Non-parametric analysis of active sites distribution of nitrided Mo/Al$_2$O$_3$ catalyst during carbazole HDN

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Introduction

The deactivation behavior of CoMo and NiMo catalysts during deep hydrodesulfurization (HDS) of gas oils owing to poisoning of nitrogen compounds has been extensively studied. The kinetics of hydrodenitrogenation (HDN) of carbazole over nitrided Mo/Al$_2$O$_3$ catalysts has two types of active sites one of which was quickly hydrogenated and the other denitrogenated with difficulty [1-3]. A kinetic model of the catalyst deactivation during the carbazole HDN was studied for the sulfided and nitrided molybdena-alumina catalysts. The kinetics of HDN of perhydrocarbazole on the Mo/Al$_2$O$_3$ nitrided at 723 K was observed to obtain rate expression of the Langmuir-Hinshelwood type for C-N hydrogenolysis in which it was the rate–determining step with equilibrium of the hydrogenation: the adsorption of perhydrocarbazole on one kind of catalytic site and of hydrogen on another. A nonparametric technique for the elucidation of the heterogeneity of a surface is available that can distinguish different sites during a reaction. The adsorbed reactant species react at different rates, the total measured rate of the reaction is the sum of the separate rates, and then the overall function of the rate versus time contains information describing the distribution of the activity of the surface sites. The numerical method applied to a Fredholm integral equation of the first kind [4-7], $r(t) = \int h(t,k) \cdot f(k) dk$, where $r(t)$ is normalized data of the reaction rate, $(f(k))$ is a activity distribution (rate constant), and $(h(t,k))$ is a kernel, in our case, the change in the concentration of strength of active species on the catalyst surface. The active site on the catalyst obeys (i) first-order kinetics and these sites work in (ii) parallel and (iii) independently. de Pontes et al. [5] and Hoost and Goodwin [6] studied isotopic transients during the methanation reaction and assumed the equation. In a previous paper [7], the non-parametric determination of the activity distribution of the catalytic sites on a sulfided 12.5% Mo/Al$_2$O$_3$ catalyst during the HDS of dibenzothiophene was studied. The equation was described as the Fredholm integral equation of the first kind.The distinct patterns supported the fact that two active sites with different rate constants imposed the C–S hydrogenolysis and hydrogenation of dibenzothiophene on the sulfided 12.5% Mo/Al$_2$O$_3$ catalysts. In this study, the activity distribution of active sites on the nitrided 12.5% Mo/Al$_2$O$_3$ catalyst during carbazole HDN was nonparametrically determined and examined. .

Experimental and Calculation method

A 12.5% Mo/Al$_2$O$_3$ catalyst was prepared using a mixture of ammonium paramolybdate and γ-alumina, calcined in air at 823 K for 3 h, and 12.5% MoO$_3$/Al$_2$O$_3$ was nitrided by a temperature-programmed synthesis with ammonia. The catalysts was treated in flowing ammonia at 49.6 μmol s^{-1} at a rate of 0.0167 K s^{-1} from 573 K to a final temperature (773, 973, or1173 K), held at that temperature for 3 h, and then cooled to room temperature in flowing NH$_3$. The HDN of carbazole on the nitrided catalyst was carried out at 573 K and a total pressure of 10.1 MPa using a fixed-bed microreactor in a high-pressure flow system. The liquid feed, consisting of 13.6 mmol L^{-1} carbazole in xylene, was introduced into the reactor at 5.56 μL s^{-1} with a hydrogen flow of 74.4 μmol s^{-1}. The HDN rate was calculated, based on the moles of carbazole converted at 573 K. The equation was programmed in C using a PC station, according to the algorithm for the implementation of the computational procedure.

Results and Discussion

In order to distinguish the active sites with the different catalytic reactivity is measured by the rate, $r(t)$, carbazole HDN over the nitrided 12.5% Mo/Al$_2$O$_3$ catalyst. For the distribution of the surface active site (Site II) of the 773 K-nitrided catalyst, two peaks are deconvoluted: the distribution (x_2) is 0.547 at a k_2 of 0.56 h^{-1}, and the distribution (x_1) of the surface active site (Site I) is 0.831 below the k_1 value of 0.19 h^{-1} (the average of 0.1 h^{-1}). The 773 K-nitrided Mo catalyst contained two distributions of the active sites; the one type of 12 times stronger active site was distributed at 39.7%, while the other type of weaker active site was distributed at 60.3 %. The strength of the active site (k_2) decreased with the increasing nitridation temperature. In the case of $h(t,k) = \exp(-kt)$ for the 873 K-nitrided catalyst, at k_2=0.896 h^{-1} (rate coefficient), the activity distribution of the surface site (Site II) is 0.956 and below k_2 = 0.22, the distribution is 0.470. The 973 K-nitrided catalyst is distributed at 24.5 % below the k_1 value of 0.20 h^{-1} (the average 0.1 h^{-1}) and is at 75.5 % at the k_2 value of 1.08 h^{-1}. Thus, the two distinct distributions support the fact that two active sites with the 10-20 times strength are present at 39.7-75.5 %, respectively, on the Mo nitride catalysts for the carbazole HDN. Thus, the two distinct distributions support that two active sites with different activities are present on the nitrided 12.5% Mo/Al$_2$O$_3$ catalysts for the carbazole HDN. The distributions of the rate constant of active sites during the carbazole HDN on three Mo nitride catalysts for $h(t,k)$ of $1/(1+kt)$ are also discussed.

Conclusion

The nonparametric determination of the activity distribution of the active sites is applied to the kinetics of the rate of carbazole HDN on the nitrided Mo/Al$_2$O$_3$ catalysts. The equation for carbazole HDN was described as a Fredholm integral equation of the first kind, $r(t) = \int h(t,k) \cdot f(k) dk$, where $r(t)$ is the rate of the HDN reaction, $h(t, k)$ is a kernel of $\exp(-kt)$, and $f(k)$ is the distribution of reactivity of the adsorbed species on the surface sites, i.e., the distribution of activity of the catalytic sites. The two distinct distributions support that two active sites with different activities are present on the nitrided 12.5% Mo/Al$_2$O$_3$ catalyst for the carbazole HDN.

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