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「課程博士用」

学 位 論 文 の 要 旨

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学位論文題目	Development of HZSM-5-based catalysts for in-situ catalytic upgrading of bio-oil derived from fast pyrolysis of biomass（バイオマスの高速熱分解に由来するバイオオイルのその場アップグレードのための HZSM-5 ベース触媒の開発）		

学位論文要旨

Fast pyrolysis of biomass to produce bio-oils has attracted great attention because it is an effective technology to convert most of biomass components directly into liquid fuel. However, the bio-oils obtained from the pyrolysis process always have highly complex oxygenated compounds with high viscosity, serious corrosivity, and rather instability. Thus, before the raw bio-oils are used as fuel or chemical feedstock, they must be upgraded, especially deoxygenated. Cracking of bio-oils over protonated zeolites such as HY, H-Beta, H-ferrierite and HZSM-5 at ambient pressure could be an effective way for the bio-oil upgrading, in which hydrogen gas is not necessary. Especially, among various protonated zeolites, HZSM-5 has been considered the most effective one in the deoxygenation of bio-oils with more aromatic species in the upgraded bio-oils. However, HZSM-5 itself is limited by low mass-transfer rates of large reactants as well as products due to its micropore structure. During the deoxygenation process, the easy blockage of open micropores always leads to the sharp catalyst deactivation. To deal with this issue, three main strategies could be applied. First one is metal modification, which is a facile method to optimize the acidity of the HZSM-5 for the promoting of deoxygenation and meanwhile, the reducing of the further reactions to form coke on the catalyst and thereby slowing down the catalyst deactivation rate. However, this method cannot reduce the diffusion limitation of the micropores in the zeolites. Thus, the second strategy, i.e., construction of HZSM-5 with a hierarchical structure, could solve diffusion limitations. The third one is the synthesis of special ZSM-5 morphologies such as HZSM-5 catalysts with hollow structure or core/shell structure. In this dissertation, the above three strategies were used for the preparation of HZSM-5-based zeolite catalysts for the in-situ upgrading of bio-oils derived from the fast pyrolysis of biomass. While, the mechanisms influencing catalytic performance and catalyst preparation were proposed and discussed. The main conclusions are summarized as follows:

(1) A study on in-situ upgrading of bio-oil from the fast pyrolysis of biomass over Cu/ZSM-5 prepared using the wet impregnation method. It is found that Cu/HZSM-5 with low Cu loading amounts preserved HZSM-5 crystalline structure as well as its acid sites and provided the best textural properties which enhanced deoxygenation performance. 0.5 wt.% Cu/ZSM-5 exhibited the best catalytic performance with a high relative amount of aromatic hydrocarbons of 73.2 % and a yield of specific aromatic hydrocarbons as high as 56.5 mg/g-biomass (d.a.f), which were much higher than those based on the parent HZSM-5. Moreover, the 0.5 wt.% Cu loaded HZSM-5 catalyst also showed excellent catalytic reusability and regeneration property.

(2) Hierarchical structured HZSM-5 catalysts were synthesized by desilication of commercial HZSM-5 in aqueous NaOH solution with the assistance of tetrapropylammonium

hydroxides (TPAOH) and applied for upgrading of bio-oil derived from fast pyrolysis of biomass. In comparison to traditional HZSM-5 and those hierarchical structured HZSM-5 zeolite catalysts prepared under other conditions, the hierarchical HZSM-5 prepared by using concentrations of 0.2 M NaOH with 0.25 M TPAOH showed the maximum catalytic performance, resulting in the highest production of aromatic hydrocarbons. With the help of a small amount of TPAOH, the formation of mesopores can be highly controlled, resulting in more surface area and suitable acid content. However, the coke generated on the catalyst surface led to the deactivation of catalysts. To solve this issue, hierarchical HZSM-5 zeolite catalysts were modified by various metals with different loading amounts. It was found that 0.25 wt.% Cu loaded hierarchical HZSM-5 further increased the yield of aromatic hydrocarbons with reduced coke formation.

(3) To further improve the catalytic performance, HZSM-5 zeolites with hollow structure were prepared by using the hydrothermal method. In the presence of tetrapropylammonium hydroxide (TPAOH), it was found that the obtained hollow HZSM-5 zeolite catalyst had a mesoporous shell. When the optimum catalyst was used for the upgrading of bio-oils derived from the fast pyrolysis of cellulose and hemicellulose, aromatic hydrocarbon yields of 78.49–78.67 % were achieved, which were much higher than the case using traditional HZSM-5 (61.06–68.26 %). Moreover, when real biomass (cedar) with an optimum biomass/catalyst weight ratio of 1:2 was used, the yield of aromatic hydrocarbons was up to 80.16%. In addition, this catalyst also exhibited excellent reusability and regeneration properties.

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