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碳纳米管负载/促进的甲苯加氢脱芳  
Pt 催化剂研究

Study of by CNT-supported / promoted Pt Catalyst for  
Hydro-dearomatization of Toluene

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**Study of CNT-supported / promoted Pt Catalyst for  
Hydro-dearomatization of Toluene**

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## 摘 要

加氢精制是石油炼制和石油化工的重要工艺过程之一,多年来一直受到催化学界的重视。随着重油和成品油加工深度及环境保护要求的提高,加氢精制,诸如加氢脱硫(HDS)、加氢脱氮(HDN)和加氢脱芳(HDA)等催化剂的工作效率仍待改进。工业上现行的 HDA 催化剂多是以  $\gamma\text{-Al}_2\text{O}_3$  为载体的负载型贵金属催化剂。作为载体的  $\gamma\text{-Al}_2\text{O}_3$ , 由于其与被担载的贵金属组分之间的相互作用较强,易形成比较稳定的、难于还原/活化的表面化合物种,不利于催化剂活性的提高。

多壁碳纳米管(Multi-walled carbon nanotubes, 简称为 CNTs, 下同)是一类新奇碳素纳米材料。典型的 CNTs 具有由  $sp^2\text{-C}$  构成的类石墨平面按一定方式叠合而成的纳米级管状结构。鉴于这类新奇管状纳米碳材料具有独特的结构和物化性质,作为一种新型碳素催化剂载体或促进剂,较之一些常规载体材料(如  $\text{Al}_2\text{O}_3$ ,  $\text{SiO}_2$ , AC 等)更具特色,近年来引起国际催化学界的日益注意,所涉及用 CNTs 作为新型催化剂载体或促进剂的研究领域包括:选择加氢、氢甲酰化、选择脱氢、氨合成、FT 合成、甲醇/低碳醇合成等。从化学催化角度考虑,多壁碳纳米管诱人的特性,除其高的机械强度、大而可修饰的表面、类石墨的管壁结构、以及纳米级的管腔外,其优良电子传递性能、对氢强的吸附能力并可期产生的氢溢流效应也很值得注意。

本文以自行制备的 CNTs 作为载体,经由等容浸渍法制备 CNTs 负载 Pt 加氢脱芳(HDA)催化剂,考察其对甲苯 HDA 的催化性能、并与常规载体(AC,  $\gamma\text{-Al}_2\text{O}_3$ )负载 Pt 参比体系作比较;利用 TEM/SEM/EDX, XRD, XPS,  $\text{H}_2\text{-TPR}$ ,  $\text{H}_2\text{-TPD}$  等多种物化表征方法对催化剂的制备过程及工作态催化剂体系进行表征研究,所获结果为深入了解 CNTs 的促进作用本质提供重要的实验和理论依据,对于一类高效新型 Pt 基加氢脱芳催化剂的设计和研发,也有重要现实意义。本文主要结果如下:

## 1. 碳纳米管负载/促进甲苯加氢脱芳 Pt 催化剂的制备和催化性能

- 1) CNTs 负载的铂催化剂(标记为:  $w\%Pt/CNTs$ ,  $w\%$ 为质量百分数)由等容浸渍法制备。Pt 负载量的优化调查实验在 0.4 MPa、373 K、 $n_{C_7H_8}/n_{H_2} = 6/94$  (mol/mol)、 $GHSV = 1.2 \times 10^5 \text{ ml}_{STP} \cdot \text{h}^{-1} \cdot \text{g}_{\text{cat}}^{-1}$  的反应条件下进行, 结果显示, 甲苯 HDA 转化率随着 Pt 负载量由 0 逐步增加而上升, 当 Pt 负载量为 1.0%(质量百分数)时甲苯 HDA 转化率达 100%, 随后趋于平稳, 表明 CNTs 负载催化剂的 Pt 负载量以 1.0%为最佳。所考察 8 种不同 Pt 负载量催化剂上甲苯 HDA 反应活性高低顺序为:  $1.2\%Pt/CNTs \approx 1.1\%Pt/CNTs \approx 1.0\%Pt/CNTs > 0.9\%Pt/CNTs > 0.8\%Pt/CNTs > 0.7\%Pt/CNTs > 0.5\%Pt/CNTs > 0.3\%Pt/CNTs$ 。对比制备实验表明, 对于  $Al_2O_3$  和 AC 负载的催化剂, 最佳 Pt 负载量分别为 1.4%和 2.4%。
- 2) 催化剂活性评价结果显示, 在  $1.0\%Pt/CNTs$  催化剂上, 0.4 MPa、373 K、 $n_{C_7H_8}/n_{H_2} = 6/94$  (mol/mol)、 $GHSV = 1.2 \times 10^5 \text{ ml}_{STP} \cdot \text{h}^{-1} \cdot \text{g}_{\text{cat}}^{-1}$  的反应条件下, 甲苯转化率达 100%, 相应的“比反应速率”[即: 单位时间(秒)内单位质量 Pt 组分(以毫摩尔 Pt 表示)上甲苯 HDA 转化量(以毫摩尔  $C_7H_8$  表示)]达到  $1.74 \text{ mmol}_{C_7H_8} \cdot \text{s}^{-1} \cdot \text{mmol}_{Pt}^{-1}$ , 是  $\gamma-Al_2O_3$  和 AC 分别负载对应物( $1.0\%Pt/\gamma-Al_2O_3$  和  $1.0\%Pt/AC$ )上这个值(分别为  $0.97$  和  $1.37 \text{ mmol}_{C_7H_8} \cdot \text{s}^{-1} \cdot \text{mmol}_{Pt}^{-1}$ )的  $1.79$  和  $1.27$  倍, 是  $\gamma-Al_2O_3$  和 AC 负载各自最佳 Pt 负载量催化剂( $1.4\%Pt/\gamma-Al_2O_3$  和  $2.4\%Pt/AC$ )上这个值(分别为  $1.17$  和  $0.73 \text{ mmol}_{C_7H_8} \cdot \text{s}^{-1} \cdot \text{mmol}_{Pt}^{-1}$ )的  $1.48$  和  $2.38$  倍。

## 2. 碳纳米管负载/促进甲苯加氢脱芳 Pt 催化剂的表征

- 1) 工作态催化剂的 XRD 图谱显示, 对于 CNTs 负载的催化剂  $1.0\%Pt/CNTs$ , 除观测到归属于 CNTs 的 XRD 特征衍射峰之外, 也出现归属于 Pt 微晶相的衍射峰, 但其强度比  $\gamma-Al_2O_3$  负载的对应物体系相应 XRD 峰的强度来得弱, 表明 Pt 组分在 CNTs 上高度分散, 其金属 Pt 处于更小的微晶、甚至非晶状态; 这与 TEM/SEM 观测到的绝大多数金属 Pt 颗粒粒径  $\leq 4 \text{ nm}$  的结果相一

致。

- 2) 催化剂的氧化态前驱物的 H<sub>2</sub>-TPR 测量结果显示, 被调查的 3 种载体负载催化剂的可还原性高低顺序为: 1.0%Pt/CNTs > 1.0%Pt/AC > 1.0%Pt/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>; 前者的“比耗氢量”(即单位质量 Pt 还原的耗氢量)是后两者相应比耗氢量分别的 1.28 和 1.61 倍。这一顺序与这些催化剂上甲苯 HDA 的“比反应速率”高低顺序相一致。
- 3) 工作态催化剂的 XPS 表征揭示, 两种碳素载体(CNTs 和 AC)负载催化剂的 Pt(4f)-XPS 谱峰的位置、峰形及其相对面积强度略有差别: 在 1.0%Pt/CNTs 催化剂表面总 Pt 量中, Pt<sup>0</sup>-物种所占摩尔百分数达 97.3 mol%, 是 AC 负载对应体系上这个值(86.8 mol%)的 1.12 倍。由此可见, 用 CNTs 代替 AC 作为 Pt 催化剂载体导致工作态催化剂表面催化活性 Pt 物种(Pt<sup>0</sup>)的浓度有所提高; 这也是以 CNTs 为载体的催化剂具有较高可还原性(见 H<sub>2</sub>-TPR 表征)的当然结果。与 AC 载体相比, 具有高度石墨化表面的 CNTs 在缓和所负载 Pt 组分与载体之间的相互作用、以抑制难还原 Pt 物种的生成方面似乎更有效。
- 4) 预还原催化剂的 H<sub>2</sub>-TPD 试样结果揭示, 与 AC 或  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> 负载的参比体系相比, CNTs 负载的 Pt 催化剂在室温至 773K 温度范围能可逆地吸附更大量的 H<sub>2</sub>。在 3 种催化剂试样上所观测 H<sub>2</sub>-TPD 谱峰在 323~773 K 温度范围的相对面积强度比为:  $S_{1.0\%Pt/CNTs} / S_{1.0\%Pt/AC} / S_{1.0\%Pt/\gamma-Al_2O_3} = 100/30/21$ ; 这个顺序与这 3 种催化剂上甲苯 HDA 的反应活性高低顺序相一致。

### 3. CNTs 载体的促进作用本质

本文结果表明, 在所考察 3 种载体负载的催化剂中, CNTs 负载催化剂 1.0%Pt/CNTs 对甲苯 HDA 反应具有最高的催化活性, 无论是相对于  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> 和 AC 分别负载等 Pt 负载量的对应物、抑或各自最佳 Pt 负载量的催化剂。然而, 对比实验却表明, 用 CNTs 代替常规载体  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> 和 AC 并不引起所负载 Pt 催化剂上低碳醇合成反应的表观活化能发生明显变化, 这暗示甲苯加氢脱芳的主要反应途径或速率决定步骤没有改变,。在另一方面, H<sub>2</sub>-TPR 和 XPS 的表征研究揭

示, 与  $\gamma\text{-Al}_2\text{O}_3$  和 AC 负载的对应体系相比, CNTs 负载催化剂更易于被还原, 工作态的 1.0%Pt/CNTs 催化剂表层催化活性 Pt 物种( $\text{Pt}^0$ )在总负载 Pt 量中所占份额较高; 这无疑有助于以 Pt 负载量为计算基准的催化剂比活性的提高, 但并非是导致不同载体负载催化剂活性差别的唯一原因。

基于  $\text{H}_2$ -TPD 实验调查结果, 能够推断, 在本文甲苯 HDA 反应条件下, 在 CNTs 载体上存在着相当大量的氢吸附物种, 这将有助于在工作态催化剂上营造较高稳态吸附氢浓度的表面氛围, 这些活泼氢吸附物种通过“氢溢流”容易传输至  $\text{Pt}^0$  催化活性位, 有助于加快甲苯加氢脱芳反应的进行。

上述结果能导向如下结论: (1) CNTs 是被担载 Pt 组分优良的分散剂, 并能缓和/削弱载体与被担载 Pt 组分之间的相互作用, 有助于后者在较低温度下还原活化、并产生较高表面浓度的催化活性 Pt 物种( $\text{Pt}^0$ ); (2) CNTs 也是优良的  $\text{H}_2$  吸附、活化、储存剂, 这有助于在工作态催化剂表面营造高浓度活泼氢吸附物种的表面氛围, 以提高表面加氢反应的速率。以上两方面的促进效应对催化剂活性的提高都有重要贡献。

**关键词:** 多壁碳纳米管, 碳纳米管负载 Pt 催化剂, 甲苯, 加氢脱芳.



## Extended Abstract

The saturation of aromatic compounds in distillate fractions and in particular in diesel fuel has received considerable attention in recent years. A high aromatic content is associated with poor fuel quality, giving a low cetane number in diesel fuel and a high smoke point in jet fuel. New legislation has been introduced to limit aromatics in diesel fuel and this has led to new catalyst and process developments. Industrial hydro-dearomatization catalytic processes have been largely carried out on noble metals/ $\text{Al}_2\text{O}_3$  hydrogenation catalysts. Notable features of alumina supports include their ability to provide high dispersion of the active metal components. However, the results have also shown that numerous chemical interactions exist between the amorphous alumina and transition metal oxides in the precursor state.

Multi-walled carbon-nanotubes (MWCNTs, 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 a series of 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 this dissertation, highly active CNT-supported Pt catalysts were prepared by the conventional incipient wetness method. Their catalytic performance for hydro-dearomatization (HDA) of toluene was evaluated, and compared with the reference systems based on  $\gamma$ - $\text{Al}_2\text{O}_3$  and activated carbon (AC). Using a number of physico-chemical methods (TEM/SEM/EDX, XRD, XPS,  $\text{H}_2$ -TPR,  $\text{H}_2$ -TPD, etc), these catalyst systems were characterized. The results shed some light on understanding the nature of promoter action by the CNTs and the prospect of developing highly active catalysts. The progresses obtained in the present work were briefly described as follows:

## 1. Preparation and performance of CNT-supported/promoted Pt catalyst for HDA of toluene

- 1) The optimization test of Pt-loading amount showed that over the eight catalyst samples with different Pt-loading amounts under reaction condition of 0.4 MPa, 373 K,  $C_7H_8/H_2 = 6/94$  (mol/mol),  $GHSV = 1.2 \times 10^5 \text{ ml}_{\text{STP}} \cdot \text{h}^{-1} \cdot \text{g}_{\text{-cat.}}^{-1}$ , the observed sequence of reactivity of toluene HDA is as follows:  $1.2\%Pt/CNTs \approx 1.1\%Pt/CNTs \approx 1.0\%Pt/CNTs > 0.9\%Pt/CNTs > 0.8\%Pt/CNTs > 0.7\%Pt/CNTs > 0.5\%Pt/CNTs > 0.3\%Pt/CNTs$ , with  $\sim 1.0\%$  (mass percentage) of Pt-loading amount optimal.
- 2) It was experimentally demonstrated that the support could significantly affect the catalyst activity for the HDA reaction. Over  $1.0\%Pt/CNTs$  catalyst under the reaction conditions of 0.4 MPa, 373 K,  $C_7H_8/H_2 = 6/94$  (mol/mol),  $GHSV = 1.2 \times 10^5 \text{ ml}_{\text{STP}} \cdot \text{h}^{-1} \cdot \text{g}_{\text{-cat.}}^{-1}$ , the observed conversion of toluene HDA reached 100%, the corresponding specific reaction rate was  $1.74 \text{ mmol}_{C_7H_8} \cdot \text{s}^{-1} \cdot \text{mmol}_{Pt}^{-1}$ . This value was 1.79 and 1.27 times as high as that ( $0.97$  and  $1.37 \text{ mmol}_{C_7H_8} \cdot \text{s}^{-1} \cdot \text{mmol}_{Pt}^{-1}$ ) of the counterparts supported by  $\gamma\text{-Al}_2\text{O}_3$  and AC, respectively, and was 1.48 and 2.38 times as high as that ( $1.17$  and  $0.73 \text{ mmol}_{C_7H_8} \cdot \text{s}^{-1} \cdot \text{mmol}_{Pt}^{-1}$ ) of the catalysts supported by  $\gamma\text{-Al}_2\text{O}_3$  and AC with the respective optimal Pt-loading amount ( $1.4\%Pt/\gamma\text{-Al}_2\text{O}_3$  and  $2.4\%Pt/AC$ ), respectively.

## 2. Characterization of CNT-supported/promoted Pt catalyst for HDA of toluene

- 1) XRD measurement of the functioning catalyst of  $1.0\%Pt/CNTs$  catalyst showed that, except the features present at  $2\theta = 26.1^\circ$ ,  $43.1^\circ$  and  $53.5^\circ$ , which were due to the diffractions of (002), (100) and (004) planes, respectively, of graphitized tube-wall of the CNTs, the peaks due to Pt were detected at  $2\theta = 39.7^\circ$ ,  $46.3^\circ$ , and  $67.3^\circ$ , which were due to the diffractions of (111), (200), and (220) planes of metallic Pt. Those peaks, especially the one at  $2\theta = 39.7^\circ$ , were considerably

weak, and obviously weaker than that of the counterpart based on  $\gamma\text{-Al}_2\text{O}_3$ , implying that the supported Pt component was highly dispersed at the surface of CNTs, and existed mostly in states of smaller micro-crystalline, even non-crystalline.

- 2) The  $\text{H}_2$ -TPR profiles taken on the three precursors of catalysts supported by the CNTs, AC and  $\gamma\text{-Al}_2\text{O}_3$ , respectively, with the same Pt-loading amount showed that the position ( $\sim 498$  K) of  $\text{H}_2$ -reduction peak of the 1.0%Pt/CNTs catalyst was somewhat lower than that (506 K or 531 K) of the system based on AC or  $\gamma\text{-Al}_2\text{O}_3$ , while its specific  $\text{H}_2$ -consumed amount (i.e., the amount of hydrogen consumed due to reduction of unit mass of Pt) was 1.28 and 1.61 times as high as that of the systems based on AC and  $\gamma\text{-Al}_2\text{O}_3$  respectively, indicating that the reducibility of the CNT-supported catalyst was much higher than that of the reference system supported by AC or  $\gamma\text{-Al}_2\text{O}_3$ .
- 3) XPS measurements revealed that using the CNTs in place of AC or  $\gamma\text{-Al}_2\text{O}_3$  as support of the catalyst led to a slight increase in concentration of catalytically active Pt-species ( $\text{Pt}^0$ ) at the surface of the functioning catalyst. On the functioning 1.0%Pt/CNTs catalyst, the observed molar percentage of  $\text{Pt}^0$ -species in the total surface Pt-amount reached 97.3%. This value is 1.12 times as high as that (86.8%) of the counterpart supported by AC. Compared to the AC support, the CNTs with highly graphitized surface seem to be more effective in mitigating chemical interactions between the supported Pt component and the support to inhibit formation of some of Pt species, which are very stable and difficult to be reduced.
- 4)  $\text{H}_2$ -TPD tests of the pre-reduced catalysts revealed that the CNT-supported Pt-catalyst could reversibly adsorb a greater amount of hydrogen under atmospheric pressure at temperatures from room temperature to 773 K, compared to the counterpart supported by AC or  $\gamma\text{-Al}_2\text{O}_3$ . The ratio of the relative area-intensities of the observed  $\text{H}_2$ -TPD profiles in the range of 323~773 K was as follows:  $S_{1.0\%Pt/CNTs} / S_{1.0\%Pt/AC} / S_{1.0\%Pt/\gamma\text{-Al}_2\text{O}_3} = 100/30/21$ ; this sequence was in line with the observed reaction activity of toluene HDA over these catalysts.

### 3. Nature of the promoting action by the CNT-support

Based upon the aforementioned results about the preparation study of catalyst and the assay of HDA activity, as well as the characterization of the functioning catalysts, it has been demonstrated that the CNT-material could serve not only as carrier, but also as an excellent promoter, for the Pt-based catalyst for HDA of toluene. It was experimentally shown that using the CNTs in place of AC or  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> as support of the catalyst caused little change in the apparent activation energy for toluene HDA reaction, likely implying that the major reaction pathway of the toluene hydrogenation-conversion was unchanged, however, it led to a slight increase in concentration of catalytically active Pt-species (Pt<sup>0</sup>) at the surface of the functioning catalyst. In addition, the Pt/CNTs catalyst could reversibly adsorb a greater amount of hydrogen under atmospheric pressure at temperatures from room temperature to 573 K. This unique feature would help to generate microenvironments with higher stationary state concentration of active hydrogen-adspecies at the surface of the functioning catalyst. Both factors mentioned above were favorable to increasing the rate of toluene HDA reaction.

**Keywords:** multi-walled carbon nanotubes, CNT-supported Pt catalyst, toluene, hydro-dearomatization.

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### 第三章 碳纳米管负载/促进的 Pt 基催化剂甲苯加氢脱芳研究

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