优秀博士学位论文摘要

微波辐射下耐硫型 Pd 催化剂的可控制备及在一步法合成二甲醚中的应用

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摘　要:针对合成气一步法制取二甲醚(Syngas to Dimethyl ether,STD)工艺的研究现状,采用微波技术开发了具有较好耐硫效果的 Pd 系二甲醚合成催化剂,具体从以下 3 方面进行了研究开发:

首先,进行了 Pd 系 STD 反应催化剂制备研究。分别以 $\gamma-Al_2O_3$、HZSM-5 和 Al-MCM-41 为载体,采用浸渍法制备了 3 个系列负载型 Pd 金属催化剂,通过调控焙烧条件、Pd 负载量、助剂类型和复合方式及助剂添加量等实现了对催化剂表面的物相及吸附特性、还原特性、表面酸性等性能的控制,探讨了催化剂 STD 反应活性与样品本身所固有特性的关系。

其次,进行了 Pd 系催化剂耐硫机理研究。以 H_2S 和噻吩为探针毒物研究硫中毒实验和再生实验后 Pd 催化剂用于 STD 反应性能,考察了催化剂载体和助剂类型对 Pd 催化剂耐硫性能的影响,运用多种表征手段对催化剂的物性结构和反应物化学结构进行表征,分别揭示了 Pd 金属表面和酸中心上的硫化物吸附形态和吸附特点;利用 GC-MS 分析确定有机硫和无机硫毒物在 $CeO_2-CaO-Pd/HZSM-5$ 催化剂表面的吸附位置,并推测出其表面的硫化物转化机理。

最后,对 $CeO_2-CaO-Pd/HZSM-5$ 催化剂的 STD 反应动力学进行了研究。选取 STD 反应活性和耐硫性能优异的 $CeO_2-CaO-Pd/HZSM-5$ 催化剂进行 STD 反应工艺条件研究,确定了优化工艺条件;在此基础上,建立 $CeO_2-CaO-Pd/HZSM-5$ 双功能催化剂颗粒的动力学方程,统计检验显示该模型可靠,模型计算值与实验值吻合良好。

关键词:二甲醚;STD;微波;耐硫;Pd 金属;固体酸;合成气

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Controllable preparation of sulfur-tolerant Pd catalysts under microwave irradiation and application of these catalystsin one-step synthesis of dimethyl ether

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Abstract: According to the development of the direct syngas to DME (STD) technology, in this work, the hybrid catalyst preparation of Palladiuman (Pd) metal-supportfor DME synthesis by microwave technology was studied and developed, which has a good effect of sulfur tolerance. All research was divided into following three sections.

Firstly, Pd metal-support catalystfor STD reaction was researched. Three series of Palladiuman catalysts supported on different carriers, $\gamma-Al_2O_3$, HZSM-5 and Al-MCM-41respectively, were prepared by impregnation. The properties of catalysts, such as surface phase structure and adsorption, reduction properties, surface acidity were controlled by changing calcination condition, Pd loading, or single and binary promoters and its added amount. The relationship between STD reactivity and the intrinsic characteristics of the catalyst were investigated.

Secondly, the sulfur-tolerant mechanism of Pd catalysts was researched. The STD activity of catalysts after the process ofsulfur poisoning with H_2S or thiophene and regeneration with syngas was investigated, the influence of carriers type and promoters type on thecatalysts' sulfur tolerance was analysis, the catalysts' structure and the reactants' chemical structureswere characterized based on various characterizations, and then the adsorption patterns and characteristics of sulfide on Pd metal active sides and acid active sides were revealed. Adsorption position of organic sulfur poisons and inorganic sulfur poisons on in $CeO_2-CaO-Pd/HZSM-5$ catalyst was determined based on GC-MS, and thepossibletransformation mechanism of sulfides on catalyst were suggested.

Finally, the kinetics of STD reaction over $CeO_2-CaO-Pd/HZSM-5$ catalyst was researched. Because owing togood STD reactivity and sulfur tolerant, STD process conditions over $CeO_2-CaO-Pd/HZSM-5$catalyst was further studied. The kinetic equations for STD reaction over $CeO_2-CaO-Pd/HZSM-5$ catalyst in a fixed-bed reactor within the process conditions above were established. Statistical test shows the data calculated by the mechanism models are consistent with the experiments, so these modelsare reliable.

Key words: dimethyl ether; STD; microwave; sulfur tolerance; Pd; solid acid; syngas