

Kinetic study for burning regeneration of coked zeolites obtained by methylation of toluene

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Highlights

- Coke is mainly formed inside zeolite pore when coke loading is low.
- Reaction rate constant for carbon combustion was constant regardless of coke loading.
- Reaction rate constant for hydrogen combustion depended on coke loading.

1. Introduction

Zeolites are one of the important catalysts in the fields of petrochemicals and widely used for production of essential raw materials in industry. In contrast, during catalytic reaction of hydrocarbons over zeolite, carbonaceous compounds (i.e., coke) formed on the catalyst. Coke formation decreased their activity due to corruption of active site and/or pore blocking of zeolite. In general, coke combustion is carried out for regeneration of the catalyst. In contrast, coke combustion produces steam by oxygenation of hydrogen in coke and temperature of catalyst bed become high because the reaction is exothermic reaction. It is well known that dealumination of zeolite easily occurs under hydrothermal atmosphere at high temperature [1], which leads to permanent degradation of zeolite. So, information concerning reaction rate of coke combustion is required for design of the regeneration process. The main purpose of this study is to clarify the effect of location of coke formed on zeolite and zeolite structure on reaction rate of coke combustion. In this study, ZSM-5 and beta zeolite with different coke loading was prepared by methylation of toluene, and location and structure of coke formed during the reaction was evaluated. In addition, kinetic results of burning regeneration of coked zeolite were analyzed.

2. Experimental

Coked ZSM-5 and beta were prepared by methylation of toluene using a fixed bed flow reactor. The temperature of the reaction was 723 K. The mass ratios of the coke to the zeolites were varied between 1.5% and 18.2 % by changing the reaction time from 30 to 390 min. Nitrogen adsorption/desorption isotherms of coked zeolites were measured for estimation of micropore volume of the coked zeolites.

Kinetic analyses for combustion of coke formed on zeolites were carried out using the multiple reaction model developed in the previous study [2]. The transient changes in the overall conversion (X_t) of coke were calculated from the decrease in weight of the coked zeolite under a stream of air diluted with nitrogen (oxygen partial pressure: 12.8 kPa) in the temperature range from 823 to 873 K. The weight change of coked zeolite was measured by thermo gravimetric analysis. By the parameter fitting of overall conversion of coke using theoretical equation, rate constant of the combustion of carbon and hydrogen in coke were estimated.

3. Results and discussion

Fig. 1 shows relationship between coke loading and micropore volume of coked zeolites. The broken line indicates calculated micropore volume of coked zeolite if all of coke is formed inside the zeolite pore. The micropore volume of coked zeolite monotonously decreased with increasing coke loading below 4 wt% for ZSM-5 and below 11 wt% for beta zeolite, and measured micropore volume of coked zeolite showed almost the same value with the calculated value. In contrast, micropore volume of coked zeolite with coke loading above 4 wt% for ZSM-5 and above 11 wt% for beta zeolite showed higher value as compared with the calculated value. It is considered that these results indicate coke is mainly formed inside pore of zeolite in the

low coke loading region and coke formation and growth mainly occurs on outer surface in high coke loading region.

Fig.2 shows Arrhenius plots of the rate constant of carbon and hydrogen combustion in coke obtained from burning regeneration using coked ZSM-5 (coke loading: 8.4 wt%). The activation energies of the rate constants for carbon and hydrogen were 156 kJ/mol and 140 kJ/mol, respectively. The values are nearly equal to the value obtained in the previous report [3]. In addition, as not shown here, the activation energies of the rate constants for carbon and hydrogen showed almost the same value regardless of coke loadings.

Fig.3 shows the effect of the coke loading on the frequency factors of the rate constants of carbon and hydrogen in coke formed on ZSM-5 and beta zeolite. The frequency factors for carbon were constant regardless of the coke loading for each zeolite. In the case of ZSM-5, frequency factors for hydrogen combustion rate constant with coke loading below 8.4 wt% showed constant value. In contrast, frequency factor for hydrogen combustion rate constant with coke loading above 8.4 wt% decreased with increasing coke loading. In addition, coked beta zeolite also showed same tendency. The rate constant for hydrogen (k_{HS}/r_0) depended on the particle size of coke because the rate constant for hydrogen is expressed in terms of the coke particle (r_0). In the low coke loading region, coke particle size was considered to be limited by pore structure because coke is mainly formed inside the pore of zeolite. In contrast, coke particle was considered to be mainly formed and grown on outer surface of zeolite. So, growth of coke particle led to the decrease in rate constant of hydrogen.

4. Conclusions

Reaction rate constant for carbon combustion showed constant value regardless of coke loading. In contrast, reaction rate constant for hydrogen depended on coke loading due to coke growth in high coke loading region. Mechanism for coke formation and coke combustion is considered to be same regardless of zeolite structure.

References

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Keywords

Coke combustion; Kinetics; ZSM-5; beta.

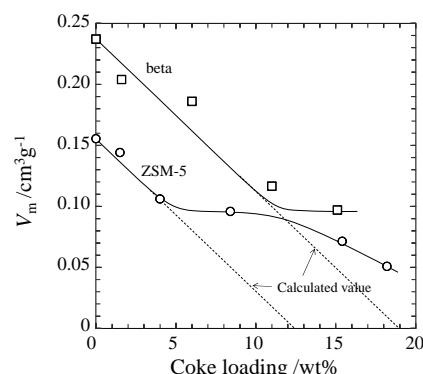


Figure 1. Effect of coke loading on micropore volume of coked zeolites.

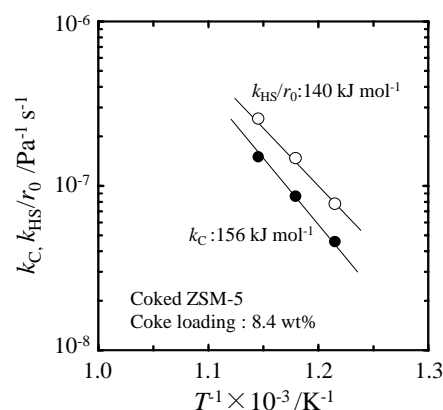


Figure 2. Arrhenius plots of reaction rate constant for carbon and hydrogen combustion.

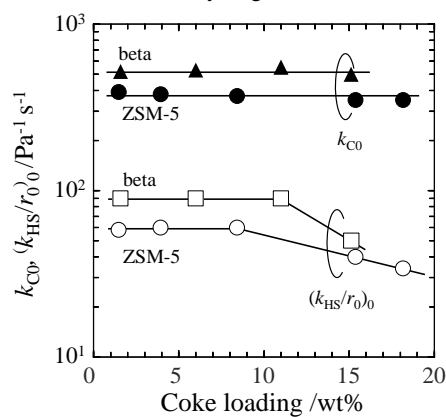


Figure 3. Effect of coke loading on the frequency factor of reaction rate constant for carbon and hydrogen combustion.