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硕 士 学 位 论 文

无钾耐硫 CO 钴钼变换催化剂的研究

The study of potassium-free sulfur-tolerant

Co-Mo supported water-gas shift catalyst

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厦门大学博硕士学位论文摘要库

摘要

水煤气变换是水蒸气 (H_2O) 和一氧化碳 (CO) 反应生成二氧化碳 (CO_2) 和氢气 (H_2) 的一个可逆、放热反应 ($\text{CO} + \text{H}_2\text{O} = \text{CO}_2 + \text{H}_2$)。钴钼变换催化剂主要应用于合成氨、合成甲醇和制氢行业的半水煤气变换。与传统工业变换催化剂 Fe-Cr 系 (中温, 400°C) 和 Cu-Zn 系 (低温, 200°C) 相比, 钴钼变换催化剂的催化特性是: 低温活性好, 活性温区宽 ($160\sim 500^\circ\text{C}$), 耐硫耐毒性强。近几年, 化工行业积极推广使用这类高效催化剂, Co-Mo 型催化剂因此在工业上获得广泛的应用和认可。

钴钼变换催化剂有两类: 一类是 Co-Mo-K/ γ - Al_2O_3 , 用于低压 ($0.8\sim 2.0\text{MPa}$) 低汽气比 (~ 0.3) 中温串低温变换系统, 因其钾流失及易反硫化, 使用寿命仅 2 年; 另一类为 Co-Mo/MgO- Al_2O_3 , 用于高压 ($\sim 8.0\text{MPa}$) 高汽气比 (~ 1.4) 变换系统, 使用寿命大于 5 年。前一类含钾催化剂国内已有 30 多个生产厂家生产, 后一类无钾催化剂国内仅有齐鲁石化研究院独家生产 (QCS 系列), 市场大多被德国 BASF 公司生产的 K8-11 产品占领。但是, 由于第二类无钾工业催化剂尚存在如下问题: (1) Co 含量较高 (达 3.5%), 制作工艺采用二步高温煅烧, 导致催化剂生产成本高; (2) 催化剂只适用于高压高汽气比变换系统, 无法适用中低压变换系统。因此本课题的立意在于开发适应高中压、高低汽气比、价格低廉的高效无钾钴钼 CO 变换催化剂。

本文通过捏合法制备镁铝尖晶石复合载体, 采用浸渍法负载钴钼活性组分, 考察镁铝比、钴钼比对催化剂活性的影响, 确定了催化剂配方, 并用 BET、XRD、XPS、ESR、Raman 和 H_2 -TPR 表征手段, 研究载体及其催化剂的性能, 初步得到如下结果:

(1) 镁铝摩尔比为 1.05 的载体具有最高的机械强度, 其相应催化剂的活性最好, 复合载体以 $\text{MgAl}_2\text{O}_4 \cdot x\text{MgO} \cdot y\text{Al}_2\text{O}_3$ 不规则的尖晶石形式存在;

(2) 确定了催化剂配方, 其中 MoO_3 8.0wt%, CoO 1.8wt%, 即 Co(1.8)-Mo(8.0)/MgO(1.05)- Al_2O_3 , 定型催化剂与德国进口催化剂 K8-11 以

及国内 QCS 型催化剂比较，具有更高的活性，尤其是在低汽气比条件下。

(3) 对载体及其催化剂的谱学表征研究得到如下结论：

a. 镁铝摩尔比接近 1.05，钴钼氧化物质量比接近 1.8/8.0，有利于氧化态催化剂中易还原的八面体配位的 Mo 物种的生成，减少难还原的四面体配位 Mo 物种的生成。

b. 硫化态催化剂中 Mo 以 Mo^{6+} 、 Mo^{5+} 、 Mo^{4+} 混合价态物种共存，S 以 S^{6+} 、 S^{2-} 混合价态物种存在；ESR 显示催化剂中存在氧包围物种 oxo-Mo^{5+} 和硫包围的 thio-Mo^{5+} 以及 Co-Mo-S 物种。当镁铝摩尔比小于 1.05 和钴钼质量比小于 1.8/8.0 时，随着两者比值的增加，低价 Mo、低价硫、 thio-Mo^{5+} 和 Co-Mo-S 的含量增加；当两者的比值超过最佳值时，则相反。

c. 硫化态催化剂中当 $\text{Co/Mo}=1.8/8.0$ （质量比）时，ESR 显示 thio-Mo^{5+} 和 Co-Mo-S 峰强度最强，Raman 显示 MoS_2 物种的峰最强，这些物种可能构成催化剂的活性相。

关键词：水煤气变换，钴钼变换催化剂，无钾，镁铝尖晶石复合载体

Abstract

The water-gas shift (WGS) is a reversible, exothermic reaction of steam with carbon monoxide (CO) to produce carbon dioxide (CO₂) and hydrogen (H₂). The supported cobalt-molybdenum catalyst is mainly employed in the water-gas shift reaction of many industrial processes, such as ammonia synthesis, methanol synthesis and hydrogen production. Compared with iron-chromium-based shift catalyst (the optimal reaction temperature is 400°C) and the copper-zinc-based low-temperature shift catalyst (the optimal reaction temperature is 200°C), Co-Mo catalyst is of some excellent catalytic characteristics, namely a higher catalytic activity at low temperature, a wider temperature range from 160°C to 500°C at which a perfect catalytic activity can maintain, and a better ability of sulfur tolerant. Recently, this type catalyst has been used extensively and now gained wide industrial acceptance.

Two classes of the Co-Mo catalyst are used in industry: one is the Co-Mo-K/ γ -Al₂O₃ catalyst, which is suitable for use under low pressure (0.8 to 2.0MPa), low steam-to-gas ratio (about 0.3) and particularly in the shift system by connecting the medium-temperature stage with low-temperature one, however, its catalytic lifetime is only two years because the catalyst is very susceptible to lose potassium during the reaction therefore resulting in anti-sulfidation of the catalyst; the other is Co-Mo/MgO-Al₂O₃ catalyst, which is mainly employed in the shift system under high pressure (about 8MPa) and high steam-to-gas ratio (about 1.4), what is better, the catalytic lifetime is over 5 years. In China, more than 30 manufactories produce the former type of the catalyst, only the Qilu Institute of Petroleum Chemical Industry is producing the latter type named QCS series that have been put into industrially use. The market was occupied by K8-11 type catalyst produced by BASF (German company) in this field. As the content

of Cobalt in both two commercial catalysts is as much as 3.5% and the preparation of them is the two-step calcining method at high temperature, in particular, these catalysts are only fit for the shift system under high pressure and high steam-to-gas ratio reaction condition, they are found to be not suitable for the shift system under medium or low pressure condition, what is worse, the price of these catalysts are very expensive because of monopoly. The goal of our research is to develop a highly active potassium-free Co-Mo supported shift catalyst, which is suitable for the shift system no matter what the reaction condition is under high or medium pressure, high or low steam-to-gas ratio condition.

The preparations of the catalysts are as follows. Firstly, a mixing-kneading method is used to prepare a complex support of the magnesium-alumina spinel, and then impregnate the complex support with the Co-Mo solution followed by calcination to produce the catalyst. The influence of both magnesium-to-alumina ratio (molecular molar ratio) and cobalt-to-molybdenum ratio on the catalytic activity has been investigated. The characteristics of both supports and catalysts have been investigated by means of BET, X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), Electron spin resonance (ESR), Laser Raman (LR) and H₂-Temperature-programmed reduction (H₂-TPR). The results are listed below:

(1) The support with the magnesium-to-alumina ratio of 1.05 has the highest mechanical strength and catalytic activity. The state of the complex support exists as an irregular spinel form of $\text{MgAl}_2\text{O}_4 \cdot x\text{MgO} \cdot y\text{Al}_2\text{O}_3$.

(2) The catalyst with the composition of 8wt% MoO₃ and 1.8wt% CoO, namely the catalyst Co(1.8)-Mo(8)/MgO(1.05)-Al₂O₃, was found to have higher catalytic activity in comparison with the same type of catalysts such as German

K8-11 and Chinese QCS, especially at low steam-to-gas ratio.

(3) The results of the characterizations of supports and catalysts are presented below:

a. When Mg/Al (molar/molar) is close to 1.05 and CoO/MoO₃(weight/weight) is close to 1.8/8, the composition of the catalyst is found to be beneficial to increase the amount of octahedral molybdenum species which is easy to reduce and simultaneously decrease the content of tetrahedron molybdenum species which is very hard to reduce in the oxide state of catalyst.

b. A mixed valence species of the molybdenum with Mo⁶⁺, Mo⁵⁺ and Mo⁴⁺ was observed to coexist in the sulfided state of the catalyst and sulfur species exist in the form S⁶⁺ and S²⁻. The characterization of ESR indicated that oxo-Mo⁵⁺ species (Mo⁵⁺ species was surrounded by oxygen), thio-Mo⁵⁺ species (Mo⁵⁺ species was surrounded by sulfur) and Co-Mo-S exist in the catalyst at the sulfided state. When Mg/Al (molar/molar) is smaller than 1.05 and CoO/MoO₃(weight/weight) is less than 1.8/8, with the increasing of both values, the contents of Mo species in low valence, S species in low valence, thio-Mo⁵⁺ and Co-Mo-S are all increasing. A contrasting observed result can be obtained when the values mentioned above are beyond the optimal ones.

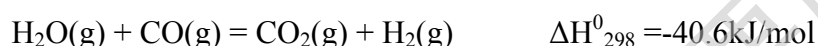
c. The characterization of ESR indicates that the peak-intensities of thio-Mo⁵⁺ and Co-Mo-S are the strongest for sulfided state of the catalyst when Co/Mo=1.8/8. The characterization of Raman represents, at the same time, the peak-intensity of MoS₂ species is the strongest. All of these species probably make up of the active phase of the catalyst.

Keywords: Water-gas shift, Co-Mo shift catalyst, Potassium-free, Magnesium-alumina spinel (MgAl₂O₄)

第一章 前言

1.1 概述

水煤气变换反应（water-gas shift reaction）是一氧化碳（CO）和水蒸汽（H₂O）在催化剂的作用下生成二氧化碳（CO₂）和氢气（H₂）的反应，该反应是可逆、放热的化学反应。反应方程式为：



此反应已在工业上广泛应用：（1）用于合成氨以及制氢工业；（2）在合成甲醇和合成汽油生产中，也用此反应来调整一氧化碳与氢的比例，以满足工艺的要求；（3）近年来，为了降低城市煤气中一氧化碳的含量，也通过此变换反应来实现^[1]。

在合成氨生产中，水煤气变换反应具有多重意义：一是由于 CO 是氨合成催化剂的毒物，因此在进行氨合成反应之前必须将其最大程度的除去；二是在合成氨中，消耗大量氢气，所以应尽可能获取更多的氢气；三是变换反应的另一产物 CO₂ 是合成碳铵和尿素的主要原料。因此最近几十年各国学者都一直在不断地研究和改进变换催化剂，以提高催化活性，降低生产成本。此外，在 C₁ 化学领域中，水煤气变换反应的催化作用是一个重要的研究课题。

制取合成氨原料气所用原料和工艺过程多种多样，导致（水）煤气中 CO 含量不尽相同，例如，以煤或焦炭为原料，采用间断式固定层煤气发生炉制得的半水煤气，含 CO 为 25%~28%，以天然气为原料，采用蒸汽转化法制得的半水煤气含 CO 13%~18%，以重油为原料制得的煤气含 CO 为 45%~49%，以煤粉加压气化制得的煤气含 CO 为 30%~40%。相应地，一氧化碳变换反应也有不同的工艺流程。50 年代以前，在常压下制取合成氨原料气，其变换大多数也是在常压下进行。此后，尤其是 60 年代以后，合成氨原料改为天然气、油田气、石油加工气、轻油等，金属材料工业水平的提高，

生产方法大多采用加压的蒸汽转化法,变换则在加压下进行,一般在 4.0MPa 以下。现在以煤、焦为原料的常压造气工厂,很多也改用加压变换,以降低能耗,用粉煤加压气化作原料气,其变换压力一般在 5.5MPa 以下,以渣油为原料最高压力已达 8.5MPa^[2]。

1.2 水煤气变换催化剂的发展

目前,工业上采用的水煤气变换催化剂大体上可分为三大类:(1)铁-铬系中温变换催化剂;(2)铜-锌系低温变换催化剂;(3)钴-钼系变换催化剂。

1.2.1 铁-铬系中温变换催化剂

Fe-Cr 系变换催化剂在合成氨厂和制氢厂一氧化碳变换过程中一直被广泛使用,其型号较多,是用量最大的催化剂,其工业操作温度通常为 300℃~530℃。铁-铬系中温变换催化剂主要由 Fe₂O₃ 和 Cr₂O₃ 氧化物以及其他一些助剂组成。1912 年,德国科学家 W. Wied^[3]利用 FeO-Al₂O₃ 做一氧化碳变换催化剂,从水煤气中制取氢气,1913 年, A. Mittasch^[4]等人研制成功 Fe-Cr 系催化剂,在德国的 BASF 公司合成氨厂首次实现工业化。

Fe-Cr 催化剂又称高温催化剂,通常其主要活性成分是 Fe₂O₃ (70~80%) 和 Cr₂O₃ (5~15%), 以及添加一些 MgO、Al₂O₃ 和 K₂CO₃ 等助剂^[5]。郭清松等^[6]研究了 Fe₂O₃ 晶型对 Fe-Cr 系中温变换催化剂的活性影响,并且通过 XRD 和 TEM 对国产催化剂 B₁₀₇ 和 BI 进行分析,发现 BI 催化剂中主体相为单一的 γ-Fe₂O₃, 而 B₁₀₇ 则为 γ-Fe₂O₃ 和 α-Fe₂O₃ 的混合物,结合活性测试,发现单一 γ-Fe₂O₃ 相的 BI 催化剂低温活性和耐热性方面都比 B₁₀₇ 好。对美国 C12-1 型进行晶相分析,其中既有 γ-Fe₂O₃ 相,也有 α-Fe₂O₃ 相,焙烧不完全的还有 α-FeOOH 等物相(脱水后得到 α-Fe₂O₃),形成以上晶相对催化剂强度起较好的作用^[2]。高温催化剂在 250~400℃ 下还原活化使用,还原态是

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