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硕士学位论文

高分散 NiO/SBA-15 和 Ni/SiO₂ 催化剂的
制备及其丙烷氧化脱氢和甲烷部分氧化
催化性能

Preparation and Catalytic Performance of
Well-dispersed NiO/SBA-15 and Ni/SiO₂ Catalysts
for Oxidative Dehydrogenation of Propane and
Partial Oxidation of Methane

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摘 要

本论文的主要目的是针对以简单的浸渍步骤制备高分散、抗烧结催化剂的方法探究，并对以柠檬酸络合法制备的催化剂进行了重点考察，为研制负载型高分散纳米尺度催化剂提供了科学基础。

在论文的第一部分（第三章）工作中，选取硝酸镍和柠檬酸镍为前驱体，采用浸渍法制备了 SBA-15 负载的 NiO 催化剂，通过 XRD、BET、TEM、H₂-TPR、O₂-TPD-MS、TP-MS 和 TG-DTG 等实验技术对相关催化剂进行了表征，实验结果表明：以柠檬酸镍为前驱体制备的催化剂可在介孔分子筛 SBA-15 孔道内部形成高含量、均匀分散的 NiO，同时能够较好地保持 SBA-15 的介孔结构。这主要是归因于金属离子与柠檬酸形成的环状螯合物可通过氢键与载体表面的硅羟基作用使得前驱盐均匀分布在 SBA-15 载体的内壁，形成一层与 SBA-15 表面作用较强的薄膜，该层薄膜在焙烧过程中因有机配体的燃烧而分解进而形成粒径较小、分散度较高的催化剂。而以硝酸镍为前驱体时，因其与 SBA-15 载体表面作用力较弱，在干燥过程中前驱体之间就已发生相互团聚，进而在焙烧过程中存在明显的烧结现象，导致形成的 NiO 颗粒较大，分散度较差。同时相比于以硝酸镍为前驱体制备的催化剂，以柠檬酸镍为前驱体制备的催化剂在 ODHP 反应中具有更好的低温催化性能，这与该催化剂中存在更多的非化学计量氧密切相关。

在论文的第二部分（第四章）工作中，选取氯化镍、硝酸镍、醋酸镍和柠檬酸镍等前驱体，同样采用浸渍法分别制备了 Ni/SiO₂ 催化剂，考察了各催化剂在 650 °C 下的 POM 反应性能，以检验催化剂在高温反应条件下的稳定性。通过 XRD、BET、TEM、H₂-TPR 等实验技术对各催化剂进行了表征，实验结果表明：以不同前驱体分别制备的 3.0 wt% Ni/SiO₂ 催化剂上归属为与 SiO₂ 载体具有强相互作用的 NiO 物种的含量按照氯化镍、硝酸镍、醋酸镍和柠檬酸镍的顺序依次递增，还原后催化剂上金属 Ni 粒子的平均粒径按相同顺序依次减小，同时各催化剂的 POM 反应稳定性也依此顺序逐渐提高。在以柠檬酸镍为前驱体制备的催化剂中，前驱盐柠檬酸镍水溶液因具有较高粘度以及与载体间的较强相互作用使前驱盐均匀吸附在 SiO₂ 载体表面，进而在焙烧过程中因有机配体的燃烧形成粒

径较小、分散度较高的催化剂，有效提高了催化剂的抗烧结能力，使得以柠檬酸镍为前驱体制备的催化剂表现出较高的 POM 反应稳定性。

关键词： NiO/SBA-15； Ni/SiO₂； 浸渍法； 高分散； 前驱体； 丙烷氧化脱氢； 丙烯， 甲烷部分氧化； 合成气

厦门大学博硕士论文摘要库

Abstract

This dissertation focuses on the studies of the technique that can be used to prepare well-dispersed and sinter-resistant catalysts by simple impregnation steps, and the catalysts prepared by citric acid coordination-impregnation method have been studied systematically in order to provide the scientific foundation for developing this catalyst.

In the first part (chapter 3), a series of NiO/SBA-15 catalysts were prepared by nickel nitrate and nickel citrate by the impregnation method. XRD, BET, TEM, H₂-TPR, O₂-TPD-MS, TP-MS and TG-DTG characterization results indicate that NiO nano-particles in the catalyst prepared by nickel citrate were highly dispersed inside the mesopores of SBA-15 whose mesopores structure have been saved completely. The chelated nickel citrate precursor interacts with silanol groups at the pore surface *via* hydrogen bonding, which results in a homogeneous distribution of precursor compound in the mesopores. After drying the chelated nickel precursor is therefore expected to have formed a thin film on the pore surface of SBA-15. Because of the hydrogen bonding this film is tightly adhered to the pore surface. Upon calcination of the thus immobilised catalyst precursor the thin film of nickel citrate breaks up and decomposes due to the combustion of the organic ligand. The resulting catalyst contains only very small NiO nano-particles situated inside the mesopores. When nickel nitrate precursor is used for catalyst preparation, the interactions of nickel nitrate with the support surface are too weak to provide sufficient anchoring of the nickel ions during drying treatment, thus giving rise to the formation of the very large NiO particles of this catalyst during calcination. Moreover, compared to the catalysts prepared by nickel nitrate, the catalysts prepared by nickel citrate have higher low-temperature catalytic performance which is closely related to the presence of more nonstoichiometric oxygen in the catalysts.

In the second part (chapter 4), in order to test the stabilities under high

temperature reaction condition, a series of Ni/SiO₂ catalysts were prepared by different nickel precursors (i.e., nickel chloride, nickel nitrate, nickel acetate and nickel citrate) by the same method, the catalytic performance at 650 °C of these catalysts were investigated in detail for the POM reaction. XRD, BET, TEM and H₂-TPR characterization results indicate that the 3.0 wt% Ni/SiO₂ catalyst prepared by nickel citrate possessed the most amount of NiO species which showed strong interaction with the support of SiO₂, the average size of whose Ni particles is the smallest after reduced, this kind of catalyst also exhibited the best POM reaction stability under high temperature reaction condition among all the Ni/SiO₂ catalysts prepared by different nickel precursors. A homogeneous distribution of precursor compound on the surface of the support generated by the high viscosity of the impregnated solution and the strong interaction between Ni species and the support of SiO₂, result in small size and high dispersion due to the combustion of organic ligand during calcination, which are suggested to be the best POM reaction stability under high temperature reaction conditions.

Keywords: NiO/SBA-15; Ni/SiO₂; Impregnation; Well-dispersed; Precursor; Oxidative dehydrogenation of propane; Propene; Partial oxidation of methane; Synthesis gas

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