

## Production of Fuels from Waste Polyethylene Derived Heavy Oil over Ni-REY Catalyst in Steam Atmosphere

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Catalytic cracking of heavy oil obtained from waste polyethylene was conducted using nickel and rare earth metal exchanged Y-type zeolite catalyst (Ni-REY) in a steam atmosphere to recover light fuels. The Ni in the catalyst showed catalysis for transportation of hydrogen atoms from steam to hydrocarbons. During the repetition of sequences of reaction and regeneration of the catalysts, MFI type zeolite was gradually deactivated. On the other hand, Ni-REY kept a constant activity, and gave the high selectivity towards (Ni-REY in steam: 78%, MFI type zeolite in N<sub>2</sub>: 35%).

### Introduction

Polyolefins, such as polyethylene (hereafter abbreviated to PE) and polypropylene (PP), is one of major waste plastics, and its amount makes up of about 70% of the total waste plastics. PE and PP were easily pyrolyzed above 718 K and 683 K, respectively, yielding aliphatic hydrocarbons with a wide range of carbon numbers [1,2]. Therefore, the obtained oils must be upgraded to high quality fuels before their use.

We reported that rare earth metal exchanged Y-type zeolite catalysts (REY) effectively converted the PE derived aliphatic heavy oil to high quality gasoline [3,4]. However, waste plastics are mostly generated from small-to-medium size enterprises and households. Therefore, it is preferable to build chemical plants for waste plastics recycling in each self-government body or prefecture [5]. Considering this point, steam is a potential candidate for the carrier gas in such plants, as it is cheap and easy to handle,

The main objective of this study is to prepare a catalyst, which shows high and stable activity for the catalytic cracking of waste PE derived heavy oil in steam atmosphere. REY was selected as a base catalyst, as it showed high stability in a steam atmosphere [6]. A part of rare earth metal in REY was exchanged with Ni, which enhances the transformation of the hydrogen of steam to hydrocarbons, yielding a Ni supporting REY catalyst (Ni-REY). The obtained catalysts were applied to the catalytic cracking of PE derived heavy oil. Furthermore, the stability of the catalyst during the sequences of reaction and regeneration was investigated.

### Materials and Methods

**Catalyst.** Ni-REY was prepared from HY and NaY type zeolites by the ion-exchange technique using nickel chloride and a mixture of rare earth metal chlorides. MFI type zeolite (ZSM-5 zeolite) with a SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ratio of 65 was also

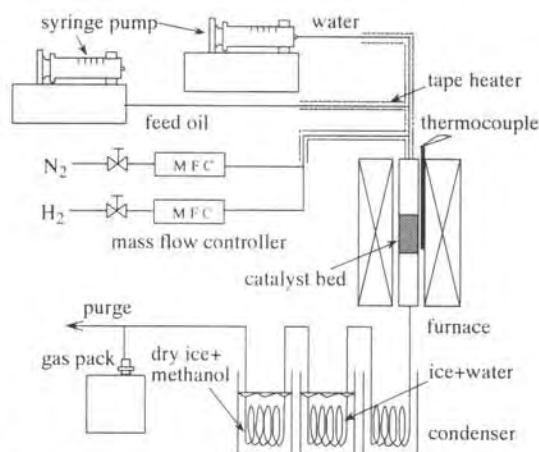


Fig. 1 Schematic view of micro reactor.

hydrothermally prepared using  $\text{Na}_2\text{SiO}_3$  and  $\text{Al}_2(\text{SO}_4)_3$  for comparison.

**Catalytic Cracking.** The feed oil used in reactions was obtained by pyrolyzing PE at 723 K (PE OIL). The catalytic cracking of PE OIL was conducted using a catalytic fixed bed reactor under the conditions of time factor  $W/F=0.25\text{--}2.9$  h and reaction temperature  $T=573\text{--}723$  K (see Fig. 1). Carrier gas used was nitrogen for MFI type zeolite, nitrogen and steam for REY and nitrogen, hydrogen and steam for Ni-REY, in order to examine the catalysis of Ni in Ni-REY for hydrogen transfer from steam to hydrocarbons. The sequence of the reaction in steam (REY and Ni-REY) or in nitrogen (MFI) and regeneration in air at 573 K was repeated to investigate the stability of the catalyst. The change in the acid amount of the catalyst during this sequence was also measured by a new ammonia TPD method (*ac*-TPD), where the desorption of ammonia proceeds under complete adsorption equilibrium conditions [7]. The composition of gaseous products was measured using a GC equipped with columns of activated carbon and Porapak-Q. Liquid products were analyzed using a Karl-Fisher moisture titrator apparatus, a GC-MS and a capillary gas chromatograph.

## Results and Discussion

**Screen test of catalyst.** Figure 2 shows typical product distributions, when the conversion was about 80% and the reaction was conducted at  $T=673$  K and  $W/F=1$  h. The results of HY, MFI and REY are also shown for comparison. Among the catalysts employed, REY used in nitrogen and Ni-REY (Ni content: 0.5 wt%) used in hydrogen showed higher selectivities towards gasoline (hydrocarbons of carbon number ranging from 5 to 11), 58 and 65%, respectively. This high selectivity was thought to be due to the

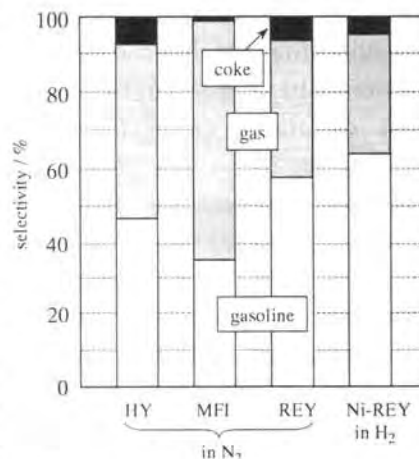


Fig. 2 Product distribution of the catalytic cracking of heavy oil.

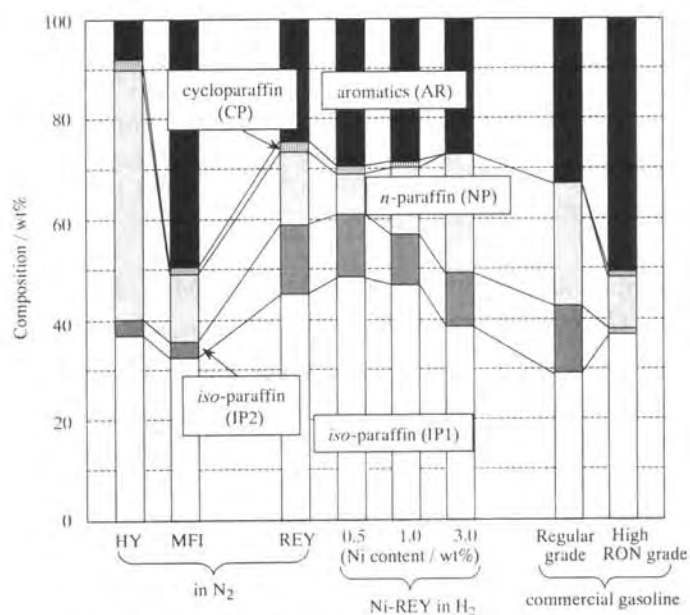


Fig. 3 Compositions of gasoline fraction produced by catalytic cracking over catalysts used. ( $T=673.2$  K,  $W/F=1$  h)

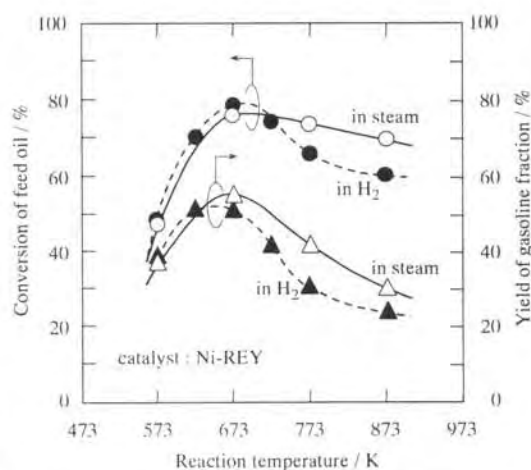


Fig. 4 Relations of conversion and gasoline yield to reaction temperature. ( $W/F=1$  h)

following two reasons: large pore diameters (0.74 nm) enabling for hydrocarbon to penetrate into, and the mild acid strength of the acid sites (active sites) of these catalysts to prevent excessive cracking.

Figure 3 represents the composition of the obtained gasoline, where IP1 denotes isoparaffins from C5 to C7, IP2 the total isoparaffins not including C5 to C7, CP the cycloparaffins, NP2 the *n*-paraffins without C5, and AR the total aromatics. Considering the RON number [8] and the air pollution problems, gasoline having large amount of IP1 and CP and small amount of NP2 and AR is preferable. Ni-REY and REY enable to produce gasolines suitable for such requirement.

#### Possibility for the usage of steam as the carrier gas.

Figure 4 shows the dependencies of the heavy oil conversion and the yield of gasoline on the reaction temperature in nitrogen and steam atmospheres for Ni-REY (Ni content: 0.5 wt%) at  $W/F=1$  h. Both of the conversion and the yield reached the maximum values at 673 K, and showed the higher values in steam atmosphere than in hydrogen due to the gasification of coke by the catalysis of Ni in steam atmosphere.

In order to confirm the long-term stability of Ni-REY, the sequence of reaction and regeneration were repeated. Reaction and regeneration were conducted at 673.2 K for 3 h in a steam atmosphere, and at 773.2 K for 3 h in an air stream, respectively. This experiment was also conducted using MFI type zeolite by changing carrier gas in the reaction from steam to nitrogen for comparison.

Figure 5 shows the changes in the strong acid amount of Ni-REY and MFI during the sequence of reaction and regeneration, where  $G/G_0$  is the ratio of the strong acid amount of the used catalyst to that of fresh one. Although the reaction was conducted in nitrogen stream for MFI, its acid amount gradually decreased due to the dealumination during the regeneration. It is evident that the stability of the acid sites of Ni-REY is higher than that of MFI type zeolite.

Figure 6 shows the changes in the conversion of heavy oil and the yields of gas, gasoline and coke for MFI type zeolite during the sequence of the reaction and regeneration. MFI type zeolite was gradually deactivated as the number of the sequence increased, due to the dealumination (see Fig. 5). Figure 7 shows the changes in the catalytic activity and the selectivity towards gasoline during the sequence of the reaction and the regeneration. Both of the conversion and the selectivity kept constant for Ni-REY and REY, indicating these catalysts were stable. To examine the stability of Ni in Ni-REY, the adsorption isotherms of  $H_2$  on Ni-

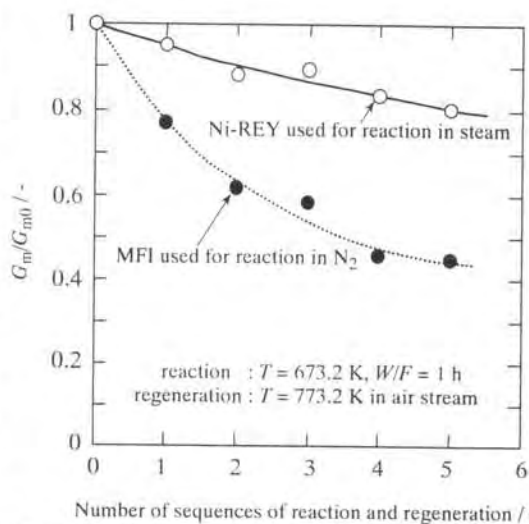


Fig. 5 Changes in the amount of strong acid sites of MFI type zeolite and Ni-REY during the sequence of the reaction and the regeneration.

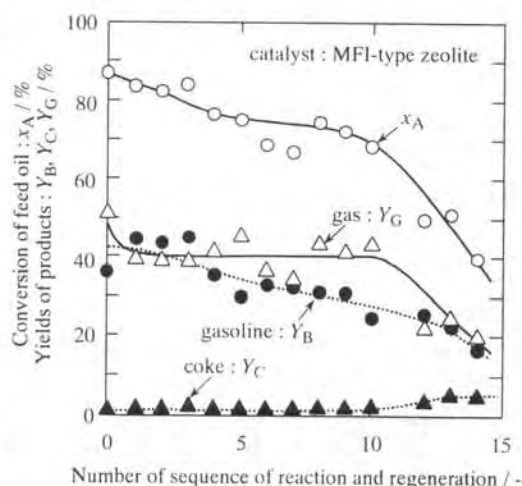


Fig. 6 Changes in catalytic activity of MFI type zeolite during the sequence of the reaction and the regeneration ( $T=673.2$  K,  $W/F=1$  h).

REY at 303.2 K below 10 torr were measured by a constant volumetric method before and after five repetitive sequences of reaction in a steam atmosphere and regeneration. The isotherms on REY were also measured. The difference between the isotherm of H<sub>2</sub> on Ni-REY and that on REY represents the amount adsorbed of H<sub>2</sub> on the surface of Ni, and was almost constant (1.13 mmol kg<sup>-1</sup>) before and after the sequences, indicating the high stability of Ni in Ni-REY during the sequences.

From the above discussions, it is confirmed that PE-derived heavy oil can be efficiently upgraded over Ni-REY in a steam atmosphere to useful fuels.

### Conclusion

Ni-REY catalyst showed high activity and selectivity towards gasoline for the catalytic cracking of heavy oil obtained from the waste polyethylene, even if the usage of steam as a carrier gas. The selectivity towards gasoline of Ni-REY was higher (78%) than that of MFI type zeolite (35%). Ni in Ni-REY was considered to act for the transportation of hydrogen atoms from steam to hydrocarbons. During the repetition of the sequence of the reaction and the regeneration, MFI zeolite was deactivated due to the dealumination, on the other hand, Ni-REY was found to show constant activity.

### Acknowledgement

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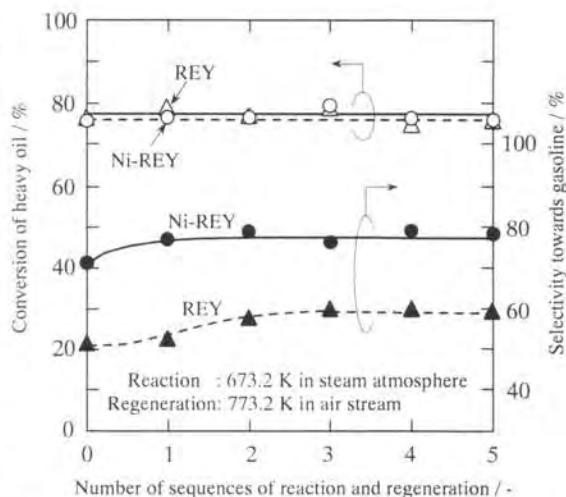


Fig. 7 Changes in catalytic activity of Ni-REY and REY catalysts during the sequence of the reaction and the regeneration.

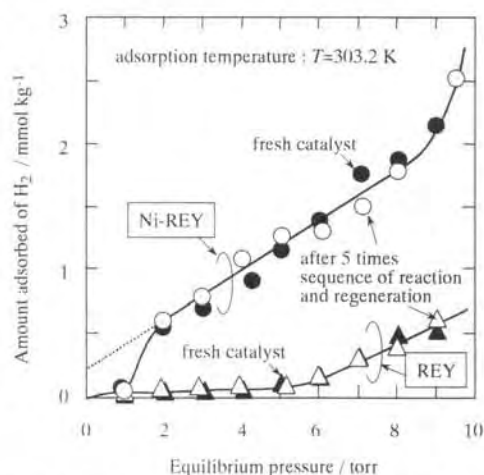


Fig. 8 Adsorption isotherms of H<sub>2</sub> on the used and the fresh catalysts for REY and Ni-REY.