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Research article

Dehydrocyclization-cracking reaction of soybean oil using zeolite-metal oxide composite-supported PtNiMo sulfided catalysts

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ABSTRACT

Zeolite (ZSM-5 with various SiO_2/Al_2O_3 ratios)-alumina composite-supported PtNiMo sulfides catalysts were prepared, and were used to produce aromatics and hydrogen selectively by dehydrocyclization-cracking of soybean oil, a new type of reaction of fat under 1 MPa H_2 in the range 420 °C–580 °C. Although liquid products were not obtained using catalysts without Pt, soybean oil was completely cracked by 1 wt% of Pt containing catalysts under 1 MPa H_2 at above 420 °C, producing gasoline with research octane number up to 92. The conversion decreased below 95% even at 500 °C using 0.5 wt% of Pt or using titania instead of alumina. When alumina support was modified by basic reagents in advance, larger amounts of CO and CO_2 were formed in comparison with the catalysts, which included the unmodified alumina, in the reaction of soybean oil, indicating that decarbonylation and decarboxylation, which can inhibit the consumption of hydrogen, occurred preferentially.

1. Introduction

Recently much attention has been focused on renewable resources, carbon neutral biomass. Different from other renewable energy, only biomass can be carbonaceous resources which complement chemical industry. Among biomass, vegetable oils have some advantages because they are liquid materials and include a large number of alkyl groups in their structure. Although fatty acid methyl ester (FAME) is derived from esterification of vegetable oils with methanol, there are some problems in this process [1]. For example, a large amount of glycerol is produced as a byproduct and unreacted methanol and alkali catalysts remain in the FAME. In recent years, not only hydrotreating of vegetable oils to obtain diesel fuels with high cetane numbers [2–7] but also catalytic cracking of them to obtain gasoline with a high octane number and light olefins, materials for petrochemicals, have been extensively investigated [8–12]. The hydrotreating produces propane and propene, which are easily used as fuel and raw material for petrochemicals, instead of producing glycerol. The gas oils obtained have high durability in oxidation compared to FAME. Therefore, hydrotreating seems to be favorable for transferring vegetable oils to fuels. On the other hand, we explored the addition of acidity to the catalysts which caused the variation in selectivity of gasoline and diesel oils by changing zeolite species under the high hydrogen pressure [2]. In the course of our study, we were interested in the treatment of vegetable oils under 1 MPa low pressure of hydrogen, where neither gas oil nor gasoline may be obtained at the normal temperature used in hydrocracking. However, there is the possibility that the higher temperature would produce not only aromatics by dehydrocyclization but also gaseous hydrogen like catalytic cracking.

This paper deals with the feasibilities of not only hydrocracking of fats under low pressure of 1 MPa but also selective dehydrocyclization-cracking of vegetable oils in order to produce gasoline including large amounts of aromatics and hydrogen simultaneously. Specifically, as shown in Figs. 1, 6 molecules of aromatics, 3 molecules of CO_2 and 1 molecule of propane are selectively obtainable from 1 molecule of vegetable oil assuming that it contains four double bonds, and then 14 molecules of hydrogen can be generated. From this assumption, approximately 1 bottle of 7 m^3 cylinder of hydrogen can be produced from 18 l can of vegetable oil.

The catalyst for hydrocracking consists of zeolite for cracking and Ni and Mo for hydrogenation of aromatics and hydrocracking of compounds with heteroatoms. In this study, alumina with mesopores was mixed with zeolite to make a composite and then Ni, Mo and Pt were supported on the zeolite-alumina composite. After presulfiding the catalyst, hydrocracking of triglyceride to carboxylic acid and its further cracking to carbon dioxide and hydrocarbons were performed. The dehydrocyclization of hydrocarbons proceeds simultaneously to form aromatics and gaseous hydrogen. Therefore the total reaction may be called dehydrocyclization-cracking reaction of fat. The effects of kind of metal, pore size, acidity and pressure on the activity and selectivity of this reaction were explored and the complete conversion of fat to valuable gas and liquid products with lower molecular weight under the low hydrogen pressure 1 MPa was achieved in this paper.

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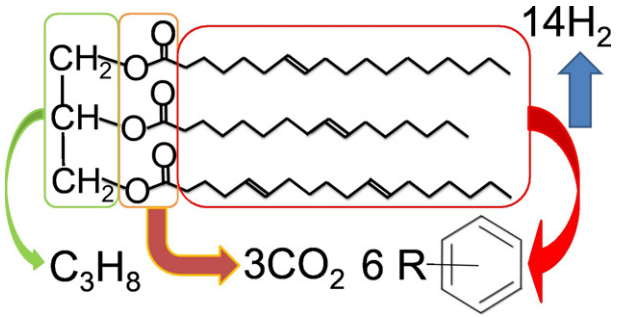

Fig. 1. Optimal reaction route for selective dehydrocyclization-cracking reaction.

2. Experimental

2.1. Materials and catalyst preparation

Zeolites used were ZSM-5 (24, 38, 90 or 1770) (MFI zeolite: SiO_2/Al_2O_3 (mol/mol) 24 (HSZ-822HOA, Tosoh), 38 (HSZ-840HOA, Tosoh), 90 (JRC-Z-90, Catalysis Society of Japan) or 1770 (HSZ-890HOA, Tosoh), cation type H^+). Industrial pure alumina (surface area 250 m^2/g, average pore diameter 8 nm, pore volume 0.70 cm^3/g), which is commonly used for hydrotreating catalyst preparation) was supplied from a petroleum company. Alumina-sol was purchased from Shokubai Kasei Co. Ltd. (Cataloid AP-1). Composite supports were composed of a zeolite (25 wt%), alumina (60 wt%) and alumina-sol (15 wt% as Al_2O_3) and were prepared by kneading method with water and successive calcination at 500 °C for 3 h in air [2]. Ni and Mo species were supported on composite supports by the conventional impregnation method using nickel nitrate hexahydrate (Nakarai Tesque Co. Ltd., $Ni(NO_3)_2 \cdot 6H_2O$) and ammonium heptamolybdate tetrahydrate (Nakarai Tesque Co. Ltd., $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$). Each catalyst calcined at 500 °C for 3 h in air included 16 wt% of MoO_3 and 3.3 wt% NiO (the Ni/Mo ratio 0.4). Subsequently, aqueous solution of $H_2[PtCl_6] \cdot 6H_2O$ was used similarly to prepare a catalyst with 1 wt% Pt.

The names of supports were determined by the abbreviation of zeolite (mainly ZSM for ZSM-5), silica/alumina ratio of zeolite in parenthesis, alumina content 60 (wt%) and the letter "A" for alumina. The samples name is shown by PtNiMo/support name.

Modification of alumina by Zn was performed using zinc acetate dehydrate ($Zn(CH_3COO)_2/2H_2O$), aqueous NH_3 ($CH_3COO:NH_3 = 1:1$) and ethanol as solvent to obtain 12 wt% of ZnO/Al_2O_3 after calcination. 12 wt% of Na_2O/Al_2O_3 or K_2O/Al_2O_3 was prepared using NaOH or KOH, CH_3COOH (NaOH or KOH:CH_3COOH = 1:1) and deionized water as a solvent. Instead of Al_2O_3, MgO (reference catalysts JRC-MGO-4, 500A, Catalysis Society of Japan) was used similarly. Composites with zeolite, modified Al_2O_3 or MgO and alumina-sol and successive supported metal catalysts were prepared using same methods described above.

Table 1
Surface area, pore volume, and average diameter of each fresh catalyst.

Catalyst	Catalyst BET			BJH		
	SA[a] (m^2/g)	PV[a] (cm^3/g)	PD[a] (nm)	Pore SA[a] (m^2/g)	PV[a] (cm^3/g)	PD[a] peak (nm)
Pt/NiMo/ZSM(24)60A	267	0.59	8.8	233	0.52	7.2
Pt/NiMo/ZSM(38)60A	272	0.58	9.7	242	0.58	8.5
Pt/NiMo/ZSM(90)60A	263	0.65	9.5	250	0.63	7.0
Pt/NiMo/ZSM(1770)60A	273	0.68	9.2	232	0.54	7.2
0.5Pt/NiMo/ZSM(24)60A	264	0.56	8.5	237	0.53	6.9
Pt/NiMo/ZSM(24)60Ti	198	0.43	4.4	172	0.38	3.9
Pt/NiMo/Z(24)60MgO	189	0.56	11.8	198	0.55	8.4
Pt/NiMo/Z(24)60Zn/A	252	0.48	7.7	208	0.46	10.5
Pt/NiMo/Z(24)60Na/A	254	0.50	7.8	228	0.47	12.1
Pt/NiMo/Z(24)60K/A	253	0.48	7.6	219	0.45	9.2
ZSM-5(24)	388	0.30	3.1	34	0.14	3.7

[a] SA; surface area, PV; pore volume, PD; pore diameter.

2.2. Characterization of catalysts

Characterizations of catalyst samples were performed according to the methods reported previously [2].

XRD patterns of catalysts were measured on a Rigaku Ultima IV diffractometer (Ni-filtered Cu-Kα radiation (λ = 1.54nm)). Peaks of ZSM-5 crystals and γ-alumina were observed in each XRD pattern of synthesized ZSM-5-Al_2O_3 composite supports, indicating that crystals of ZSM-5 zeolites were maintained. It is thought that zeolite crystals were dispersed in Al_2O_3 particles constructing hierarchical structures with microporous zeolite in the inner part and mesoporous Al_2O_3 in the outer shell of the catalysts.

The pore size distribution of a calcined sample was measured using N_2 adsorption and desorption equipment (BELSORP mini II, Nihon BEL Co. Ltd.). The Brunauer-Emmett-Teller (BET) method was used to estimate total surface area, pore volume and average pore diameter. The Barrett-Joyner-Halenda (BJH) method was used to estimate the distribution of mesopores with larger than 3.3 nm pore diameter.

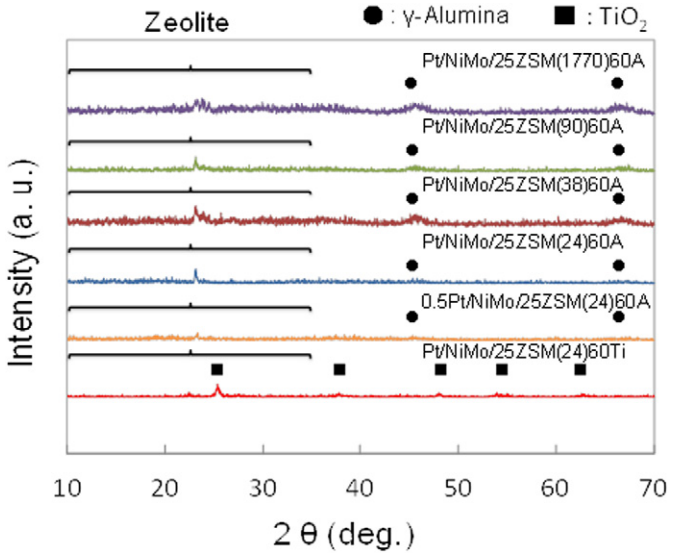

Fig. 2. XRD patterns of PtNiMo/ZSM-Oxide composite catalysts.

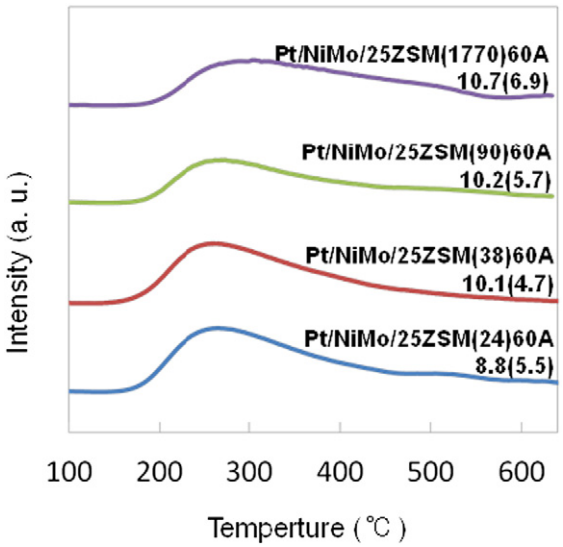

Fig. 3. NH_3-TPD profiles of each catalyst.