氧化铈的结构对其热稳定性及催化丙烷氧化脱氢反应性能的影响

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摘要: 采用湿化学法制备了低维氧化铈的纳米棒和纳米颗粒, 通过原位 X 射线粉末衍射、透射电镜和 N₂ 物理吸附等技术研究了氧化铈纳米结构对其热稳定性的影响。结果表明, 氧化铈纳米棒的稳定性更高。采用浸渍法制备了氧化铈负载的氧化钒催化剂, 并用于丙烷氧化脱氢反应中, 发现以氧化铈纳米棒为载体的催化剂表现出更高的丙烯选择性, 这可能是由于棒状结构的开放性有利于产物丙烯的直接扩散。

关键词: 氧化铈; 纳米结构; 热稳定性; 丙烷; 氧化脱氢

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Structural Effects of Cerium Oxides on Their Thermal Stability and Catalytic Performance in Propane Oxidation Dehydrogenation

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Abstract: The low-dimensional ceria nanorods and nanoparticles were prepared by wet chemical methods. The structural effect on the thermal stability of CeO₂ has been well investigated by in situ X-ray powder diffraction, transmission electron microscopy, and N₂ physisorption, revealing a superior stability of CeO₂ nanorods. CeO₂-supported V₂O₅ catalysts were prepared by the incipient wetness impregnation method and their catalytic performance in the oxidative dehydrogenation of propane was evaluated. The V₂O₅/CeO₂ nanorods catalysts display an improved selectivity for propene, probably arising from the immediate diffusion of propene product due to the open characteristic of rod-like structure.

Key words: cerium oxide; nanostructure; thermal stability; propane; oxidation dehydrogenation

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CeO₂ 作为一种具有独特 *f* 层电子结构的稀土材料, 广泛应用于催化^[1~4]、燃料电池电极^[5]、化妆品^[6]、陶瓷和涂层材料等领域。在多相催化领域,

CeO₂ 因具有独特的储放氧能力而备受关注。近来的 Mai 等^[7]和 Lawrence 等^[8]的研究表明无论是作为催化剂还是催化剂载体, CeO₂ 纳米结构都表现出比块

体材料更优越的性能。人们采用多种方法制备了纳米棒^[7,9,10]、纳米颗粒^[11–13]、纳米立方体^[7]和纳米管^[14–16]等不同形貌的 CeO_2 。然而, 纳米颗粒高的表面/体相比和表面张力, 可能降低纳米结构的热稳定性。许多报道致力于研究纳米尺寸的 CeO_2 在高温下作为催化剂载体的烧结现象^[17–19]。Andrievskii 等^[20]发现纳米结构的热稳定性取决于制备方法和形貌。本文采用常见的方法制备了 CeO_2 纳米颗粒和纳米棒, 通过原位 X 射线衍射 (XRD)、透射电镜 (TEM) 和 N_2 物理吸附等方法进行了表征; 同时, 以丙烷氧化脱氢为探针反应, 评价了纳米 CeO_2 负载的 V_2O_5 催化性能。

采用共沉淀法制备 CeO_2 纳米颗粒。将 100 g $\text{CO}(\text{NH}_2)_2$ 和 32.2 g $(\text{NH}_4)_2\text{Ce}(\text{NO}_3)_6$ 在烧杯中混合, 溶解于超纯水后加热到 90 °C, 持续搅拌下反应 12 h, 得到的黄色沉淀用超纯水洗涤, 并在 80 °C 干燥过夜。采用水热法制备 CeO_2 纳米棒: 24 g NaOH 和 0.64 g $\text{Ce}_2(\text{SO}_4)_3$ 分别溶解在超纯水中, 混合后搅拌 20 min, 转移到 100 ml 带聚四氟内衬的不锈钢反应釜中, 于 160 °C 水热反应 14 h, 抽滤洗涤得到的浅黄色滤饼, 在 80 °C 干燥过夜。将得到的两个样品放入石英舟, 于空气气氛中分别在 200, 400, 600 或 800 °C 焙烧 4 h。采用浸渍法制备 $\text{V}_2\text{O}_5/\text{CeO}_2$ 催化剂: 取一定量的 NH_4VO_3 溶解于草酸溶液中, 然后加入所制 CeO_2 粉末, 在 120 °C 干燥 12 h 即得催化剂样品。实验中所有试剂均购买于国药试剂公司。

样品形貌在荷兰 FEI Tecnai F20 型 TEM 上观察, 加速电压 200 kV。XRD 实验在德国 Bruker D8 型 X 射线衍射仪上进行, Cu 靶 K_α ($\lambda = 0.15432$ nm) 和 Mo 基底。在高真空 (1×10^{-5} Pa) 条件下, 以 1 °C/min 升到指定温度, 保持 10 min, 开始摄谱。 N_2

物理吸附实验在美国 Micromeritics ASAP 3020 型吸附仪上进行, 实验前样品在 150 °C 脱气 12 h。

催化剂评价在石英反应器中进行, 样品用量 150 mg, 通入 30 ml/min 的原料气 (C_3H_8 8.3%, $\text{C}_3\text{H}_8:\text{O}_2$ (摩尔比) = 1:1, He 平衡), 稳定在 450 °C 进行反应。反应产物通过安捷伦 7890A 型气相色谱在线分析。

图 1 为制备的纳米 CeO_2 样品的 TEM 照片。可以看出, 制备的 CeO_2 样品为直径 20~30 nm 均匀分布的棒状结构。晶面间距 0.27 和 0.31 nm 分别对应 CeO_2 晶相的 (002) 和 (111) 晶面, 与文献[21,22]结果一致, 其尖锐的衍射峰表明样品具有一定的结晶度。共沉淀法制备的 CeO_2 样品是尺寸约 7 nm 的均匀粒子, 并且从 HRTEM 照片上可以看到 CeO_2 晶相的各晶面指数。

图 2 为不同焙烧温度下 CeO_2 纳米棒和纳米颗粒的原位 XRD 谱。位于 28°, 33°, 47°, 56° 和 69° 处五个宽化的衍射峰对应于面心立方萤石结构的 CeO_2 晶相 (JCPDS 34-0394)。这些衍射峰随温度的升高而向小角度有所移动。 CeO_2 纳米颗粒衍射峰随着温度的升高而变得更加尖锐, 且在 600 °C 时出现明显的烧结现象。通过分析最强峰 (111) 晶面的半宽高, 可以发现, 随温度从 600 °C 升至 1000 °C, 纳米颗粒的粒子尺寸从 6.1 nm 增至 19.8 nm (见表 1)。而对于纳米棒, 当温度升高到 600 °C 时, CeO_2 晶相的衍射峰强度逐渐降低, 并出现一些新的衍射峰 (如 26°, 37° 和 45°), 可归属为非计量比氧化铈 ($\text{CeO}_{2-\delta}$), 例如 Ce_4O_7 , Ce_7O_{12} ($\text{CeO}_{1.698}$), Ce_7O_{12} , $\text{CeO}_{1.67}$, Ce_2O_3 和 Ce_6O_{11} , 反映了高温下氧物种的释放。

由谢乐公式算得各样品晶粒尺寸随温度的变化见表 1。可以看出, 纳米棒的晶粒尺寸基本上保持在

图 1 CeO_2 纳米结构的 TEM 照片

Fig. 1. TEM images of CeO_2 nanostructures. (a) TEM of CeO_2 nanorods; (b) HRTEM of CeO_2 nanorods (inset: a fast Fourier transform); (c) TEM of CeO_2 nanoparticles; (d) HRTEM of CeO_2 nanoparticles.

图 2 不同温度焙烧后 CeO_2 纳米结构的原位 XRD 谱

Fig. 2. In situ XRD patterns of CeO_2 nanostructures calcined at various temperatures. (a) CeO_2 nanoparticles; (b) CeO_2 nanorods. RT—Room temperature.

25~29 nm, 而这些波动可能与纯相 CeO_2 相转变为非计量比的化合物有关; 但纳米颗粒的尺寸明显增大了两倍, 表明其稳定性更低. 另外, 从室温到 600 °C, 纳米棒和纳米颗粒的比表面积分别降低了 30% 和 59%, 而经过 800 °C 焙烧 4 h 后, 纳米棒仍达 17.3 m^2/g 的比表面积, 是纳米颗粒的三倍, 进一步表明纳米棒的稳定性更高.

图 3 800 °C 焙烧过 CeO_2 纳米结构的 TEM 照片

Fig. 3. TEM images of CeO_2 nanostructures after 800 °C calcination. (a) TEM of CeO_2 nanorods; (b) HRTEM of CeO_2 nanorods; (c) TEM of CeO_2 nanoparticles; (d) HRTEM of CeO_2 nanoparticles.

表 1 CeO_2 纳米结构的比表面积和晶粒尺寸随温度变化结果

Table 1 Specific surface area and crystal size of CeO_2 nanostructures calcined at different temperature

Temperature (°C)	$A_{\text{BET}}/(\text{m}^2/\text{g})$		Crystal size (nm)	
	Nanorods	Nanoparticles	Nanorods	Nanoparticles
RT	57.3	153.3	—	6.1
200	57.1	149.6	—	6.2
400	46.1	135.5	—	6.3
500	—	—	—	6.4
600	40.0	63.2	25.7	6.9
700	—	—	29.9	7.9
800	17.3	5.7	29.6	10.1
900	—	—	26.2	14.8
1000	—	—	25.0	19.8

图 3 为 800 °C 焙烧后 CeO_2 纳米结构的 TEM 照片. 由图可见, 纳米棒虽然很大程度上保持着棒状结构, 但是由于一些结点的形成, 最终变为一种长南瓜结构. 这可能是由于在 CeO_2 相转变为非计量比化合物的过程中为了缓解高温产生的应力, 保持热力学系统的稳定而发生了体积收缩. 焙烧处理对纳米颗粒的形貌产生了很大的影响, 出现了明显的团聚现象, 图 3(d) 中标识了纳米颗粒中烧结颗粒间的晶界, 也与 XRD 结果相符.

低碳 (C2~C4) 烯烃是聚合物生产中最重要 的化学原料, 其需求的不断增长推动了对高效 生产工艺的研究, 其中丙烷氧化脱氢作为一种 替代工艺, 可以在低温下获得理论上的丙烯 产率. CeO_2 纳米结构由于存在高浓度氧空 位而广泛用作氧离子导体^[23,24]. 表 2 为纳 米 CeO_2 样品负载不同量的 V_2O_5 催化丙 烷氧化脱氢的活性及丙烯的选择性. 可以看 出, 各纳米棒负载催化剂活性位点 V_2O_5 上 的丙烯转化频率 (turn over frequents, TOF) 高 于维持在 6.5 h^{-1} 的纳米颗粒, 且当 V_2O_5 负 载量为 2.5% 时, TOF 达最大

表 2 各 V_2O_5/CeO_2 催化剂上丙烷氧化脱氢反应性能Table 2 Propane oxidation dehydrogenation performance of V_2O_5/CeO_2 catalysts

Sample	TOF (h^{-1})		C_3H_8 selectivity (%)	
	Nanorods	Nanoparticles	Nanorods	Nanoparticles
1.0% V_2O_5/CeO_2	9.1	6.8	11.5	8.4
2.5% V_2O_5/CeO_2	10.7	5.9	35.0	20.3
5.0% V_2O_5/CeO_2	10.1	7.6	62.4	40.2
10% V_2O_5/CeO_2	5.6	6.0	69.7	61.3

Reaction conditions: catalyst 0.15 g, 450 °C, 8.3% propane, $C_3H_8:O_2$ molar ratio = 1:1, total flow 30 ml/min, He as balance.

值为 $10.7 h^{-1}$ 。同时, 系列纳米棒催化剂上丙烯选择性也更高, 如 5% V_2O_5/CeO_2 催化剂的丙烯选择性为 62.4%, 是同等条件下纳米颗粒的 1.5 倍。基于棒状结构的开放性, 我们认为其优异的选择性源于丙烯分子在棒状结构活性位点上的有效扩散, 从而抑制了丙烯的深度氧化。丙烯产率在 V_2O_5 的表面浓度为 $5\sim 7 nm^{-2}$ 时达到最大值, 也与 Daniell 等^[25]的结果相符。与文献[26,27]报道的 Al_2O_3 , SiO_2 和 ZrO_2 等负载的 V_2O_5 催化剂上丙烷氧化脱氢反应性能相比, CeO_2 活性较 Al_2O_3 和 ZrO_2 的稍低, 但高于 SiO_2 的, 且丙烯选择性更高。

综上所述, 通过水热法和共沉淀法分别制备了尺寸均匀的 CeO_2 纳米棒和纳米颗粒。结果表明, CeO_2 纳米棒具有更高的热稳定性, 经 800 °C 焙烧后, 纳米棒变为多节结构。另外, 随温度的升高, CeO_2 纳米棒形成了多种非计量比的 CeO_2 晶相。在丙烷氧化脱氢反应中, 负载 V_2O_5 的 CeO_2 纳米棒表现出更高的丙烯选择性。 CeO_2 纳米棒热稳定性和催化性能提高的机制, 还有待于进一步的研究。

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英 译 文

English Text

Cerium oxide as one typical rare earth material has a special *f*-shell electronic structure, having been widely used in various applications of catalyst [1–4], fuel cell electrolyte [5], fluorescent materials, cosmetics [6], ceramics and coating materials. In the research field of heterogeneous catalysis, CeO_2 nanostructures are greatly attractive owing to the unique capacity to store and release oxygen under the reaction conditions. Recently, considerable researches have shown that nanostructured CeO_2 gives a superior performance to bulk CeO_2 when they are used as either catalyst or support [7,8]. The researchers have explored many methods to prepare different morphologies of CeO_2 nanostructures such as nanorods [7,9,10], nanoparticles [11–13], nanocubes

[7], nanotubes [14–16], etc. However, the infinite size of nanoparticles triggers a high surface-to-volume ratio and surface tension, probably lowering the thermal stability of CeO_2 nanostructures. Many reports have focused on the sintering phenomenon in nano-sized CeO_2 as the catalyst support for some high-temperature processes [17–19]. It is reported that the stability of nanomaterials greatly depends on their morphologies and manufacture [20]. We applied the commonly used methods to produce CeO_2 nanoparticles and nanorods. A direct comparison on their thermal stability was allowed by using in-situ X-ray diffraction (XRD), transmission electron microscopy (TEM), and nitrogen physisorption. Finally, the catalytic applications of CeO_2 nanomaterials as the support for V_2O_5 nanoparticles were evaluated.

CeO_2 nanoparticles and nanorods were prepared via coprecipitation and hydrothermal methods, respectively. $\text{CO}(\text{NH}_2)_2$ (100 g) and of $(\text{NH}_4)_2\text{Ce}(\text{NO}_3)_6$ (32.2 g) were dissolved in the ultrapure water. Both solutions were added simultaneously to a glass beaker, heated to 90 °C and then maintained for 12 h with stirring. The yellow precipitate was removed, washed thoroughly with ultrapure water, and dried overnight at 80 °C. To prepare the nanorods, 24 g of NaOH and 0.64 g of $\text{Ce}_2(\text{SO}_4)_3$ were separately dissolved in the ultrapure water and then mixed together. The system was stirred for 20 min before transferred to a 100 ml Teflon-lined stainless steel autoclave. The hydrothermal treatment at 160 °C was performed for 14 h. After the solution was filtered out, we thoroughly washed the pale yellow cake and dried overnight at 80 °C. The obtained samples were moved to a quartz boat and calcined at different temperatures (200, 400, 600, and 800 °C) in air for 4 h. Two series of $\text{V}_2\text{O}_5/\text{CeO}_2$ catalysts with various loadings were prepared via the incipient wetness impregnation method. A certain amount of NH_4VO_3 was dissolved in oxalic acid solution, and then the CeO_2 powder was immersed into the solution. The mixture was dried at 120 °C for 12 h. All reagents in this report were purchased from Sinopharm Group Co. Ltd.

TEM measurements were performed on a FEI Tecnai F20 microscope with an accelerating voltage at 200 kV. XRD tests were taken on a Germany Bruker D8 Discover diffractometer using Cu target K_α as light source ($\lambda = 0.15432$ nm) and a metal Mo holder. In high vacuum (1×10^{-5} Pa) conditions, the sample was heated to a certain temperature at a ramp of 1 °C/min and kept for 10 min before the diffraction patterns were collected. Nitrogen physisorption experiments were carried out on a Micromeritics ASAP 3020 instrument. The samples were degassed in vacuum at 150 °C for 12 h to remove physically adsorbed components.

The catalytic activities were evaluated in a quartz micro-reactor by using 150 mg of sample. The reactant (30 ml/min, C_3H_8 8.3%, $\text{C}_3\text{H}_8:\text{O}_2$ (molar ratio) = 1:1, He as balance) was introduced into the reactor after the temperature stabilized at

450 °C. The chemical composition of the product mixture was analyzed by an online gas chromatograph (Agilent 7890A).

The TEM images of as synthesized CeO_2 nanostructures are shown in Fig. 1. The obtained nanorods feature a homogeneous distribution of diameter ranging from 20 to 30 nm (Fig 1(a)). The lattice spacing distances of 0.27 and 0.31 nm reveal the (002) and (111) planes, respectively, of the CeO_2 phase. The sharp lattice fringes suggest a certain degree of crystallinity, agreeing with the literature on hydrothermal synthesis of CeO_2 nanorods [21,22]. The nanoparticles that derived from the coprecipitation method display uniform particle sizes of around 7 nm and the HRTEM images report all typical lattice distances corresponding to the CeO_2 crystal phase (Figs. 1(c) and (d)).

Figure 2 depicts the in situ XRD patterns of CeO_2 nanorods and nanoparticles at different temperatures. Five broadening peaks at 28°, 33°, 47°, 56°, and 69° indicate the presence of cubic CeO_2 phase with the fluorite structure (JCPDS 34-0394). Such representative peaks shift downward to some extent with the increasing temperature. For the nanoparticles, the diffraction peaks of CeO_2 gradually sharpened with the increasing temperature and sintering of nanoparticles become significant when the temperature is higher than 600 °C. After the analysis by the width at half height of the strongest (111) peak, we can observe an increase in particle size of CeO_2 from 6.1 to 19.8 nm with the elevating temperature from 600 to 1000 °C (Fig. 2). For the nanorods, the intensity of CeO_2 phase gradually lowered and several small peaks (e.g. 26°, 37°, and 45°) appeared as the temperature reached 600 °C. The new peaks can be attributed to the nonstoichiometric cerium oxides ($\text{CeO}_{2-\delta}$) such as Ce_4O_7 , $\text{CeO}_{1.695}$, Ce_7O_{12} , $\text{CeO}_{1.675}$, Ce_2O_3 , and Ce_6O_{11} , revealing the release of oxygen species at high temperature.

The specific surface area and crystal size of CeO_2 nanostructures calcined at different temperatures are shown in Table 1. The particle size of nanorods remains almost unchanged at 25–29 nm and the vibration can be related with the phase transformation of pure CeO_2 to various non-stoichiometric phases. However, the value of nanoparticles significantly increases nearly by twice, showing an inferior stability to the nanorods. The nanorods sample also displays the better stability of porosity than nanoparticles. As the temperature was elevated from room temperature to 600 °C, the surface areas of nanorods and nanoparticles were decreased for around 30% and 59%, respectively. After calcined at 800 °C for 4 h, the nanorods still kept a surface area of 17.3 m²/g being three times that of nanoparticles.

Figure 3 shows the TEM images of CeO_2 nanostructures calcined at 800 °C for 4 h. The characteristic of nanorods still keep to a large extent but some kinks form to produce a long squash structure. The reason can be attributed to the volume

shrinkage of phase transformation into the nonstoichiometric phase in order to release the produced stress and maintain a thermodynamically stable system. Calcination treatment has a strong effect on the morphology of nanoparticles to cause the significant agglomeration, in agreement with the XRD results in Fig. 2. HRTEM images identify the grain boundary among several particles due to the sintering of nanoparticles.

Low-carbon (C2–C4) olefins are the most important chemical feedstocks in polymer industry and the uprising worldwide demand continuously drives the investigation on highly efficient production technologies. Oxidative dehydrogenation of propane as an alternative route can be run at low temperatures with a theoretically high yield of propene. Nanostructured CeO₂ is well known as an oxygen-ion conductor due to its large amount of oxygen vacancies [23,24]. Table 2 gives the steady-state activity and propene selectivity of CeO₂-supported V₂O₅ catalysts with various loadings. With the increasing loading of V₂O₅, the activity of nanorods (mmol propene per mmol V₂O₅ per hour) over nanoparticles which remains at 6.5 h⁻¹ while that over nanorods approaches to the maximum, i.e. 10.7 h⁻¹, at the loading of 2.5%. Moreover, the series of nanorods display a superior selectivity for propene. For example, the 5% V₂O₅/CeO₂ nanorods sample gives 63% propene selectivity being around 1.5 times that of 5% V₂O₅/CeO₂ nanoparticles. Considering the open-

ing characteristic of nanorods as the support, we may attribute the reason to the efficient diffusion of produced propene molecules from the active sites to prevent the deep oxidation to some degree. Propylene yield achieved the maximum when V₂O₅ surface density was 5–7 nm⁻², which were consistent with Daniell's [25] results. Meanwhile, comparing with the oxidative dehydrogenation of propane performance of in the literature [26,27], V₂O₅/CeO₂ had a higher activity than that of V₂O₅/SiO₂, and lower than V₂O₅/Al₂O₃ and V₂O₅/ZrO₂, but with a selectivity advantage.

In conclusion, CeO₂ nanorods and nanoparticles with the uniform size were prepared by hydrothermal and precipitation methods, respectively. The nanorod sample possesses a higher thermal stability of both porosity and morphology. A kink-rich structure of nanorods can be observed after the calcination treatment at 800 °C. The in situ XRD identified the formation of more sorts of non-stoichiometry cerium oxides. Nanorods display the superior propene selectivity to nanoparticles when they were used as the support for V₂O₅ to catalyze the oxidative dehydrogenation of propane. A detailed investigation will be made to clarify the mechanism of improved thermal and catalytic performance.

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