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Full Length Article

High-selective-hydrogenation activity of W/Beta catalyst in hydrocracking of 1-methylnaphalene to benzene, toluene and xylene

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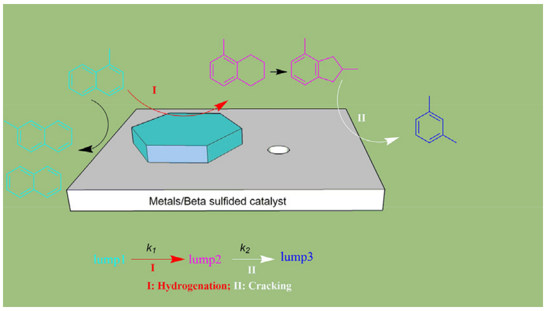
GRAPHICAL ABSTRACT



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ABSTRACT

Hydrocracking of 1-methylnaphthalene to light aromatic hydrocarbons, such as benzene (B), toluene (T) and xylene (X), at 420 °C and 6 MPa was studied over a series of sulfided Metals/Beta catalysts (Metals = NiMo, NiW, CoMo, CoW, Mo, W). Based on reaction results, a six-lump reaction kinetic model was proposed and a mathematic kinetic model was established which agreed well with the experimental data. All the kinetic constants of every step reaction in the reaction model were obtained. Hydrogenation activity of catalysts not only be affected by metal species and their contents, but also be influenced by metal-zeolite interaction. Strong acidity resulting strong interaction between acid centers and metal centers decreased the hydrogenation activity of catalysts. When the amount of loaded metal oxides increases, the Brönsted acid concentration of zeolite decreases. Selective-hydrogenation activity is a key factor to BTX yield and W-based catalysts showed higher selective hydrogenation activity than other catalysts. Both experiments and the kinetic model showed that 25W/Beta catalyst had the highest BTX yield (53 wt%), attributed to its relatively high selective-hydrogenation activity of W and suitable metal-zeolite interaction.

1. Introduction

Light cycle oil (LCO, in diesel boiling point range), mainly composed of bicyclic aromatic hydrocarbons, is produced in large scale through the fluid catalytic cracking (FCC) process [1]. Due to its high aromatic hydrocarbons content, LCO cannot be blended directly into diesel pools but can be used as a blend-stock in heavy fuel oil for viscosity adjustment. Since the market demands for heavy fuel oil and

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Nomenclature

F_{10}	Molar flow rate of 1-methylnaphthalene fed to reactor, mol/h
F_j	Molar flow rate of lump *j*, mol/h
F_T	Total molar flow rate of all reactants, mol/h
F_H	Molar flow rate of hydrogen, mol/h
G_{10}	Mass flow rate of 1-methylnaphthalene which is fed to reactor, g/h
M_1	Relative molecular mass of 1-methylnaphthalene, g/mol
T	Space time, h
r_j	Reaction rate of formation of lump *j*, mol/g·h
ν	The stoichiometric efficient

k_i	Reaction rate constant in reaction number *i*, m^3/g·h
C_j	Concentration of lump *j*, m^3/g·h
C_{T0}	Concentration of total reactants which is fed to reactor, mol/m^3
Y_j	Defined as F_j/F_{10}
Y_H	Defined as F_H/F_{10}
N_{exp}	Number of experiments
PleaseCheck	Concentration of toluene which is fed to reactor, mol/m^3
M_1'	Relative molecular mass of toluene, g/mol
k_i'	Reaction rate constant of reaction i',m^3/g·h
Y_j'	Y_j' defined as F'_j/F'_{10}, $j = 1,2,3$

diesel decrease steadily in recent years, it is highly desirable to convert bicyclic aromatic hydrocarbons in the LCO into high-value products, i.e., monocyclic aromatic hydrocarbons such as benzene (B), toluene (T) and xylene (X), because the demands for them are steadily increasing [2,3].

To produce BTX, one aromatic ring in the bicyclic aromatic hydrocarbons must be selectively opened to form one phenyl ring with alkyl chains (Scheme 1). Selective hydrogenation (HYD) and hydrocracking (HC) are common ring opening reactions used for effective conversion of the bicyclic aromatic hydrocarbons to monocyclic aromatics [2]. And, bi-functional catalysts such as metals supported on acid catalysts have mostly been applied [4,5]. To achieve high selectivity of monocyclic aromatic, high selective hydrogenation activity is inevitable which only accelerates part hydrogenation of bicyclic aromatic, and suitable acidity is also indispensable which promotes the β-scission of alkylbenzene to BTX.

Recently, transition metals and Beta zeolite are widely used in hydrocracking reaction, attribute to their high hydrogenation activity, peculiar pore structure and suitable acidity [6–8]. Numerous efforts have been made to further improve the selectivity of BTX. Such as, modification of supports [8–11], controlling of metal: acid ratio [12–14] and metal-acid proximity [15,16]. Lee et al. [3] studied the morphology effect of Beta zeolite and found that Ni_2P/nano-sized Beta showed superior activity in both hydrogenation and cracking activity than Ni_2P/micrometer-sized Beta. Kim et al. [17] suggested that sylylated Beta zeolite can encourage the maximum conversion and selective ring opening yield due to optimal balance of metallic and acidic function.

It is widely accepted that the comprehension of inherent correlation between catalyst characteristics and reaction selectivity is essential to design high selective catalyst. However, there is no paper clearly clarifying that relationship because of the high complexity of the LCO hydrocracking and interaction between two catalytic centers [18]. For example, high hydrogenation activity can promote the conversion of bicyclic aromatic hydrocarbons but also reinforce the saturation of monocyclic aromatics (decrease the selectivity of BTX). And the selectivity of BTX cannot reflect the selective hydrogenation activity of catalyst because acidic supports also take an important part in hydrocracking process. Excessive loaded metals can decrease the strength and number of acid sites, especially for Brönsted acid sites, which are necessary for selective ring opening. Meanwhile, excessively acid sites could lead to the serious secondary cracking [19,20]. The metal-support interaction also affects the degree of reduction of the metal and then influences the activity of catalyst in hydrogenation reactions [6,21,22]. Up to now investigators have not developed a credible method to quantitatively evaluate the balance of hydrogenation and cracking activity.

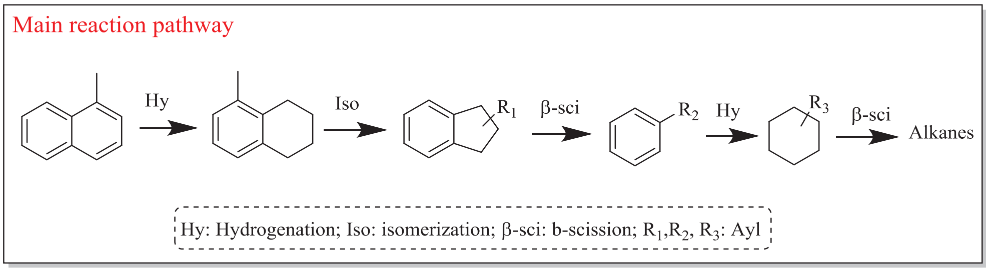
Kinetic study is useful in understanding of the reaction mechanism and in comparing the activities of different catalysts, whereas kinetic study of hydrocracking reaction catalyzed by a catalyst with high acidity is rarely reported. Therefore, it is needed to establish the kinetic model of the hydrocracking process of bicyclic aromatic hydrocarbons, because it is useful for quantitative evaluation of the functions of the metallic catalytic sites and the acid catalytic sites in the hydrocracking process, and it can be used to guide the preparation of good selective LCO hydrocracking catalysts.

In this work, hydrocracking of 1-methylnaphalene (1-MN) was used as the probe reaction for the hydrocracking of bicyclic aromatic hydrocarbons, and was performed in a fixed-bed reactor using a series of transition metals/zeolite as the bi-functional catalysts. A reaction model and the corresponding mathematical kinetics model were proposed. And the effects of transition metal and zeolite support on the selective hydrocracking of bicyclic aromatic hydrocarbons were investigated by the means of kinetic model's parameters.

2. Experimental

2.1. Catalyst preparation

Zeolite Beta with different SiO_2/Al_2O_3 ratios was prepared by the method reported in literature [23]. Typically, silica gel (98 wt% SiO_2, Qingdao Chemical Reagent Co., Ltd.), sodium hydroxide (NaOH), sodium aluminate ($NaAlO_2$) were used as silicon, alkaline and aluminum sources respectively. First, 3.00 g tetraethylammonium hydroxide and 0.70 g NaOH were dissolved in 12.00 g H_2O, and then stirred for a while to form a clear solution. Next, 0.37 g $NaAlO_2$ was added and stirred for



Scheme 1. The main reaction pathway of hydrocracking of 1-methylnaphalene.