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碳纳米管负载/促进合成气制低碳混合醇
Mo-Co-K 硫化物基催化剂研究

Study on Mo-Co-K Sulfide-based Catalysts supported / promoted by
MWCNTs for Mixed Alcohols Synthesis from CO/H₂

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**Study on Mo-Co-K Sulfide-based Catalysts
supported / promoted by CNTs for
Mixed Alcohols Synthesis from CO/H₂**

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扩展式中文摘要

低碳醇是最重要的煤基洁净合成燃料和化工原料产品之一。这类 C_{2+} -含氧物已经被证明是具有更高辛烷值, 较低 NO_x 、臭氧、CO 和芳香烃蒸气排放物的优质、洁净动力燃料。上个世纪 80 年代中期以来, 有关 MoS_2 -基催化剂上合成气制低碳醇的研究已相当广泛而深入, 有一系列开创性研究论文发表, 其结果大大增进人们对这类催化剂及相应催化反应体系的认识。然而, 现有的低碳醇合成工艺单程转化率及生成 C_{2+} -醇的选择性仍较低, 大多数体系合成的主要产物是甲醇、而非 C_{2+} -醇, 使其商业应用大受限制。高度活泼、尤其对 C_{2+} -醇生成高度选择的新催化剂的研制及相应高效合成过程的开发, 一直是许多研究工作追求的目标。

在另一研究前沿, 多壁碳纳米管(简称为 CNTs)自 1991 年被发现以来, 人们对它的兴趣与日俱增。这类具有纳米级管状结构的新型纳米碳材料系由碳六元环组成的类石墨平面、按一定方式叠合而成; 它们具有石墨化的管壁、纳米级的管腔、由 sp^2 -C 构成的表面、高的导电/导热性能、以及对氢的吸附活化并促进其溢流的优良性能, 所有这些特点使 CNTs 很有希望作为一些催化剂的优良载体、或高效促进剂。

在本研究工作中, CNTs-基材料负载或促进的负载型和共沉淀型 Mo-Co-K 硫化物催化剂被制备, 催化剂的组成被优化, 利用一系列物理化学技术(诸如: TEM/EDX, SEM, XRD, XPS, H_2 -TPR 及 H_2 (or CO)-TPD 等)对催化剂进行了表征, 在固定床加压稳态连续流动反应系统就这类催化剂及相关参比体系对 CO 加氢转化为低碳醇的催化活性作了比较评价; 结果显示, 与一些常规载体(诸如: 活性炭(AC)、 $\gamma-Al_2O_3$ 等)负载的同类负载型催化剂或与不含 CNTs 的共沉淀型对应物相比, 所制备 CNTs 基材料负载或促进的催化剂上 CO 加氢制低碳醇的催化活性和 C_{2+} -醇的生成选择性均高得多。本文结果对于深入了解作为载体或促进剂的 CNTs-基材料的促进作用本质和合成气高效制低碳醇的耐硫催化剂的研制, 兼具理论和实践意义。本文得到下述若干重要结果:

I. CNTs 基材料负载合成气制低碳醇 MoCoK 硫化物基催化剂研究

I-1. CNTs 和 Co-修饰 CNTs 材料的制备和表征

CNTs 的制备 按本组先前报道的方法、以 CH_4 为碳源、纳米 Ni-MgO 为催化剂、在常压固定床反应装置上进行制备, 所制得 CNTs 经 TEM/SEM/HRTEM 和 XRD 等技术/方法表征, 证实其为鱼骨型多壁碳纳米管, 外径在 15~45 nm 范围, 内径为 3~5 nm, 比表面积~140 m^2/g 。

Co-修饰 CNTs 的制备 用自行制备的 CNTs 作为基质, 经由化学还原沉积法制备, 所制得材料(记为 $y\%$ (质量百分数)Co/CNTs)经 TEM/EDX、SEM 和 XRD 技术进行表征, 结果证实: 金属 Co 十分均匀地分布在 CNTs 基质表面, Co_x^0 晶粒粒径在 4~7 nm 范围; C 和 Co 是丰度最高的两种表面元素, 其含量分别为 52.66 atomic% 和 35.08 atomic%, Pd 的含量在 EDX 检测极限以下。

I-2. 负载型 Mo-Co-K 硫化物基催化剂的研制

Co/Mo 摩尔比的优化: 在固定 Mo 负载量为 6.2%、K 负载量为 1.5%, 变动 Co/Mo 摩尔比(由 0/1, 0.5/1, 1/1, 2/1 至 3/1)的 6 种 CNTs 负载催化剂上, 2.0 MPa, 583 K, $V(\text{H}_2)/V(\text{CO})/V(\text{N}_2) = 45/45/10$, $\text{GHSV} = 2400 \text{ ml}_{\text{STP}} \cdot \text{h}^{-1} \cdot \text{g}_{\text{cat}}^{-1}$ 的反应条件下进行比较调查, 结果显示, 低碳醇合成得率随着 Co/Mo 摩尔比由 0 逐步升高而上升, 在 Co/Mo = 1/1(摩尔比)附近达到极大, 随后转而下降, 表明 CNTs 负载催化剂的 Co、Mo 相对含量以 Co/Mo = 1/1(摩尔比)为佳, 相应催化剂的组成为 11.6% $\text{Mo}_1\text{Co}_1\text{K}_{0.6}/\text{CNTs}$ 。

Mo_1Co_1 负载量的优化 在优化 Co/Mo 摩尔比基础上, 保持 Co/Mo = 1/1(摩尔比)不变, 在上述反应条件下考察催化剂活性与 Mo_1Co_1 负载量的相关性, 结果表明 Mo_1Co_1 , 所考察 5 种催化剂上低碳醇合成反应活性高低顺序为: 11.6% $\text{Mo}_1\text{Co}_1\text{K}_{0.6}/\text{CNTs}$ > 13.3% $\text{Mo}_1\text{Co}_1\text{K}_{0.6}/\text{CNTs}$ > 17.4% $\text{Mo}_1\text{Co}_1\text{K}_{0.6}/\text{CNTs}$ > 9.9% $\text{Mo}_1\text{Co}_1\text{K}_{0.6}/\text{CNTs}$ > 5.8% $\text{Mo}_1\text{Co}_1\text{K}_{0.6}/\text{CNTs}$, 以 11.6% $\text{Mo}_1\text{Co}_1\text{K}_{0.6}/\text{CNTs}$ 为佳。

K/Mo 组成比例的优化 在优化 Co/Mo 摩尔比和 (Mo_1Co_1) 负载量的基础上, 考察 K(前驱态为 K_2CO_3)添加量对催化剂活性的影响, 结果表明, K/Mo =

0.6(摩尔比)时低碳醇合成得率达到极大值。

不同载体负载 $\text{Mo}_i\text{Co}_j\text{K}_k$ 硫化物基催化剂上低碳醇合成的反应活性 实验结果显示：在 CNTs 负载催化剂 $11.6\%\text{Mo}_1\text{Co}_1\text{K}_{0.6}/\text{CNTs}$ 上，2.0 MPa, 583 K, $V(\text{H}_2)/V(\text{CO})/V(\text{N}_2) = 45/45/10$, $\text{GHSV} = 2400 \text{ ml}_{\text{STP}}\cdot\text{h}^{-1}\cdot\text{g}_{\text{-cat}}^{-1}$ 的反应条件下，CO 转化率达 3.34%，相应总醇 C-基选择性为 83.7%(其中 C_{2+} -醇生成选择性为 62.3%)，相应的“比反应速率”[即：单位时间内、单位质量 $\text{Mo}_i\text{Co}_j\text{K}_k$ 组分(以毫摩尔 Mo 表示)上 CO 的转化量(以微摩尔 CO 表示)] 达到 $0.69 \mu\text{mol}\cdot\text{CO}\cdot\text{s}^{-1}\cdot(\text{mmol}\cdot\text{Mo})^{-1}$ ，是 $\gamma\text{-Al}_2\text{O}_3$ 、AC 和 SiO_2 分别负载相同($\text{Mo}_1\text{Co}_1\text{K}_{0.6}$) 负载量(即 11.6%)催化剂上相应比反应速率的 5.31 倍、2.30 倍和 6.90 倍，是 3 种参比载体各自最佳 $\text{Mo}_i\text{Co}_j\text{K}_k$ 组成及相应负载量催化剂(即： $26.1\%\text{Mo}_1\text{Co}_1\text{K}_{0.8}/\gamma\text{-Al}_2\text{O}_3$ 、 $50.3\%\text{Mo}_1\text{Co}_1\text{K}_{0.8}/\text{AC}$ 和 $22.2\%\text{Mo}_1\text{Co}_1\text{K}_{0.8}/\text{SiO}_2$)上比反应速率的 3.45 倍、3.45 倍和 2.88 倍。

I-3. Co-修饰 CNTs 负载 Mo-Co-K 硫化物基催化剂上低碳醇合成的反应性

实验发现，用 Co-修饰 CNTs 代替未经修饰的单纯 CNTs 或活性炭(AC)作为 Mo-Co-K 硫化物基催化剂的载体导致 CO 加氢转化活性明显提高和 C_{2+} -醇的生成选择性大为改进。在其组成经优化的 $11.6\%(\text{Mo}_1\text{Co}_1\text{K}_{0.6})/(6.4\%\text{Co}/\text{CNTs})$ 催化剂上，5.0 MPa, 613 K, $V(\text{H}_2)/V(\text{CO})/V(\text{N}_2) = 45/45/10$, $\text{GHSV} = 3600 \text{ ml}_{\text{STP}}\cdot\text{h}^{-1}\cdot\text{g}_{\text{-cat}}^{-1}$ 反应条件下，总醇(C_{1-4} 醇)的时空产率达到 $154.1 \text{ mg}\cdot\text{h}^{-1}\cdot\text{g}_{\text{-cat}}^{-1}$ (相应 CO 转化率为 12.6%)，是单纯 CNTs 和 AC 各自最佳 $\text{Mo}_i\text{Co}_j\text{K}_k$ 组成及相应负载量催化剂 [$11.6\%(\text{Mo}_1\text{Co}_1\text{K}_{0.6})/\text{CNTs}$ 和 $50.3\%(\text{Mo}_1\text{Co}_1\text{K}_{0.8})/\text{AC}$] 上相应观测值(87.7 和 $66.1 \text{ mg}\cdot\text{h}^{-1}\cdot\text{g}_{\text{-cat}}^{-1}$) 分别的 1.76 和 2.33 倍。乙醇成为 CO 加氢转化的最主要产物，其 C-基选择性达 31.6%，相应的总醇 C-基选择性为 70.5%， C_{2+} -醇/ C_1 -醇= 3.6(C-基选择性比)。

I-4. CNTs-基材料负载 Mo-Co-K 硫化物基催化剂的表征

实验发现，用 Co-修饰的 CNTs(即 $6.4\%\text{Co}/\text{CNTs}$)代替单纯 CNTs 或 AC 作为 Mo-Co-K 硫化物基催化剂的载体并不引起 CO 加氢转化反应的表观活化能发生明显变化，但却导致工作态催化剂表面催化活性 Mo 物种(Mo^{4+})在总承载 Mo 量

中所占比率明显增加,这为 H₂-TPR 和 XPS 表征结果所证实。在另一方面, H₂-TPD 测量揭示,在常温常压下 6.4%Co/CNTs 负载的催化剂 [11.6%(Mo₁Co₁K_{0.6})/(6.4%Co/CNTs)] 对 H₂ 的吸附容量是单纯 CNTs 或 AC 负载参比体系 [11.6%(Mo₁Co₁K_{0.6})/CNTs 和 50.3%(Mo₁Co₁K_{0.8})/AC] 的 2.17 和 2.86 倍;据此可以推断,在低碳醇合成反应条件下,在工作态催化剂表面存在着较大数量的吸附活泼氢物种,这有助于营造较高稳态浓度活泼氢的表面氛围,这些吸附氢物种容易通过碳纳米管促进的氢溢流,传输至 Mo-Co-K 催化活性位,于是有助于提高低碳醇合成过程中一系列表面加氢过程的反应速率。

II. CNTs 促进合成气制低碳醇共沉淀型 Mo-Co-K 硫化物催化剂研究

II-1. CNTs 促进共沉淀型 Mo-Co-K 硫化物基催化剂上低碳醇合成的反应性

用自行制备的多壁碳纳米管(CNTs)作为促进剂,制备一类 CNTs 促进共沉淀型 Mo-Co-K 硫化物基催化剂。实验结果显示,适当添加少量 CNTs 到 Mo-Co-K 硫化物基催化剂中能显著地提高 CO 加氢的转化活性和低碳醇的生成选择性。在其组成经优化的 Mo₁Co₁K_{0.3}-10%CNTs 催化剂上,5.0 MPa、623 K、V(CO):V(H₂):V(N₂) = 45:45:10、GHSV = 3600 mL_{STP}·h⁻¹·g_{cat}⁻¹ 的反应条件下,CO 的转化率达 21.6%,相应总醇(C₁₋₄ 醇)时空产率为 241.5 mg·h⁻¹·g_{cat}⁻¹,是不含 CNTs 促进剂的对应物(Mo₁Co₁K_{0.3})上这些值(17.1%和 131.0 mg·h⁻¹·g_{cat}⁻¹)分别的 1.26 和 1.84 倍;前者 C₂₊-醇/C₁-醇 = 2.0 (C-基选择性比),展现其作为优质车用动力燃料添加剂和化工基础原料重要应用前景,而后者 C₂₊-醇/C₁-醇值只为 1.6。

II-2. CNTs 促进共沉淀型 Mo-Co-K 硫化物基催化剂的表征研究

实验表征结果显示,少量 CNTs 促进剂的适当加入并不导致 Mo₁Co₁K_{0.3} 硫化物基催化剂上 CO 加氢反应的表现活化能发生明显变化;较之不含 CNTs 的对应物体系, CNTs 促进的催化剂更易于在较低温度下还原活化(在本文 H₂-TPR 测试条件下,含 CNT 体系单位质量 Mo₁Co₁K_{0.3} 还原的“比耗氢量”是不含 CNT 对应物的 4.1 倍;前者在 448 K 温度下开始还原,峰温为 623 K,后者当温度升至 648 K 才开始还原,峰温为 685 K),并导致工作态催化剂表层催化活性 Mo 物种(Mo⁴⁺)

在总 Mo 量中所占份额明显提高 [工作状态催化剂的 XPS 分析显示, 含 CNTs 体系表面 Mo^{4+} 物种的摩尔分数达 88.1%, 是不含 CNTs 对应物相应值(77.3%)的 1.14 倍]。在另一方面, CNT 促进催化剂展现出对 H_2 更强的吸附活化能力(H_2 -TPD 对比测量显示, 在常温常压下同 CNTs 体系对 H_2 的化学吸附容量是不含 CNTs 对应物的 4.5 倍)、并能在相当大程度上使水煤气变换副反应受到抑制(在本文 5.0 MPa 压力级别的反应条件下, 在 573~633 K 温度范围, 含 CNTs 体系上副反应产物 CO_2 的选择性保持在 16.5 C% ~ 12.5 C% 水平; 而相同条件下在不含 CNT 的对应物上, CO_2 的选择性高达 33.9 C% ~ 28.5 C%; 前者不及后者的一半); 上述这些因素对催化剂活性的提高和低碳醇生成选择性的改进都有重要贡献。

结 论

本文结果显示, CNTs-基材料(包括单纯 CNTs 和金属 Co-修饰 CNTs)不仅能作为合成气制低碳醇 Mo-Co-K 硫化物基催化剂的载体, 也是其优良的促进剂。在上述两种情形下, 不论是作为载体的 Co-修饰的 CNTs, 或是作为促进剂的单纯 CNTs, 适当组合它们到 Mo-Co-K 硫化物基质催化剂中并不引起 CO 加氢转化反应表观活化能发生明显变化(这似乎暗示 CO 加氢转化的主要反应途径或速率决定步骤没有改变), 但却导致工作状态催化剂表面催化活性 Mo 物种(Mo^{4+})在总 Mo 量中的所占份额明显增加、以及化学吸附氢物种(H(a))的浓度大为提高。这两方面的效应在促进 CO 加氢转化活性的提高和低碳醇生成选择性的改进两方面都起重要作用; 此外, CNTs-基材料促进的催化剂工作状态表面上高稳态浓度氢吸附物种的存在使水煤气变换副反应在相当大程度上受到抑制, 这对低碳醇产率的提高也有一定贡献。为更深入了解 CNTs-基材料的促进作用本质、尤其弄清低碳醇生成选择性因何得以改进的作用机理, 进一步的研究工作、特别是低碳醇合成反应条件下工作状态催化剂上吸附物种和反应中间物种的原位表征信息, 是高度需要的。

关键词: 多壁碳纳米管, 金属钴修饰碳纳米管, 碳纳米管载体, 碳纳米管促进剂, Mo-Co-K 硫化物基催化剂, CO 加氢, 低碳醇合成.

厦门大学博硕士学位论文摘要库

Extended Abstract

The higher alcohols (C_{2+} -alcohols) have been considered as one kind of the most important species among coal-based clean synthetic fuels and chemical feedstocks. These C_{2+} -oxygenates have been confirmed to be a better and cleaner automobile fuel with high octane number, and lower emissions of NO_x , ozone, CO, and aromatic vapors. Higher alcohol synthesis (simplified as HAS) on MoS_2 -based catalysts has been extensively studied since the mid-1980s. A number of pioneer works have been published on this subject. Progress in this field has considerably contributed to the growing understanding of the nature of these catalytic reaction systems. Nevertheless, the existing technology of HAS is still on a small scale. The single-pass-conversion of the feed syngas and selectivity to C_{2+} -alcohols both were relatively low. Under the used reaction conditions, most systems produce methanol as the main product instead of C_{2+} -alcohols. Development of catalysts with high efficiency and selectivity to C_{2+} -alcohols has been one of the key objectives for R&D efforts.

To the other front, multi-walled carbon-nanotubes (CNTs, simplified as CNTs) have been drawing increasing attention recently. This new form of nanostructured carbon has a much higher degree of structural perfection, and possesses several unique features, such as, highly graphitized tube-wall, nanosized channel and sp^2 -C-constructed surface. They also display high thermal and electrical conductivity, and excellent performance for adsorption and spillover of hydrogen, which make this kind of nanostructured carbon materials full of promise as a novel catalyst support or promoter.

In the present work, the supported or co-precipitated catalysts of Mo-Co-K sulfide based on CNT-based materials or promoted by CNTs were prepared and characterized through a series of physico-chemical techniques, such as TEM/EDX, SEM, XRD XPS, H_2 -TPR (temperature-programmed reduction) and H_2 (or CO)-TPD (temperature-programmed desorption) measurements. The catalysts displayed higher catalytic activity and selectivity for HAS from syngas, as compared to the reference

systems, including the catalysts supported by AC (a conventional activated carbon support), and the CNT-free co-precipitated counterpart. The results shed some light on understanding the nature of promoter action by the CNT-support/promoter and the prospect of developing highly active catalysts. Several significant results are described as follows:

I. Study on Mo-Co-K sulfide catalysts supported by Co-modified CNTs for HAS

With the home-made CNTs (“Herringbone-type”, with the outer diameter of 15~45 nm, the inner diameter of 3~5 nm, and specific surface area of $140 \text{ m}^2 \cdot \text{g}^{-1}$) as substrate material and using chemical reduction-deposition method, a type of metallic cobalt-decorated CNTs, noted as $y\%$ (mass percentage)Co/CNTs, was prepared. TEM/EDX, SEM and XRD measurements demonstrated that the metallic cobalt was evenly coated on the CNT substrate, with granule-diameter of the Co_x^0 -crystallites of 4~7nm. Carbon and cobalt were the predominant two elements, with the content at 52.66 atomic% and 35.08 atomic% respectively, and Pd surface-content was under detection limit by the EDX.

Using the $y\%$ Co/CNTs as support, a type of supported Mo-Co-K sulfide catalysts, noted as $x\%$ ($\text{Mo}_i\text{Co}_j\text{K}_k$)/($y\%$ Co/CNTs), for HAS was developed. It was experimentally shown that using the Co-modified CNTs in place of simple CNTs or AC or $\gamma\text{-Al}_2\text{O}_3$ as the catalyst support led to a significant increase in activity of CO hydrogenation-conversion and improvement in the selective formation of C_{2+} -alcohols. Under the reaction condition of 5.0 MPa, 613 K, $\text{CO}/\text{H}_2/\text{N}_2 = 45/45/10$ (v/v) and $\text{GHSV} = 3600 \text{ ml}_{\text{STP}} \cdot \text{h}^{-1} \cdot \text{g}_{\text{-cat.}}^{-1}$, the observed STY of C_{1-4} -alcohols reached $154.1 \text{ mg} \cdot \text{h}^{-1} \cdot \text{g}_{\text{-cat.}}^{-1}$ at 12.6% conversion of CO over the catalyst of 11.6% ($\text{Mo}_1\text{Co}_1\text{K}_{0.6}$)/(6.4%Co/CNTs), which was 1.76 and 2.33 times as high as that (87.7 and $66.1 \text{ mg} \cdot \text{h}^{-1} \cdot \text{g}_{\text{-cat.}}^{-1}$) of the reference systems supported by simple CNTs and AC respectively. Ethanol became the predominant product of the CO hydrogenation, with carbon-based selectivity ratio of C_{2-4} -alcohols to CH_3OH reaching 3.6 in the products.

It was experimentally found that using the Co-modified CNTs in place of simple

CNTs or AC as the catalyst support caused little change in the apparent activation energy for the hydrogenation conversion of CO, but led to a significant increase in the molar percentage of catalytically active Mo-species (Mo^{4+}) in the total Mo-amount at the surface of the functioning catalyst (as shown by XPS measurements of the functioning catalyst), and pronounced enhancement of the dissociatively adsorbed hydrogen H(a) and chemisorbed CO(a) at the surface of the functioning catalyst (as evidenced by H_2 (or CO)-TPD tests). It could be inferred that, under the reaction condition of HAS, there existed a considerably larger amount of adsorbed H-species and CO-species on the functioning catalyst of $11.6\%(\text{Mo}_1\text{Co}_1\text{K}_{0.6})/(6.4\%\text{Co}/\text{CNTs})$, thus in favour of increasing the rate of a series of surface hydrogenation reactions in HAS. Those factors mentioned above all play important roles in promoting the enhancement of activity of CO hydrogenation-conversion and the improvement of the selectivity of HAS.

II. Study on co-precipitated Mo-Co-K sulfide catalysts promoted by CNTs for HAS

Using the home-made CNTs as promoter, a type of sulfurized Mo-Co-K catalysts (symbolized as $\text{Mo}_i\text{Co}_j\text{K}_k\text{-}x\%\text{CNTs}$) was prepared by co-precipitation method. Their catalytic performance for HAS from syngas was evaluated and compared with that of the CNT-free counterpart $\text{Mo}_i\text{Co}_j\text{K}_k$. It was experimentally shown that appropriate incorporation of a minor amount of the CNTs into the $\text{Mo}_i\text{Co}_j\text{K}_k$ led to a significant increase in the catalyst activity for CO hydrogenation-conversion and an improvement in the selective formation of the higher alcohols. Under the reaction conditions of 5.0 MPa, 623 K, $V(\text{H}_2)/V(\text{CO})/V(\text{N}_2) = 60/30/10$, $\text{GHSV} = 3600 \text{ ml}_{\text{STP}}\cdot\text{h}^{-1}\cdot\text{g}_{\text{-cat.}}^{-1}$, the observed space-time-yield (STY) of total (C_{1-4}) alcohols reached $241.5 \text{ mg}\cdot\text{h}^{-1}\cdot\text{g}_{\text{-cat.}}^{-1}$ at CO percent-conversion of 21.6% over the catalyst of $\text{Mo}_1\text{Co}_1\text{K}_{0.3}\text{-}10\%\text{CNTs}$, which was 1.84 times as high as that ($131.0 \text{ mg}\cdot\text{h}^{-1}\cdot\text{g}_{\text{-cat.}}^{-1}$) of the CNT-free counterpart, $\text{Mo}_1\text{Co}_1\text{K}_{0.3}$; ethanol became the dominant product of the CO hydrogenation-conversion. It is also experimentally found that the water-gas-shift (WGS) side-reaction was inhibited to a greater extent over the CNT-promoted catalyst.

The results of catalyst characterization indicated that addition of a minor amount of the CNTs into the $\text{Mo}_1\text{Co}_1\text{K}_{0.3}$ caused little change in the apparent activation energy for the catalyzed hydrogenation-conversion of CO, but led to a significant increase in the molar percentage of catalytically active Mo-species (Mo^{4+}) in the total Mo-amount at the surface of the functioning catalyst.

The results of H_2 -TPD (temperature programmed desorption) measurements showed that significant difference existed between the CNT-promoted coprecipitated $\text{Mo}_1\text{Co}_1\text{K}_{0.3}$ catalyst and the CNT-free counterpart, in their adsorption/desorption behavior towards hydrogen. The observed relative area-intensity of the H_2 -TPD peak associated with the strongly adsorbed species (perhaps dissociatively chemisorbed H-species) on the CNT-promoted catalyst was 4.5 times as high as that of the CNT-free counterpart. Thus, it could be inferred that, under the conditions of the HAS, there existed a considerably larger amount of reversibly chemisorbed H-species at the functioning surface of the CNT-promoted catalyst, which would generate surface micro-environments with high stationary-state concentration of H-adspecies on the catalyst, thus increase the rate of a series of surface hydrogenation reactions in HAS. In addition, high stationary-state concentration of H-adspecies on the surface of catalyst would effectively inhibit WGS side-reaction. These factors mentioned above contribute considerably to an increase in the product yields.

In conclusions, the present work shows that the CNT-based material could serve not only as carrier, but also as an excellent promoter, for the sulphided $\text{Mo}_i\text{Co}_j\text{K}_k$ -based catalyst for HAS from syngas. In the two cases mentioned above, either for Co-modified CNTs as support or for simple CNTs as promoter, their incorporation into the sulphided $\text{Mo}_i\text{Co}_j\text{K}_k$ host catalyst caused little change in the apparent activation energy for the catalyzed hydrogenation-conversion of CO (likely implying that the major reaction pathway of the CO hydrogenation-conversion was not significantly changed), but led to a significant increase in the molar percentage of catalytically active Mo-species (Mo^{4+}) and pronounced enhancement in the

concentration of chemisorbed hydrogen-species at the surface of the functioning catalyst. These factors all play important roles in promoting the enhancement of activity of CO hydrogenation-conversion and the improvement of the selectivity of higher alcohol synthesis. For better understanding of nature of the promoting action by CNT-based materials, especially the mechanism of improving selective formation of the higher (C₂₊) alcohols, further studies, especially *in-situ* characterization of reaction intermediates under the HAS reaction condition, are highly needed.

Key words: Multi-walled carbon nanotubes, Co-modified carbon nanotubes, sulphided Mo-Co-K catalyst, CO hydrogenation, higher alcohol synthesis.

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