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硕士学位论文

负载型磷化物催化剂的制备及其在生物质加氢脱
氧中的应用

Perparation of supported phosphide
catalysts and theirs application in biomass
hydrodeoxygenation

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摘要

生物质能因其原料存储丰富，可再生等优势可作为很好的替代能源。但生物质存在大量含氧化合物，极大的影响了热稳定性，限制了其广泛应用。因此需对生物质进行加氢精制处理。过渡金属磷化物催化剂因其具有良好的加氢脱氧性能，近几年来受到广泛关注和研究。

本论文采用溶胶凝胶法和柠檬酸凝胶法分别制备Pd@Ni₂P/SiO₂和FeMoP/SiO₂催化剂。通过CO化学吸附、XRD、XPS、NH₃-TPD、STEM等表征对催化剂进行分析，考察了Pd@Ni₂P/SiO₂和FeMoP/SiO₂催化剂对苯酚加氢脱氧以及丙三醇氢解反应的催化性能。

研究表明，Pd@Ni₂P/SiO₂催化剂颗粒分散均匀 (6.75 ± 1.54 nm)。由于Pd粒子的存在使形成Ni₂P的还原温度降低约200℃。并且Pd和Ni $\delta^+(0 < \delta < 2)$ 物种属于金属活性位点和酸中心，促进C-O键的断裂，使苯酚的转化率和环己烷的选择性更高。而Pd $\delta^-(0 < \delta < 1)$ 物种的存在使电子能够充分迁移，使催化剂表面H₂解离促进加氢反应，使得苯酚转化率比单纯Ni₂P/SiO₂高。在453 K和493 K，氢压为2.0 MPa时具有很好的苯酚HDO活性，两者转化率都在95%以上，主要产物分别为环己醇（65%），环己烷（95%）。

与传统的程序升温还原(TPR)法制备的催化剂相比，柠檬酸凝胶法制备出来的FeMo(1)P催化剂粒子分散均匀 (3.34 ± 0.77 nm)。Fe、Mo共存影响催化剂粒子的分散性。研究表明，FeMo(x)P催化剂中的金属中心 (Fe δ^+ 和Mo⁵⁺)同时具有金属活性和酸性中心功能促进C-O键的断裂和加氢反应的进行，并影响产物选择性的分布。Pd $\delta^-(0 < \delta < 1)$ 物种的存在促进金属与P之间电子的充分转移，使得金属活性位点和Pd δ^- 物种之间起到协同作用促进加氢反应的进行。结合XPS，NH₃-TPD和TEM结果可知，FeMo(x)P/SiO₂催化剂中的Fe δ^+ 价态分布呈现先增后减的趋势，而Mo⁵⁺价态会随着Mo比例的增加而增加。在苯酚加氢脱氧反应中，当反应条件为573K，0.2MPa，FeMo(x)P摩尔比例分别为1:1:1和1:0.5:1时，苯和环己烯的选择性分别达到79.5%和78.0%。氧化物物种的存在使得FeMo(3)P/SiO₂催化剂的酸性位点增加，促进丙三醇中的C-O键断裂。在丙三醇氢解反应中，当反应条件为493K，

2.0MPa, FeMo(x)P摩尔比例分别为1:0.5:1和1:3:1时, 1, 3-丙二醇和正丙醇的选择性分别达到32.5%和69.5%。

关键词：磷化物；苯酚；加氢脱氧；丙三醇氢解

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Abstract

Biomass has been used as an alternative source of energy due to its rich storage, renewable and other advantages. However, oxygen containing compounds in biomass greatly affects the thermal, and limits its wide application. Therefore, it is necessary to carry out hydrodeoxygenation for biomass. Among these catalysts investigated for hydrorefining, transition metal phosphide catalyst with excellent catalytic performance for hydrodeoxygenation has been paid more and more attention in recent years.

Pd@Ni₂P/SiO₂ and FeMoP/SiO₂ catalysts were prepared by sol-gel method and citric acid-gel method in this paper, respectively. The catalysts were characterized and analyzed by CO chemisorption, XRD, XPS, NH₃-TPD, TEM. And evaluations of catalytic performance over Pd@Ni₂P/SiO₂ and FeMoP/SiO₂ for phenol hydrogenation or glycerol hydrogenolysis were also performed, respectively.

The study shows that the Pd@Ni₂P/SiO₂ catalyst particles disperse evenly (6.75 ± 1.54 nm). Due to the presence of Pd particles, the reduction temperature of the formation of Ni₂P is reduced by about 200. And Pd and Ni^{δ+} (0 < δ < 2) species provide the metal active site and acid center, which promotes the C-O bond breaking, and leads to higher phenol conversion and cyclohexane selectivity.

The presence of P^{δ-} (0 < δ < 1) species can facilitate the electronic transfer, so that H₂ over the catalyst surface can dissociate to promote the hydrogenation reaction. So the conversion of phenol is higher than that on the pure Ni₂P/SiO₂.

At 493 K, and 2.0 MPa, Pd@Ni₂P/SiO₂ has high phenol conversion, above 95%, and the selectivity of the cyclohexane is 95%. At 453 K, phenol conversion is 95%, and the selectivity of the cyclohexanol is 65%.

Compared with the traditional catalyst prepared by temperature programmed reduction (TPR) method, the FeMo(1)P catalyst particles prepared by citric acid-gel method is dispersed evenly (3.34 ± 0.77 nm). The coexistence of Mo and Fe

affect the dispersion of catalyst particle. The study shows that metal ($\text{Fe}^{\delta+}$ and Mo^{5+}) over $\text{FeMo}(x)\text{P}$ catalyst also has active and acid to promote the cleavage of C-O bond and hydrogenation reaction, and influence the distribution of product selectivity. And the presence of $\text{P}^{\delta-}$ ($0 < \delta < 1$) species can facilitate the electronic transfer between metal and P species, so that the active sites and $\text{P}^{\delta-}$ species can cooperate to promote the catalytic reaction. Combing with XPS, NH_3 -TPD and TEM results show that

$\text{FeMo}(x)\text{P}/\text{SiO}_2$ catalyst of $\text{Fe}^{\delta+}$ distribution shows a trend of first increasing and then decreasing. While the Mo^{5+} distribution increases with the increasing of Mo ratio. For the phenol hydrogenation, under the reaction conditions of 573K, 0.2MPa hydrogen pressure, and the mole ratio of $\text{FeMo}(x)\text{P}$ is 1:1:1 and 1:0.5:1, the selectivity of benzene and cyclohexene is 79.5% and 78.0%. The oxidizing species make

$\text{FeMo}(3)\text{P}/\text{SiO}_2$ catalyst increases the acid sites, and promote the cleavage of C-O bond at the glycerol. For the glycerol hydrogenolysis under the reaction condition of 493K, 2.0MPa hydrogen pressure, and the mole ratio of $\text{FeMo}(x)\text{P}$ is 1:0.5:1 and 1:3:1, the selectivity of 1,3-propylene glycol and propanol is 32.5% and 69.5%, respectively.

Keywords: Phosphide; Phenol; Hydrodeoxygenation; Glycerol hydrogenolysis

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