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论文

Cu(Ⅰ)/SO_4^{2-}/ZnO和Cu(Ⅰ)/$S_2O_8^{2-}$/ZnO催化剂的制备与表征

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摘要:

采用浸渍法对无定形ZnO分别用稀H_2SO_4和$(NH_4)_2S_2O_8$溶液处理, 制备了SO_4^{2-}/ZnO和$S_2O_8^{2-}$/ZnO固体酸. 通过固体离子交换法制备了Cu(Ⅰ)/SO_4^{2-}/ZnO和Cu(Ⅰ)/$S_2O_8^{2-}$/ZnO两种催化剂, 并采用XRD, FTIR, TPD和TPR等进行了表征. 研究结果表明, 用稀H_2SO_4和$(NH_4)_2S_2O_8$溶液分别浸渍处理无定形ZnO, 经过500-600 ℃高温焙烧后得到的SO_4^{2-}/ZnO和$S_2O_8^{2-}$/ZnO固体酸表面形成了$Zn_3O(SO_4)_2$物种; py-FTIR结果表明, 两者均具有B酸中心和L酸中心; 进一步的NH_3-TPD研究结果证明, 制备的固体酸NH_3脱附峰均出现在543 ℃附近, 属于高强度固体酸. 结构分析认为, 由于SO_4^{2-}强烈的电子诱导作用, SO_4^{2-}和ZnO形成的桥式配位物种产生了B酸中心和L酸中心, 而其螯合配位形成的物种没有酸性. SO_4^{2-}/ZnO和$S_2O_8^{2-}$/ZnO固体酸与CuCl进行离子交换所制备的Cu(Ⅰ)/SO_4^{2-}/ZnO和Cu(Ⅰ)/$S_2O_8^{2-}$/ZnO催化剂的Cu(Ⅰ)易于还原, 对甲醇氧化羰基化合成碳酸二甲酯(DMC)表现出较高的活性和选择性, DMC选择性为98.3%, 时空收率可达到1.9 g(g·h).

关键词: 固体酸 多相催化 铜催化剂 氧化锌 固体离子交换

Preparation and Characterization of Cu(Ⅰ)/SO_4^{2-}/ZnO and Cu(Ⅰ)/$S_2O_8^{2-}$/ZnO Catalysts

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Abstract:

Two novel solid acids of SO_4^{2-}/ZnO and $S_2O_8^{2-}$/ZnO were prepared by impregnating H_2SO_4, $(NH_4)_2S_2O_8$ solution respectively on amorphous zinc oxide and calcining at 500—600 ℃, and then used as carriers to prepare Cu(Ⅰ)/SO_4^{2-}/ZnO and Cu(Ⅰ)/$S_2O_8^{2-}$/ZnO catalysts *via* solid-state ion-exchange. The solid acids and catalysts were characterized by XRD, FTIR, TPD and TPR. It is observed that $Zn_3O(SO_4)_2$ was formed during the preparation of the solid acids, and both of Lewis and Br nsted acid sites were formed on SO_4^{2-}/ZnO and $S_2O_8^{2-}$/ZnO. NH_3-TPD shows that both SO_4^{2-}/ZnO and $S_2O_8^{2-}$/ZnO were very strong solid acids because the temperature of NH_3 desorption peaks were above 543 ℃. It is suggested by molecule structure analysis that the form of acid sites is due to the strongly electronic inductive effect of SO_4^{2-}, the bridge-coordination complex of ZnO and SO_4^{2-} causes the formation of Brønsted and Lewis acid sites on the surface, but the chelate-coordination complex of ZnO and SO_4^{2-} has not any contribution to acid sites. Prepared by solid-state ion-exchange with the solid acids and CuCl at high temperature in N_2 follow, Cu(Ⅰ)/SO_4^{2-}/ZnO and Cu(Ⅰ)/$S_2O_8^{2-}$/ZnO catalysts, in which Cu(Ⅰ) was easy to be reduced, showed an excellent catalytic behavior in the oxidative carbonylation of methanol to dimethyl carbonate(DMC). Both of the catalysts showed high catalytic activity and selectivity: 98.13% selectivity of DMC based on methanol and 1.87 g/(g·h) space-time yield, respectively.

Keywords: Solid acid Heterogeneous catalysis Copper-based catalyst Zinc oxide Solid-state ion-exchange

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