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不同形式 SiO_2 负载纳米镍催化剂制备及 POM 高温
反应稳定性研究

Several Forms of SiO_2 Supported Nano-Ni Catalysts
Preparation and Their POM Reaction Stability at
High Temperature

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The Master Dissertation of Science in Xiamen University

**Several Forms of SiO₂ Supported Nano-Ni Catalysts
Preparation and Their POM Reaction Stability at
High Temperature**

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摘要

甲烷部分氧化(POM)制合成气反应具有能耗低,效率高等优点,有望成为制备合成气的新工艺。Ni基催化剂因具优良的POM反应活性和相对低廉的价格,一直备受研究者的关注,但Ni基催化剂易因烧结,积碳等(其中以Ni/SiO₂催化剂为甚),致使催化剂性能迅速降低直至失活,即,催化剂的稳定性,限制了它的应用。本文采用了溶胶凝胶法、常规浸渍法、表面活性剂改性浸渍法等方法制备了不同形式的SiO₂负载的纳米Ni催化剂,着力于研究这些催化剂样品的活性、选择性和稳定性,并利用BET、XRD、SEM、TEM、H₂-TPR、XPS、FT-IR和TG等多种表征手段对催化剂的比表面积、物相结构、氧化还原性质等进行研究,以促进对Ni/SiO₂催化剂的活性、选择性和稳定性与活性组分的尺度、分散性及Ni-SiO₂间的相互作用的关系的认识和理解。主要研究结果如下:

采用溶胶凝胶法制备了单分散SiO₂球负载小尺度的纳米Ni催化剂。在考察的Ni负载量~3.5和~9.0wt%下,溶胶凝胶法制Ni/SiO₂催化剂上Ni颗粒(3~5 nm)均处于高分散状态,而常规浸渍法制以商用SiO₂和纳米SiO₂球为载体的Ni/SiO₂催化剂上Ni物种粒径则显著变大(大于30 nm)。POM反应性能评价结果表明,溶胶凝胶法制Ni/SiO₂催化剂具有优越的POM反应催化性能和反应稳定性,在所考察的连续反应50 h内保持稳定的CH₄转化率(~82%)和合成气选择性(CO选择性~88%, H₂选择性~80%),而浸渍法制Ni/SiO₂催化剂经连续反应10 h后,CH₄转化率明显下降(60%以下),CO和H₂的选择性也明显降低(65%以下)。二者差异的原因与Ni纳米颗粒的大小和分散性有密切关系。Ni粒径越小,其与载体间的相互作用越强,从而表现出更好的抗烧结和抗积碳能力,最终使得催化剂在具有优良的POM反应活性和选择性的同时,也具有更高的反应稳定性。

采用表面活性剂改性浸渍法,即添加合适的表面活性剂于浸渍液中,改变添加量,制备活性组分尺度可控的商用SiO₂负载Ni催化剂。实验结果表明,阳离子型表面活性剂因与Ni(II)间电荷相斥,会对Ni/SiO₂催化剂上活性组分的分散起负面作用;而添加非离子型或阴离子型表面活性剂则可促进催化剂表面上活性组分Ni的分散。通过增大表面活性剂PVP、PEG和PEO等添加量,可使Ni/SiO₂

催化剂表面上 Ni 颗粒分布均匀、粒径减小（最小低至 4 nm 以下），与 SiO₂ 载体间存在较强相互作用的 Ni 物种含量增加，进而使催化剂表面上 Ni 分散性提高。POM 反应性能评价结果表明，Ni 粒径在 15 nm 之下，一般具有良好的催化性能和使用寿命。反应 30 h 内，CH₄ 转化率维持在~80%，CO 和 H₂ 选择性分别维持在~86%和~79%；连续反应 120 h 后，CH₄ 转化率降至~72%，CO 选择性降至~82%，H₂ 选择性几乎没有变化。表面活性剂对活性组分的分散及其粒径大小调控的促进作用的主要原因可总结为，（1）与 Ni(II)的络合，使浸渍液中孤立的 Ni 络合物的比例增大，齐聚或低聚物的比例减少，进而使表面上 Ni、Ni 间距加大，降低载体表面上 Ni 颗粒的团聚。表面活性剂 PVP 的影响大于 PEG 和 PEO；（2）降低浸渍液的表面张力，使亲水的活性组分 Ni 可以进入载体 SiO₂ 表面的低洼处或孔道的深处，降低样品焙烧中载体骨架的收缩和 Ni 颗粒的团聚程度，促进并加强 Ni-载体间的相互作用，使得 Ni 颗粒具有尺度小、分布均匀的特性。

采用“先壳后核”法，利用 Ni(II)与 N-[3-(三甲氧基硅基)丙基]乙二胺的配位作用，将 Ni 物种均匀地引入具有空腔的 SiO₂ 壳层内制得核壳结构 Ni@SiO₂ 催化剂，金属 Ni 高度均匀地分散于空心 SiO₂ 球内壁，粒径大小均匀(小于 4 nm)，Ni 颗粒的团聚几率得以较显著的降低，在 POM 反应中表现出良好的催化性能和反应稳定性。

对几种不同形式的 SiO₂ 负载纳米 Ni 催化剂在 POM 反应中的稳定性进行了探讨。结果表明，溶胶凝胶法制单分散 SiO₂ 球负载的 Ni 催化剂具有活性组分粒径小而分布均匀的特点，在所考察的几种 Ni/SiO₂ 催化剂样品中，具有较优越的高温反应稳定性和 POM 催化性能。通过比较几种不同方法制备的 Ni/SiO₂ 催化剂样品的催化性能和反应稳定性，结合表征实验结果，得出结论为，高比表面积和高孔体积负载型催化剂有助于其反应稳定性的提高；载体上活性组分粒径越小，分散性越高，粒径大小分布越均匀，越有利于提高催化剂的 POM 反应性能；活性组分与载体间相互作用的增强，有助于提高催化剂的反应稳定性，增强催化剂的抗积碳和消积碳能力，从而抑制催化剂的失活。

关键词：甲烷部分氧化； Ni/SiO₂ 催化剂；稳定性；溶胶凝胶法；表面活性剂改性浸渍法；“先壳后核”法

Abstract

The reaction of partial oxidation of methane (POM) to syngas is high efficiency and low energy consumption. POM reaction is expected to be the new technology for production of syngas. The Ni-based catalysts have attracted extensive attention because of both the high activity for the POM reaction and their relatively low cost. However, the Ni-based catalysts, especially for silica supported Ni, are always quickly deactivated due to the sintering of Ni metal particles, carbon deposition and etc. The unstability of Ni-based catalysts limit their application in production of syngas. In this dissertation, we focus on the study of the activity, selectivity and stability for the different forms of silica supported Ni catalysts, prepared by sol-gel method, impregnation method, surfactant modified impregnation method and etc. In order to reveal the relationship between the catalytic performance and physico-chemical properties of these catalysts, BET, XRD, SEM, TEM, H₂-TPR, XPS, FT-IR and TG techniques were used to characterize these catalysts in detail. The main results of this study are summarized as follows:

The monodispersed silica sphere supported Ni catalysts were prepared by sol-gel method. Though the Ni loading increased from ~3.5wt% to ~9.0wt%, the Ni particles (3~5 nm) were still high dispersed over the surface of the Ni/SiO₂ catalysts prepared by sol-gel method. But the Ni particles (> 30 nm) were obviously aggregated on the surface of Ni/SiO₂ catalysts prepared by impregnation method. The catalysts prepared by sol-gel method showed good catalytic performance and stability for POM reaction, the CH₄ conversion was maintained at ~82% and the selectivity to CO and H₂ were kept at ~88% and ~80%, respectively, with the time on stream for 50 hours. In the test of these catalysts prepared by impregnation method, the conversion of CH₄ decreased to less than 60%, and the selectivity to CO and H₂ were both decreased to less than 65%. The size and dispersion of Ni particles were related to the catalytic performance and stability of the catalysts. The catalysts prepared by sol-gel method were high resistant to aggregate of Ni particles and carbon deposition because of the strong

interaction between small Ni particles with silica support, which helped to improve the catalytic activity and selectivity of the catalysts, also could enhance the reaction stability of the catalysts.

The commercial silica supported high dispersed Ni catalysts were prepared by surfactant modified impregnation method, for which the surfactants were dissolving into the impregnation solution during the catalysts preparation. The size of Ni nanoparticles was controlled by modulating the addition amount of surfactants. Experimental results showed that the cationic surfactant could not promote the dispersion of active component because of charge repulsion. However, the non-ionic surfactant and anionic surfactant both could effectively promote the dispersion of active component. The Ni particles size over Ni/SiO₂ catalysts decreased to uniformly less than 4 nm with the increasing addition of surfactants PVP, PEG or PEO, leading to generation of more Ni species that strongly interacted with silica support. The dispersion of Ni species was obviously improved. The results of POM performance indicated that the catalysts generally showed good catalytic performance when the Ni particles size was less than 15 nm. The CH₄ conversion was maintained at ~80% and the selectivity to CO and H₂ were kept at ~86% and ~79%, respectively, with the time on stream for the initial 30 hours. After reaction for 120 hours, the CH₄ conversion and CO selectivity decreased to ~72% and ~82%, respectively, the H₂ selectivity was invariant. For that the dispersion and particles size of Ni species could be controlled by modulating the addition amount of surfactant, the reasons could be summarized as follows: (1) The complexation between surfactant molecule and Ni(II) decreased the amount of Ni oligomers species and increased the distance between Ni and Ni species, so the aggregate of Ni could be suppressed. The surfactant of PVP could more effectively help to decrease the size of Ni species than PEG or PEO. (2) The surface tension of impregnation solution decreased after surfactants dissolving in, then the hydrophilic Ni species could infiltrate into the pore of silica support. The contraction of the catalysts skeleton and the aggregation of Ni species could be inhibited. The interaction of Ni-support was enhanced, leading to the generation of small Ni particles with uniform size.

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