Dealkylation of alkyl polycyclic aromatic hydrocarbons in vacuum gas oil

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Abstract: Dealkylation of hexadecylnaphthalene (HDN) proceeded in the practical vacuum gas oil (VGO) over a silica monolayer loaded on alumina as a solid acid catalyst after the removal of basic nitrogen-containing compounds by treatment with an acidic ion-exchange resin. Even after the treatment, the catalytic activity gradually decreased with time on stream. The initial activity was regenerated in a flow of oxygen at 773 K. On the other hand, the stability of conversion was enhanced with the reaction temperature, and the high selectivity and stability were observed at 723 K.

Keywords: dealkylation, alkyl polycyclic aromatic hydrocarbons, catalyst deactivation.

1. Introduction

VGO contains alkane, alkene and alkyl polycyclic aromatic hydrocarbons, with a small amount of nitrogen, sulfur and metal containing substances. We have found that dealkylation of alkyl polycyclic aromatic hydrocarbons over a silica monolayer loaded on alumina as s solid acid catalyst produced polycyclic aromatic hydrocarbons without side chains and alkanes with keeping chain length [1]. The polycyclic aromatic hydrocarbons can be converted into benzene derivatives, and the alkane can be utilized as diesel fuel. Therefore, this reaction can contribute the effective use of heavy oils.

However, in the presence of practical vacuum gas oil (VGO), basic nitrogen-containing compounds suppressed the catalytic activity. A method has been developed to adsorb the basic compounds using an acidic ion-exchange resin, Amberlyst-15 DRY®. The dealkylation was found to proceed at 673 K after the removal of basic substances[1], but still the catalyst degradation was observed. The purpose of this study is to find mechanism for deactivation of the catalyst and methods for the stabilization of catalyst activity. For the former, calcination in oxygen was tested, whereas for the latter, the influence of reaction temperature was studied in detail in the presence of practical VGO.

2. Experimental

The silica monolayer catalyst was prepared by a method of chemical vapor deposition on alumina, JRC-ALO-6 (Catalyst Society Reference Catalyst). After degassing the alumina in a glass vacuum line at 673 K, tetramethoxysilane [$Si(OCH_3)_4$] as a precursor of silica were introduced at 593 K. After the weight of solid reached to the objective value corresponding to full coverage by the silica monolayer, the sample was calcined in oxygen at 673 K [1].

VGO was obtained by vacuum distillation of crude oil up to 1008 K, was diluted with benzene for reducing the viscosity and mixed with HDN to form the reactant mixture with the composition VGO: HDN: benzene= 0.48: 0.048: 0.48, as weight ratio; evaluation of the reactivity was carried out to measure the conversion of HDN in the mixture. For removal of basic compounds, an acidic ion exchange resin, Amberlyst-15 DRY® which had been dried at 353 K overnight was added into the mixture (resin: mixture = 1: 10, as weight ratio). Then, the solution was stirred at room temperature for 4 h, and the resin was collected by filtration. These steps were repeated 3 times.

In the dealkylation of HDN, 0.21 g of the catalyst was packed in a fixed bed flow type apparatus, and the reactant mixture (1.2 g h^{-1}) was supplied with an H_2 stream (1 MPa, 50 mL min^{-1}) at 673-773 K. The liquid product was collected at 273 K and analyzed using a two-dimensional gas chromatograph equipped with a flame ionization type detector. Regeneration of the catalyst was carried out in a flow of O_2 (30 mL min^{-1}) at 773 K for 4 h. Then, the dealkylation reaction and catalyst regeneration ware repeated.

3. Results and discussion

As reported before[1], the dealkylation of HDN proceeded in the mixture of VGO, benzene and HDN after the treatment with Amberlyst-15 DRY to remove the basic contaminants. However, even in these conditions (673 K), the HDN conversion decreased with the time on stream (● in Figure 1). This is speculated to be due to the poisoning of active site by the compounds other than the basic substances which had presumably been removed by the ion exchange resin treatment. After calcination of the catalyst at 773 K in O_2, the HDN conversion was recovered, and the following dependence of activity on the time on stream was repeatedly observed. This demonstrates a way to recover the initial activity.

On the other hand, Figure 2 shows the influence of reaction temperature on the HDN conversion and its time course. The conversion was increased with the temperature, of course, and the stability of conversion was also improved. From the viewpoint of stability, thus, the high reaction temperature is favored, but the selectivity can be suppressed. Figure 3 shows the composition of outlet solution after the reaction at 8 h at each reaction temperature. The naphthalene yield increased with the temperature. Hexadecane yield at 723 K was higher than 673 K, but it decreased at 773 K. Simultaneously, considerable amount of light alkanes were observed, indicating that the undesired cracking of hexadecane proceeded at too high temperature.

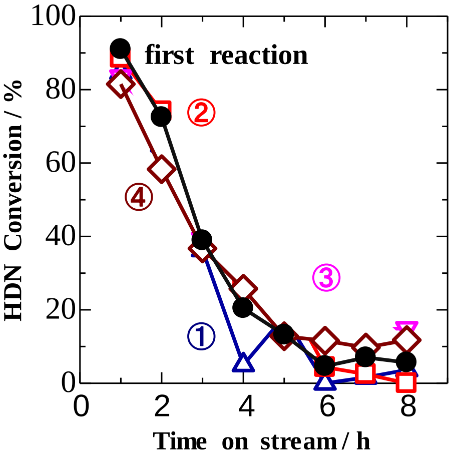

Figure 1. Time course of conversion of HDN in VGO at 673 K. The number in circle indicates the number of regeneration at 773 K.

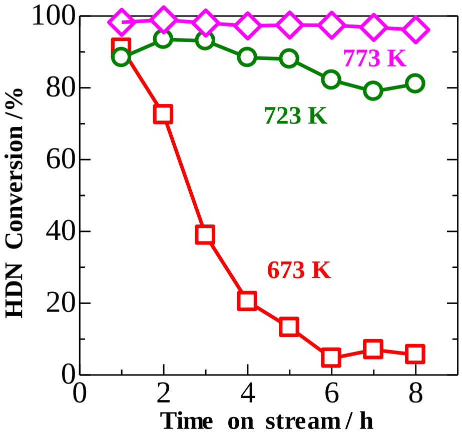

Figure 2. Time course of conversion of HDN in VGO at various temperatures.

4. Conclusions

Even after the removal of basic inhibitors, the deactivation of silica monolayer catalyst was observed during the dealkylation of alkyl polycyclic aromatic hydrocarbons in the feed of VGO at 673 K. The initial activity was regenerated by calcination in a flow of oxygen at 773 K. The stability of activity was enhanced by selecting >723 K of the reaction temperature, but undesired cracking of alkanes proceeded at 773 K. The stable catalytic activity and high selectivity were observed at 723 K.

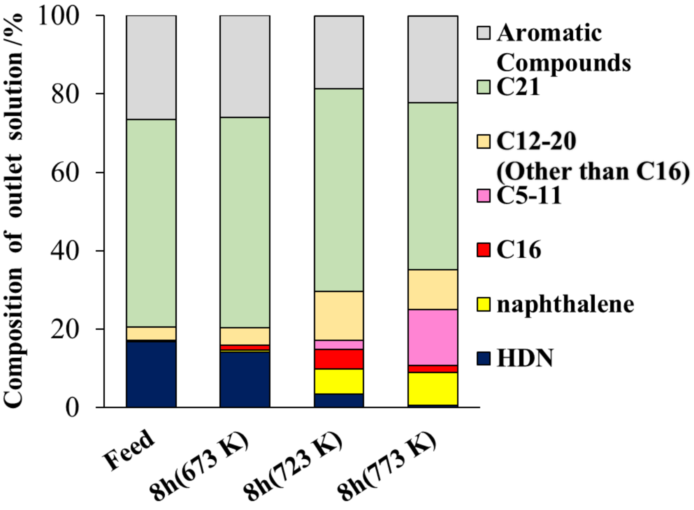

Figure 3. Composition of outlet solution obtained by dealkylation of HDN in VGO at various reaction temperatures.

References

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