is a type of thermochemical decomposition occurring at temperatures between 400–650 °C in the absence of oxygen. Pyrolysis is one of the most promising methods to convert cheap, local, and abundant lignocellulosic biomass into gases, liquids (called bio-oil) and solids (called bio-char)^{9)–11)}. In particular, fast pyrolysis of biomass is an effective method which obtains a high liquid yield achieved through rapid heating rate, short residence time, and rapid quenching of vapors¹²⁾. The yield structure is highly dependent on the feedstock and the process conditions employed, but liquid yields of up to 70–75 wt% from wood can be achieved¹³⁾. In addition, the bio-oil must be modified chemically or ‘upgraded’ by removal and modification of unwanted compounds, most of which contain oxygen as phenols and carboxylic acids. Therefore, *in-situ* upgrading using catalysts is highly desirable, generally referred to as catalytic fast pyrolysis, to reduce the cost of the process.

Fluid catalytic cracking of heavy oils and polyolefins commonly use pure zeolites (H-ZSM-5, H-Beta, HY, HMCM-41) as the catalysts¹⁴⁾. Hydrodeoxygenation (HDO) as well as hydrodenitrogenation (HDN) and hydrosulfurization (HDS) of FCC gasoline occurs on catalysts such as NiMo/SiO₂–Al₂O₃, NiMo/USY, PtPd/SiO₂–Al₂O₃ and PtPd/USY^{15),16)}. PtPd/Beta catalyst is also effective for the hydroisomerization of alkane¹⁷⁾. Cracking and HDO on PtPd-modified acid zeolites occur through carbocationic intermediates activated by Lewis and Brønsted sites, which have advantages over mechanisms involving the free radical intermediates characteristic of thermal pyrolysis such as: (i) lower temperature and, consequently, energy saving; (ii) shorter residence time, enabling higher production for the same reactor volume; and (iii) higher selectivity for commercially interesting products. Generally, the presence of Pt on the zeolite support accelerates HDO and hydroisomerization, and the presence of Pd reduces sintering of Pt particles, based on formation of PtPd heterometallic bonds¹⁷⁾. However, catalytic fast pyrolysis of Jatropha waste and *in-situ* upgrading of the obtained bio-oil has not been investigated using any these catalysts such as PtPd/USY.

In the present study, three typical catalysts such as PtPd/ZSM, PtPd/Beta and PtPd/USY were prepared and used for catalytic fast pyrolysis of Jatropha waste, obtained after extraction of Jatropha oil, using a stainless steel reactor. The characteristics of regenerated catalysts were compared with those of fresh catalysts, and the most effective catalysts were evaluated for pyrolysis and concomitant upgrading of Jatropha waste.

2. Experimental

2.1. Catalyst Preparation

Three different types of zeolite were used as microporous supports. The support surface was coated with two types of metal complex, trans-diammine-dinitropalladium(II) (Pd(NO₂)₂(NH₃)₂), and tetraammine-platinum(II) chloride hydrate (Pt(NH₃)₄Cl₂ × H₂O), which were provided by Soekawa Chemicals. Metal-modified microporous catalysts were prepared by the impregnation technique. The details of support preparation and the impregnation procedure including catalyst regeneration are explained below.

2.1.1. Support Preparation

Beta zeolite (Si/Al₂ = 22.5, Zeolyst) powder was first calcined at 500 °C for 6 h with a heating rate of 3 °C/min. Calcined powder was uniaxially pressed into pellets under 40 MPa. Next, all pellets were broken and sieved. The size range of broken support was 2.0–3.35 mm. Other cylindrical-shape pellet zeolites (2 mm (dia.) × 5.5 mm, such as USY (Si/Al₂ = 20) and ZSM (Si/Al₂ = 30)) were purchased from JGC Corp. and used without pretreatment.

2.1.2. Impregnation Procedure

In the one-step preparation method, 0.5 wt% Pt and 0.5 wt% Pd in de-ionized water were prepared and poured onto the microporous support simultaneously. The mixture was gently stirred in a flask before drying at 60 °C for 12 h and then moved to a crucible at 100 °C for 6 h for drying completely. Calcination was carried out in a muffle furnace at 500 °C for 5 h with a heating rate of 4 °C/min followed by reduction in an autoclave at 250 °C for 5 h under a 4 MPa hydrogen atmosphere. In the two-step preparation method, 0.5 wt% Pt was first dissolved in de-ionized water, followed by mixing with the zeolite support, drying, and calcination as performed in the one-step impregnation method. Then, after calcination, the Pt-zeolite was impregnated with 0.5 wt% Pd solution in de-ionized water. The mixture was again dried and calcined. Finally, the calcined PtPd-modified zeolite was reduced under a 4 MPa hydrogen atmosphere in an autoclave at 250 °C for 5 h.

2.1.3. Catalyst Regeneration

To study the efficiency of the catalyst, the used catalysts after reaction were regenerated as follows. Used catalyst covered with carbon was calcined at 600 °C for 5 h with a heating rate of 4 °C/min followed by reduction at 250 °C for 5 h in an autoclave under a 4 MPa hydrogen atmosphere.

2.2. Catalytic Fast Pyrolysis

Jatropha waste was pyrolyzed in a stainless steel reactor with a diameter of 6 cm and height of 40 cm (Fig. 1). Four traps, one ice trap and three liquid nitrogen traps, and a plastic gas reservoir of volume 100 L were connected with the reactor. The ratio of Jatropha to catalyst was 1 : 1 by weight. Approximately

1: Jatropa waste, 2: N₂ flow, 3: Thermocouple, 4: Catalyst bed, 5: Mesh filter, 6: Electric furnace, 7: Iced trap, 8: Liquid nitrogen trap, 9: Plastic waste gas reservoir.

Fig. 1 Illustration of the Stainless-steel Reactor System

20 g of quartz sand and 15 g of catalyst were first put into the reactor. Then the reactor was heated up to 600 °C under N₂ at a flow rate of 1900 mL/min. After reaching 600 °C, the Jatropa waste was poured into the reactor from the No.1 inlet of Fig. 1 immediately. Products, gas and liquid phase, were collected in the traps and plastic gas reservoir. The liquid and solid char products were weighed and the liquid products were rinsed out from the trap tubes using a mixture of 1 : 1 by volume of dichloromethane and methanol.

2. 3. Analysis

2. 3. 1. Catalyst Characterization

The dispersion and particle sizes of the reduced platinum and palladium particles were measured by the CO chemisorption method using a BEL-CAT apparatus (Bel Japan Inc.). Before chemisorption of CO, the catalysts were pretreated in He for 35 min and then reduced for 30 min in a 5 % H₂/Ar gas flow at 50 mL/min at 400 °C and flushed with He for 15 min at 400 °C in a reaction chamber. After this pretreatment, the samples were cooled down to 50 °C under He gas flow and CO pulse measurements were carried out under a 5 % CO/He gas flow at 50 mL/min. Finally, the Pt and Pd particle sizes were determined from the CO pulse data, in which the amount of CO chemisorbed on Pt was assumed to be close to that on Pd, due to the same content of 0.5 wt%.

The X-ray diffraction (XRD) patterns of fresh and used catalysts were obtained with a Philips 1850 diffractometer in step mode employing CuK α radiation ($k = 0.154$ nm). The X-ray tube was operated at 40 kV and 40 mA. The average metal and metal oxide particle sizes (denoted by “ d ”) were calculated with the Sherrer formula: $d = 0.90\lambda / (\beta \cos \theta)$, where λ is the

X-ray wavelength (1.542) and β is the width in radians at the half height of the diffraction peak.

BET surface area, total pore volume (V_p), and mean pore diameter (d_p) of all catalysts were determined by N₂-physisorption using a BELSORP MAX apparatus (Bel Japan Inc.) at liquid-N₂ temperature. V_p and d_p were estimated from the BET surface area¹⁸⁾. The reducibility of the prepared catalysts was studied by H₂-temperature-programmed reduction (TPR). Before the analysis, 50 mg of the sample was placed in a quartz tube and purged with Ar at 100 °C for 1 h to remove any impurities from the catalyst surface. The sample was cooled to room temperature in a He flow, then the TPR measurement was carried out using a 5 % H₂/Ar (v/v) mixture (flow rate 30 mL/min) at a heating rate of 5 °C min⁻¹ from room temperature to 800 °C, and the H₂ consumption was recorded with a thermal conductivity detector (TCD).

NH₃ temperature-programmed desorption (TPD) experiments were carried out for fresh and used catalysts such as PtPd-modified USY(20), ZSM(30), and Beta(22.5) using a special NH₃-TPD apparatus (BELCAT, Bel Japan Inc.), which was connected to a TCD for measuring the solid acidity of the catalysts. After pretreatment under He flow at 500 °C for 60 min, adsorption of NH₃ at 100 °C for 90 min, and desorption of the weakly adsorbed NH₃ under He flow at 100 °C for 30 min, TPD profiles were recorded under He flow between 100 °C and 800 °C (heating rate: 10 °C min⁻¹).

2. 3. 2. Proximate and Ultimate Analysis of Jatropa Waste

Proximate analysis of Jatropa waste has been performed in argon using a thermogravimetric analyzer (TGA) (TG 2000, Bruker AXS)¹⁹⁾. Approximately 10 mg of sample was heated from 40 to 800 °C at a typical ramp rate of 20 °C/min at a total flow rate of 50 mL/min. The moisture content was considered to account for the weight loss when the sample was heated up to 160 °C. Two step devolatilization began after the temperature reached 160 °C and was completed at 600 °C. TGA pyrolysis showed a gradual loss in mass above 600 °C which can be attributed to volatile metal loss and carbonate decomposition. Ultimate analysis was performed using a CE INSTRUMENTS EA1110 analyzer. The results of the proximate and ultimate analyses are summarized in Table 1.

2. 3. 3. Products Analysis

After the reaction, the liquid products were extracted with dichloromethane/MeOH and the organic phase was analyzed by off-line flame ionization detector (FID) gas chromatography (Agilent Technologies 7890A GC system, UA-DX30 column) and GC/MS (Agilent Technologies 5975C insert XL MSD). FID analysis used dioxane as the internal standard. The gaseous products were collected in a plastic bag and analyzed by off-line TCD gas chromatography. Porapak Q and

MS 5A columns were used for the TCD. FID analysis of gaseous hydrocarbon product was performed using a KCl-PLOT column. The amount of carbon deposited over the catalyst surface was analyzed by thermogravimetric analysis under air. Thus, the yields of gas, liquid (oil), and char were estimated from the sum of the carbon in Jatropha waste initially introduced. The carbon selectivity for each of the liquid products was estimated from the relative area % by GC/MS analysis. The acid value was measured with an automatically operated titration apparatus Methrom 905 Titrand.

3. Results and Discussion

3.1. Catalyst Properties

The catalysts were prepared by the one-step method (1S) in all tables and figures. Particle size and textural properties, such as BET surface area, pore volume (V_p), and pore diameter (d_p), of the catalysts are given in **Table 2**. The particle sizes of Pt (0.0152–0.482 nm) on the support surface of the catalysts were smaller than those of Pd (0.0275–0.874 nm). Surface area, pore volume, and pore diameter of these catalysts were 266.4–443.0 m² g^{−1}, 0.169–0.436 cm³ g^{−1}, and 1.52–4.11 nm, respectively. In these cases, both V_p and d_p were estimated from the BET surface area, but not the BJH methods. Therefore, even the d_p value of ZSM(30) was 2.58 nm, a little higher than by other

methods.

The XRD patterns of the fresh catalysts of PtPd-modified zeolite, pre-reduced under H₂, are presented in **Fig. 2(a)**. The zeolite structures were detected for the USY and ZSM supports, as compared with typical zeolite patterns (**Figs. 2(b)**²⁰ and **2(c)**²¹). XRD patterns were not clear for the Beta support²². Bimetallic PtPd as well as metallic Pt and Pd were not clearly detected, due to the small content (each 0.5 wt%).

The NH₃-TPD patterns of fresh PtPd-modified zeolite catalysts are shown in **Fig. 3(A)** and indicated two-stage desorption of NH₃. The low peak at 100–350 °C (l-peak) represented weak acid sites or physically adsorbed ammonia and the high peak at 350–550 °C (h-peak) represented strong acidic sites²³. **Table 3** shows the number of acid sites expressed as mmol NH₃ g^{−1} of catalyst with respect to the l-peak and h-peak and peak temperatures. The total acid properties of the l-peak and h-peak were in the order of PtPd/ZSM(30) (2.06 mmol g^{−1}) > PtPd/USY(20) (1.79 mmol g^{−1}) > PtPd/Beta(22.5) (0.93 mmol g^{−1}), as ascertained by the total number of acid sites and peak temperature of the h-peak.

To confirm the reducibility of the surface oxide of the catalysts, some catalysts were investigated by TPR. **Figure 4** illustrates the TPR spectrums of three catalysts, PtPd/Beta(22.5), PtPd/ZSM(30) and PtPd/USY(20) catalysts. Poorly identified peaks at 78.6–82.6 °C were attributed to reduction of palladium oxide particles²⁴, indicating that PdO in these zeolites can be fully reduced by diluted H₂ even at low temperature (Pd²⁺ to Pd⁰)²⁵. Pt reducibility (Pt²⁺ to Pt⁰) occurred at higher temperatures of 175–191 °C and these peaks indicated the reduction of PtO/PtO₂ to metallic platinum²⁶.

3.2. Preliminary Pyrolysis

Pyrolysis of Jatropha waste was first carried out in the absence of catalyst at 600 °C. The rinsed products from the traps of the stainless steel reactor appeared as black liquid. Analysis by GC-MS detected many

Table 1 Proximate and Ultimate Analyses of Jatropha Waste

Proximate analysis [%]	
moisture	4.95
volatile matter	81.0
ash content	0.76
fixed carbon	11.39
Ultimate analysis [%]	
C	46.39
H	6.55
N	4.53
O	42.53

Table 2 Catalyst Properties

Catalyst ^{a)}	Particle size ^{b)} [nm]		Physical properties		
	Pt	Pd	S_{BET} [m ² g ^{−1}]	Pore volume [cm ³ g ^{−1}]	Pore diameter [nm]
ZSM(30)	–	–	353.0	0.227	2.58
PtPd/USY(20)	0.151	0.275	424.8	0.436	4.11
PtPd/USY(20)-Re1	0.154	0.279	403.9	0.433	4.28
PtPd/USY(20)-Re2	–	–	409.1	0.437	4.27
PtPd/Beta(22.5)	0.482	0.874	443.0	0.169	1.52
PtPd/Beta(22.5)-Re1	0.197	0.357	438.6	0.166	1.51
PtPd/Beta(22.5)-Re2	–	–	374.0	0.143	1.53
PtPd/ZSM(30)	0.0152	0.0275	266.4	0.250	3.76
PtPd/ZSM(30)-Re1	0.334	0.605	279.0	0.262	3.76
PtPd/ZSM(30)-Re2	0.137	0.248	265.4	0.255	3.84

a) Pt: 0.5 wt%, Pd: 0.5 wt%. The numbers in parentheses denote Si/Al₂ ratio.

b) The sizes are estimated by CO adsorption.

(a): Experimental data, (b)-(d): Reference data.

Fig. 2 X-ray Diffractograms of Fresh Catalysts after Pre-reduction

(A): Fresh, (B): Spent.

1: PtPd/USY(20), 2: PtPd/Beta (22.5), 3: PtPd/ZSM(30).

Fig. 3 NH_3 -TPD of Fresh and Spent Catalysts

Table 3 Effect of Regeneration on the Parameters of the NH_3 -TPD Curves for the Zeolite Catalysts^{a)}

Catalyst	l-peak [mmol g^{-1}] (Temp. [$^{\circ}\text{C}$])	Used/Fresh ratio	h-peak [mmol g^{-1}] (Temp. [$^{\circ}\text{C}$])	Used/Fresh ratio
PtPd/USY(20)	0.62 (228)	0.79	0.31 (410)	1.00
PtPd/USY(20)-Re2	0.49 (221)		0.31 (420)	
PtPd/Beta(22.5)	1.50 (232)	0.54	0.29 (405)	0.50
PtPd/Beta(22.5)-Re2	0.81 (235)		0.15 (436)	
PtPd/ZSM(30)	1.60 (239)	0.38	0.46 (492)	0.36
PtPd/ZSM(30)-Re2	0.60 (239)		0.17 (449)	

a) Catalyst: 0.5 wt% Pt-0.5 wt% Pd/support, reaction temp.: 600°C . The NH_3 -TPD data of PtPd/USY(20), PtPd/Beta(22.5) and PtPd/ZSM(30) were obtained using each fresh catalyst before reaction. "Re2" denotes the catalyst pre-reduced after the second regeneration.

organic peaks. To simplify the data based on GC-MS analysis, the product components were classified into 9 categories based on their major chemical functional groups as follows: [aromatic hydrocarbon], [phenol], [alcohol and ketone], [ether], [acid and ester], [aliphatic hydrocarbons (alkane and alkene)], [*N*-heterocycle], [*N*-nonheterocycle] and [others]. The relative percentage of each group is shown in **Table 4**. The total percentage of each functional group was 10.8, 15.0, 6.00, 1.61, 38.9, 8.94, 9.92, 8.89 and 0.00 %.

3. 3. Effect of Three Different Types of Catalysts

The effect of catalyst preparation methods was examined by preliminary runs. PtPd/USY(20) was impregnated with 0.5 wt% Pt and 0.5 wt% Pd by both 1-step (1S) and 2-step (2S) impregnation methods. After pyrolysis in the stainless steel reactor of Jatropha residue and catalyst with ratio of 1 : 1 by weight, brown liquid

product was obtained and GC-MS analysis was carried out. The carbon selectivity for [aromatic hydrocarbon] of (1S) was 51.7 %, whereas the selectivity of (2S) was 46.0 %. These values are much higher than the value of 10.8 % without catalyst. The GC-MS analysis of all other products showed no considerable differences between the (1S) and (2S) preparation methods. The oil yields of all liquid products were almost the same (range: 36-40 %). Based on these results, the 1-step preparation method was used in subsequent reactions.

In the presence of PtPd-modified catalysts, Jatropha waste was pyrolyzed in the stainless steel reactor at 600 °C using Jatropha waste and catalyst at the ratio of 1 : 1 by weight. Liquid products were analyzed by GC-MS. Relative selectivities of produced waste oil are shown in **Table 4**. The aromatic hydrocarbon selectivities were in the order PtPd/ZSM(30) (73.7 %) > PtPd/Beta(22.5) (68.6 %) > ZSM(30) (64.8 %) > PtPd/USY(20) (48.7 %) > Pt/USY(20) (46.6 %) > PtPd/SiO₂-Al₂O₃ (33.8 %) > none (10.8 %). For phenols, the order was PtPd/USY(20) (24.2 %) > PtPd/SiO₂-Al₂O₃ (19.5 %) > Pt/USY(20) (16.8 %) > none (15.0 %) > PtPd/Beta(22.5) (8.98 %) > ZSM(30) (8.28 %) > PtPd/ZSM(30) (5.87 %). For acid and esters, the order was none (38.9 %) > PtPd/SiO₂-Al₂O₃ (9.92 %) > Pt/USY(20) (7.47 %) > PtPd/ZSM(30) (4.98 %) > ZSM(30) (2.36 %) > PtPd/USY(20) (0.49 %) > PtPd/Beta(22.5) (0.23 %). For *N*-containing compounds (sum of [*N*-heterocycle] + [*N*-nonheterocycle]), the order was none (18.8 %) > PtPd/USY(20) (18.6 %) > ZSM(30) (18.3 %) > PtPd/SiO₂-Al₂O₃ (17.0 %) > Pt/USY(20) (15.8 %) > PtPd/ZSM(30) (10.0 %) > PtPd/Beta(22.5) (9.83 %).

Examination of **Table 4** indicates that modified zeo-

1: PtPd/USY(20), 2: PtPd/Beta(22.5), 3: PtPd/ZSM(30).

Fig. 4 TPR Profiles of the Typical Catalysts

Table 4 Product Selectivities in the Fast Pyrolysis of Jatropha Waste Using Fresh and Regenerated Catalysts

Catalyst	Organic products ^{a)}									Relative acid value ^{d)}
	1	2	3	4	5	6	7	8	9	
Non	10.8	15.0	6.00	1.61	38.9	8.94	9.92	8.89	0.00	1
Pt/USY(20)	46.6	16.8	6.15	2.94	7.47	3.92	10.9	4.92	0.37	0.188
PtPd/SiO ₂ -Al ₂ O ₃	33.8	19.5	4.91	7.44	9.92	7.44	8.01	9.02	0.00	0.193
PtPd/USY(20)	48.7	24.2	7.98	0.00	0.49	0.00	11.7	6.88	0.00	0.092
PtPd/USY(20)-Re1 ^{b)}	35.1	25.6	10.7	2.63	0.32	0.00	12.0	13.7	0.00	0.095
PtPd/USY(20)-Re2	47.5	24.2	4.78	2.05	4.07	0.00	8.76	8.72	0.00	0.076
PtPd/Beta(22.5)	68.6	8.98	5.02	7.18	0.23	0.13	2.25	7.58	0.00	0.017
PtPd/Beta(22.5)-Re1	43.2	23.9	3.54	3.66	1.41	0.00	8.31	16.0	0.00	0.095
PtPd/Beta(22.5)-Re2	36.9	24.6	8.16	0.91	2.75	2.39	6.02	18.3	0.00	0.131
ZSM(30)	64.8	8.28	2.22	0	2.36	4.04	11.7	6.67	0	-
PtPd/ZSM(30)	73.7	5.87	5.49	0.00	4.98	0.00	6.53	3.47	0.00	0.129
PtPd/ZSM(30)-Re1	59.0	11.6	3.63	2.26	1.66	0.00	16.3	5.61	0.00	0.078
PtPd/ZSM(30)-Re2	56.5	12.1	5.51	1.67	4.43	0.48	9.33	8.96	1.07	0.086
PtPd/ZSM(30)(550 °C) ^{c)}	48.8	11.1	8.76	2.70	8.49	0.70	11.7	7.72	0.00	0.238

a) 1: Aromatic hydrocarbon, 2: Phenol, 3: Alcohol and ketone, 4: Ether, 5: Acid and ester, 6: Alkane and alkene, 7: *N*-heterocycle, 8: *N*-nonheterocycle and 9: Others.

b) "Re1" and "Re2" denote the reactions after the first and the second regeneration.

c) PtPd/ZSM(30)(550 °C) denotes pyrolysis at 550 °C.

d) Relative acid value of product liquid was estimated as the ratio to the value of non-catalyst conditions.

lite catalysts were somewhat effective for formation of aromatic hydrocarbons through *in-situ* upgrading. Both product selectivities and relative acid value of waste oil to the value of non-catalyst conditions are presented as indicators of the catalyst effectiveness^{*1)}. In fact, the acid values decreased to 12.9-1.73 % when using catalysts.

More details of the organic compounds in each group are shown in **Table 5**. The aromatic hydrocarbons included monoaromatics such as benzene, toluene, xylenes, and polyaromatic hydrocarbons (PAHs)²⁷⁾, such as naphthalene and methylnaphthalene. The relative ratios of monoaromatics to PAH compounds were determined as 0.873 for PtPd/ZSM(30), 0.0955 for PtPd/Beta(22.5) and 1.266 for PtPd/USY(20). The main phenolic compounds were phenols and alkylphenols. The *N*-heterocycles were typically indole and quinoline, and the *N*-nonheterocycles were aniline and hexadecanenitrile. Other products are also summarized in detail in **Table 5**.

Yields of Jatropa conversion obtained from pyrolysis with various catalysts are shown in **Fig. 5**. The yield of oil products was 49 % without catalyst, compared to 39, 44 and 41 % with PtPd/ZSM(30), PtPd/Beta(22.5) and PtPd/USY(20), respectively. In addition, the O/C ratio of oil product, estimated by GC analysis, was 0.068, 0.057 and 0.031 pyrolyzed with PtPd/ZSM(30), PtPd/Beta(22.5) and PtPd/USY(20), respectively.

3. 4. Effect of Catalyst Regeneration

The PtPd/ZSM(30), PtPd/Beta(22.5) and PtPd/USY(20) catalysts were regenerated after use for pyrolysis as explained in the experimental section. The regenerated catalyst was used for pyrolysis of Jatropa residues under the same conditions (at 600 °C under N₂ flow at 1900 mL/min in the stainless steel reactor). The first regeneration (Re1) and the second regeneration (Re2) of PtPd/ZSM(30) led gradually to decreased catalyst performance as shown in **Table 4**. The order of aromatic hydrocarbon selectivity was fresh (73.7 %) > Re1 (59.0 %) > Re2 (56.5 %). Using the Re1 and Re2 catalysts, phenolic (2) and *N*-containing products (7 and 8) increased, but acid compounds were not increased, so that the relative acid value was slightly improved after regeneration. As displayed in **Fig. 6**^{*2)},

the yield of oil products using PtPd/ZSM(30) catalyst remained constant at 38-40 % before and after regeneration. **Figure 7(A)** seems to show that the XRD intensity ratio slightly decreased to 0.967 after the second regeneration of PtPd/ZSM(30), indicating that almost all the ZSM structure still remained.

Using PtPd/Beta(22.5), the order of aromatic hydrocarbon yield was fresh (68.6 %) > Re1 (43.2 %) > Re2 (36.9 %). The relative acid value was dramatically increased after regeneration, possibly due to the increases in phenolic (2) and acid (5) products. The yield of oil products using PtPd/Beta(22.5) catalyst slightly decreased from 43.9 % for fresh catalyst to 37.0-40.9 % after regeneration. Change in XRD intensity ratio was not clear (**Fig. 7(B)**), but part of the Beta structure remained, because of the Beta peak observations for Re1 and Re2. Using regenerated PtPd/USY(20), the order of aromatic hydrocarbon yield was fresh (48.7 %) > Re2 (47.5 %) > Re1 (35.1 %). All product selectivities were approximately constant after regeneration, so that the relative acid value slightly changed. The yield of oil products using PtPd/USY(20) catalyst decreased from 40.5 % for fresh catalyst to 35.6-36.2 % after regeneration. XRD intensity ratio slightly decreased to 0.591 after the second regeneration (**Fig. 7(C)**). The use of regenerated PtPd/ZSM(30) still produced bio-oil with higher aromatic hydrocarbon content than that using regenerated PtPd/Beta(22.5) and regenerated PtPd/USY(20). These experimental results demonstrate that PtPd/ZSM(30) is a good candidate catalyst with high efficiency for catalytic fast pyrolysis of Jatropa waste.

Particle size and surface properties, including BET surface area, pore volume and pore diameter of the regenerated catalysts, are summarized in **Table 2**. The Pt and Pd particle sizes of these zeolites were 0.0152 to 0.482 nm, even after regeneration, which were almost the same as fresh catalysts. Surface area of regenerated PtPd/ZSM(30) remained constant, whereas the surface areas of PtPd/USY(20)-Re1 and -Re2 were slightly lower than the fresh catalyst. Both surface area and pore volume of PtPd/Beta(22.5) decreased with repeated regeneration. Pore volumes remained constant even after regeneration and pore diameters were approximately constant for the other catalysts.

The TG/DTG measurement of coke could be performed under air flow for two types of used catalysts derived from fresh and regeneration catalysts. **Figures 8(A)** and **8(B)** show the TG/DTG curves of the three fresh catalysts. Two peaks were identified at 449 °C and 518 °C on the PtPd/USY(20)-fresh catalyst, with coke content of 0.117 g (g of catalyst)⁻¹. One peak was identified at 487 °C on the PtPd/Beta(22.5)-fresh and one peak at 435 °C on the PtPd/ZSM(30)-fresh catalyst, with coke contents of 0.088 and 0.060 g (g of catalyst)⁻¹, respectively. Peak temperatures

^{*1)} Under non-catalyst conditions, the acid value of the obtained oil with solvent was 7.8 mgKOH/g, which could be mainly attributable to products such as free fatty acid and acetic acid. These acid compounds were decreased and the acid value of product oil reduced with catalyst. Therefore, the relative acid value is a good indicator of the acid removal ability of the catalyst.

^{*2)} In **Fig. 6**, regeneration was carried out using the same catalyst systems as the fresh catalyst and these oil yields were reproducible for the three catalysts, but part of the char yield was not reproducible. Further study is required to check the catalyst reproducibility.

Table 5 Relative Proportions (area %) of Catalytic Fast Pyrolysis of *Jatropha* Residues

No.	Organic products	Area %					
		PtPd/ USY(20)	PtPd/USY (20)-Re2	PtPd/Beta (22.5)	PtPd/Beta (22.5)-Re2	PtPd/ZSM (30)	PtPd/ZSM (30)-Re2
[Aromatic hydrocarbons]							
1	Benzene	12.14	11.61		1.2	7.79	2.72
2	Toluene	15.07	23.04	1.80	10.67	18.27	15.97
3	<i>o</i> -Xylene				1.09	5.03	5.13
4	Indene			4.18	3.98	3.24	4.52
5	Naphthalene	18.88	9.9	23.70	7.78	25.97	13.42
6	Naphthalene, 1-methyl-	0.78	1.88	3.74	0.61	9.80	5.51
7	Naphthalene, 2-methyl-	1.83	1.02	6.13	0.36		1.75
8	Naphthalene, 1,6-dimethyl-			2.31		1.54	0.27
9	Naphthalene, 2,6-dimethyl-			0.37			1.27
10	Biphenylene			1.60			0.33
11	Fluorene			1.18		0.93	0.29
12	9H-Fluorene, 9-methylene-					1.08	0.29
13	Anthracene and pyrene			23.61			
[Phenols]							
14	Phenol	17.90	24.17	5.91	10.8	5.87	6.73
15	Phenol, 3-methyl-			1.09	3.21		1.87
16	Phenol, 4-methyl-	6.35			7.07		3.48
17	Phenol, 2,4,6-tris(1-methylethyl)-			1.43	3.52		
18	Phenol, 2,6-bis(1,1-dimethylethyl)-4-ethyl-			0.55			
[Alcohols, ketones]							
19	3-Octanone			4.52		1.47	
20	Benzaldehyde, 3,5-dichloro-2-hydroxy-			0.50			
21	Dichloroacetaldehyde	4.55			4.42	4.02	2.90
22	4,5-Dichloro-1,3-dioxolan-2-one	3.43	7.19		2.6		1.50
[Ethers]							
23	1-Propene, 1-methoxy-			3.38			
24	Benzofuran			2.28	0.91		0.16
25	2-Ethoxytetrahydrofuran			1.52			0.64
[Acids, esters]							
26	3-Benzo[g]quinoxalin-2-yl-propionic acid			0.23			
27	Acetic acid, bromochloro-				1.17	4.98	4.44
28	Propenoic acid, 2-trifluoroacetyl-amino-	0.49					
[Alkanes, alkenes]							
29	Heptadecane			0.13	0.42		
[N-heterocycles]							
30	Quinoline			0.89	0.26	3.39	2.95
31	Indole				0.46	3.14	5.14
32	Pyrrole, 1- <i>t</i> -butyl-2,4-diphenyl-			1.36	1.81		
33	Piperidine, 2-propyl-, (<i>S</i>)-	3.76			0.72		
34	Pyrrolidine, 2-ethyl-1-methyl-	3.02	1.27		1.25		
35	Pyrrolidine, 2-butyl-1-methyl-	1.69	2.17		1.52		
36	2,2'-Dipiperidine	3.25					
[N-nonheterocycles]							
37	1,1,4,7,10,10-Hexamethyltriethylenetetramine		1.86	4.61		3.47	
38	Hexadecanenitrile			2.97			1.50
39	5-Phenyl-1,2,3,4-thiadiazole	4.07			2.09		
40	Propanenitrile, 3-chloro-	0.45	10.18		9.14		11.3
41	Benzene, 1-isocyano-2-methyl-	1.54			1.68		
42	Aniline				2.53		
43	l-Valine, <i>N</i> -(carboxymethyl)-	0.82					2.40

were 477 °C and 534 °C for the used PtPd/USY(20)-Re2 catalyst after the second regeneration, slightly higher than those of the fresh catalyst, but the coke content (0.118 g (g of catalyst)⁻¹) was almost the same. One peak was still identified at 509 °C for PtPd/Beta(22.5)-Re2, which is higher than the fresh catalyst, but the coke content (0.073 g (g of catalyst)⁻¹) was

slightly lower than the fresh catalyst. A new peak is detected at 553 °C as well as the peak at 439 °C for PtPd/ZSM(30)-Re2, but the coke content (0.059 g (g of catalyst)⁻¹) was almost the same as the fresh catalyst. These findings are summarized in **Table 6**. By relating these peaks to the coke characteristics, the peaks located at lower temperature (around 430-480 °C) were

assigned to slightly developed coke, whereas the peaks located around 480-560 °C corresponded to more condensed coke, with a lower H/C ratio²⁸. These cokes match types I and II in Bauer and Karge's classification²⁹, according to their degree of development towards polyaromatic structures. To compare the results obtained in Fig. 8, the different shape selectivity of the catalysts studied and the effect on oxygen-coke contact in combustion must be taken into account^{30,31}.

In general, combustion with such well-defined peaks may be explained by the differentiated combustion of the coke in the meso- and macropores of the catalyst

(the peak located at lower temperature) and the coke located in the zeolite crystal channels (the peak at higher temperature). Under pyrolysis reaction conditions, the coke might be formed on the internal and external acidic sites of the zeolite crystals. The difference in the nature of the coke was established by comparing the contents of coke types I and II, obtained by the DTG curves in Fig. 8 and Table 6. The coke of the PtPd/ZSM(30)-fresh catalyst consisted of only type I, whereas the coke of the PtPd/ZSM(30)-Re2 catalyst consisted of both types I and II. In contrast, the cokes of both PtPd/Beta(22.5)-fresh and Re2 catalysts were only of type II, and as for the PtPd/USY(30)-Re2 as well as the

Conditions: Waste/Cat. = 1, Temp. 600 °C, N₂ flow = 1900 mL/min.

Fig. 5 Yields of Oil, Gas and Char in Pyrolysis of Jatropa Waste Using the Stainless-steel Reactor

Conditions: See caption of Fig. 5.

Fig. 6 Yields of Oil, Gas and Char in Pyrolysis of Jatropa Waste Using Fresh and Spent Catalysts

(A): PtPd/ZSM(30), (B): PtPd/Beta(22.5), (C): PtPd/USY(20) Re-1 denotes the first regeneration and Re-2 denotes the second regeneration.

Fig. 7 X-ray Diffractograms of Fresh and Spent Catalysts after Pre-reduction

(A): TG of spent catalyst, (B): DTG of spent catalyst, (C): TG of second regeneration catalyst (Re-2), (D): DTG of regeneration catalyst (Re-2).
Measurement conditions: sample 10 mg; air flow rate 30 mL/min; temperature range 30-800 °C; heating rate 20 °C/min.

Fig. 8 TG and DTG Profiles Recorded for Spent Catalysts in Air

Table 6 Effect of Zeolite Type on the Parameters of the TG/DTG Curves for the Different Catalysts^{a)}

Catalyst	Coke [g _{coke} /g _{cat}]	Temp. peak 1 [°C]	Temp. peak 2 [°C]
PtPd/USY(20)-Fresh	0.117	449	518
PtPd/USY(20)-Re2	0.118	477	534
PtPd/Beta(22.5)-Fresh	0.088	-	487
PtPd/Beta(22.5)-Re2	0.073	-	509
PtPd/ZSM(30)-Fresh	0.060	435	-
PtPd/ZSM(30)-Re2	0.059	439	553

a) Catalyst: 0.5 wt% Pt-0.5 wt% Pd/support, reaction temp.: 600°C. "Fresh" denotes the pyrolysis reaction was carried out using fresh catalyst. "Re2" denotes the reaction using the used catalyst after the second regeneration.

fresh catalyst.

The NH₃-TPD patterns of used zeolite catalysts after the second regeneration are shown in **Fig. 3(B)**, indicating the two-stage desorption of NH₃. **Table 3** gives the number of acid sites expressed as mmol NH₃ g⁻¹, peak temperature, and the used/fresh ratio³²⁾. The l-peak temperature of each regeneration catalyst was between 220 °C and 240 °C, which is about the

same as that of the fresh catalyst, whereas the used/fresh ratio of acid site number of the l-peak was PtPd/USY(20)-Re2 (0.79) > PtPd/Beta(22.5)-Re2 (0.54) > PtPd/ZSM(30)-Re2 (0.38). The h-peak temperatures of PtPd/USY(20)-Re2 and PtPd/Beta(22.5)-Re2 were slightly raised, compared with those of fresh catalysts, whereas the h-peak temperature of PtPd/ZSM(30)-Re2 decreased compared with the fresh catalyst. The used/

fresh ratio of acid site number of the h-peak was PtPd/USY(20) (1.0) > PtPd/Beta(22.5) (0.50) > PtPd/ZSM(30) (0.36). The total acid property of the l- and h-peaks was apparently associated with coke formation³³.

3.5. Role of Zeolite Support

The three zeolite structures seem to persist, at least in part, even after the second regeneration as shown in Fig. 7. The correlation between aromatic hydrocarbon selectivity and relative acid value in Table 4 is summarized in Fig. 9, where the result for PtPd/SiO₂-Al₂O₃ is given as a typical non-zeolite. Even after the second regeneration, the selectivities of the zeolite-based catalysts were higher than for SiO₂-Al₂O₃-based catalysts, but the relative acid values in the zeolites were lower, indicating the effective involvement of the zeolite structures.

The results in Tables 3 and 4 show moderate deterioration of catalytic activity as well as surface acidity for PtPd/ZSM(30) after the first and second regeneration, but the aromatic hydrocarbon selectivity was still higher compared to that of the beta and USY-based catalysts. Moreover, Table 6 and Fig. 8 show that the amount of coke deposition was lower on the ZSM-based fresh and regenerated catalysts than on the other two catalysts, and the peak 1 temperature was also lower compared to that of PtPd/USY(20). Such good performance of the H-ZSM-5 zeolite probably depended on the three-dimensional structure without cages at the channel

intersections, combined with a good compromise between shape selectivity (10-membered ring) and site acidity strength, so that these zeolite properties minimized the formation of coke precursors and their development^{33,34}. One possible scheme is displayed in Fig. 10(A), where a major part of the pyrolysis reaction occurs on the outer surface of the catalyst, whereas some reactions such as pyrolysis of glucose derived

PtPd are omitted. U, B, and Z denote PtPd/USY(20), PtPd/Beta(22.5) and PtPd/ZSM(30), respectively. Re1 and Re2 denote the first and second regeneration. SA denotes SiO₂-Al₂O₃. Z(550 °C) denotes pyrolysis at 550 °C using PtPd/ZSM(30).

Fig. 9 Correlation between Aromatic Hydrocarbon Selectivity and Relative Acid Value

(A): PtPd/ZSM(30), (B): PtPd/USY(20), (C): PtPd/Beta(22.5).

Fig. 10 Postulated Catalysis and Regeneration Schemes

from cellulose proceed inside the zeolite crystalline channels, which have stronger acid sites associated with the h-peak of NH_3 -TPD compared to the outer surface (l-peak). These properties seem to originate mainly from the medium-size micropore and the surface acid structure of H-ZSM-5 zeolite³⁵. After regeneration at 600 °C, most of the coke on the outer surface was removed, whereas most of the coke strongly attached inside the channels was not removed, which would be consistent with the appearance of the new TG peak 2 at 553 °C, as shown in **Fig. 8(D)** and **Table 6**. Since the outer surface would be more important in pyrolysis than the inside channels, the catalyst activity after the second regeneration remained similar to that after the first regeneration (**Table 4**).

The USY zeolite has a large 12-membered ring micropore with cages at the channel intersection and lower acid amount than H-Beta and H-ZSM-5³⁶, which leads to less deterioration of surface acidity compared to H-Beta as well as H-ZSM-5 (**Tables 3 and 4**). In this case, we assume that most organic compounds would be formed by pyrolysis inside the channel and the coke accumulated inside the channel, but due to the very moderate acid nature and large channel structure, most of the coke was removed after the first and the second regeneration. As a result, both the activity and the coke amount of the regenerated catalyst (PtPd/USY(20)-Re1 and Re2) would be approximately close to that of fresh catalyst (**Tables 4 and 6**). This scheme is displayed in **Fig. 10(B)**.

In contrast, H-Beta zeolite has a 12-membered ring micropore structure similar to USY, but the total acid properties of H-Beta (2.31 mmol g⁻¹) are more than twice that of USY¹⁷) (1.11 mmol g⁻¹), which would lead to only formation of more condensed coke (peak 2) without slightly developed coke (peak 1) and, after the second regeneration at 600 °C, the peak 2 temperature increased from 487 to 509 °C, as shown in **Table 6**. Both surface area and pore volume of PtPd/Beta(22.5) decreased with repeated regeneration as shown in **Table 2**. These findings indicate that condensed coke could accumulate in the cages and channels, even after regeneration, as shown in **Fig. 10(C)**. As a result, selectivity for aromatic hydrocarbon decreased, whereas selectivity for phenols and relative acid values increased, as the regeneration was repeated (**Table 4**). Therefore, PtPd/ZSM(30) seems to be a better candidate for pyrolysis of *Jatropha* waste compared to PtPd/Beta(22.5) and PtPd/USY(20).

4. Conclusions

Three zeolite-based catalysts, PtPd/ZSM(30), PtPd/USY(20) and PtPd/Beta(22.5), were evaluated for pyrolysis of *Jatropha* waste using a stainless steel reactor. Using the fresh catalyst, the selectivity for aro-

matic hydrocarbons was in the order: PtPd/ZSM(30) (73.7 %) > PtPd/Beta(22.5) (68.7 %) > PtPd/USY(20) (48.7 %). After the second regeneration, the order became: PtPd/ZSM(30) (56.5 %) > PtPd/USY(20) (47.5 %) > PtPd/Beta(22.5) (36.9 %). The analysis of fresh and regenerated catalysts by XRD, NH_3 -TPD, and TG/DTG, as well as product selectivity showed that the characteristics for coke deposition and removal were associated with the zeolite structure and surface acid property. We assume that, due to pore size regulation, H-ZSM-5 promoted the pyrolysis reaction on the outside surface rather than in the inside channels, resulting in easy coke removal. In USY zeolite with 12-membered ring (12 MR), the reaction could occur inside the channels, but the moderate acid nature resulted in only slightly developed coke formation, which could be removed after regeneration. In contrast, in beta zeolite with 12 MR, the total surface acidity might be more than twice that of USY, resulting in more condensed coke formation, which was difficult to remove by regeneration. The partially deactivated H-ZSM-5 or USY-based catalyst retained almost constant activity, with a slight change in product distribution. Thus, under these pyrolysis conditions, PtPd/ZSM(30) seems to be a better candidate for pyrolysis of *Jatropha* waste compared to PtPd/Beta(22.5) and PtPd/USY(20). Further study is currently underway to improve the aromatic hydrocarbon selectivity through one-pot pyrolysis using the stainless steel reactor.

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要 旨

ジェットロファ廃材の熱分解における PtPd 修飾ゼオライト (ZSM-5, ベータ, USY) の効果

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ジェットロファ残査からのバイオオイル製造を目的として、三つの代表的な修飾ゼオライトを用いた熱分解をステンレス反応管、窒素雰囲気中、600℃で行った。ジェットロファ/触媒重量比=1で、芳香族炭化水素選択率の序列は、PtPd/ZSM(30) (73.7%)>PtPd/ベータ (22.5) (68.6%)>PtPd/USY(20) (48.7%)であった。加えて、再生触媒での効果も検討した。フレッシュおよび再生触媒の解析をXRD, NH₃-TPD, TG/DTG, 比表面積測定等で行い、炭素析出および除去再生の挙動はゼオライトの

細孔構造や固体酸性に影響されることを推定した。実際、10員環では細孔内よりむしろ外表面で熱分解が起こる。12員環で合計酸量が中程度のUSYでは、主反応は細孔内であるが、再生により除去しやすい炭素が蓄積する。また、同じ12員環でもUSYの2倍以上の酸量を持つベータゼオライトでは、除去にくい炭素がより多く析出する傾向であった。こうして、これら熱分解条件下では、PtPd/ZSM(30)触媒がPtPd/ベータ(22.5)やPtPd/USY(20)より相対的に好ましいことを推定した。

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