

以水热法合成的 ZrO_2 负载 Au 催化剂上的低温水煤气变换反应

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摘要: 采用一种简便的水热法合成了一系列 ZrO_2 , 并采用沉积-沉淀法制得相应 1.0% Au/ ZrO_2 催化剂, 在模拟甲醇重整气气氛下评价了它们的低温水煤气变换 (WGS) 反应催化性能. 结果发现, 于 150 °C 水热合成的 ZrO_2 负载的 Au 催化剂活性最佳, 240 °C 反应时 CO 转化率达 87%, 明显高于相同反应条件下 Au 负载量较高的 Au/ Fe_2O_3 , Au/ CeO_2 及 Au/ $CeZrO_4$ 催化剂. 采用 X 射线衍射、原子吸收光谱、 N_2 物理吸附脱附及扫描电子显微镜等手段对样品进行了表征. 结果表明, Au/ ZrO_2 催化剂的总孔体积及平均孔径越大、圆形片状形貌越规整, 其低温 WGS 催化活性就越高.

关键词: 水热法; 水热合成温度; 金; 二氧化锆; 负载型催化剂; 水煤气变换反应

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Low-Temperature Water-Gas Shift Reaction over Au/ ZrO_2 Catalysts Using Hydrothermally Synthesized Zirconia as Supports

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Abstract: Au/ ZrO_2 catalysts with a nominal gold loading of 1.0% were prepared by a deposition-precipitation method employing a series of ZrO_2 samples synthesized by a convenient hydrothermal route as supports. These catalysts were evaluated for low-temperature water-gas shift reaction under a model reformed methanol gas atmosphere. The effect of the hydrothermal synthesis temperature of zirconia on the catalytic activity of Au/ ZrO_2 was investigated. The optimal hydrothermal synthesis temperature of ZrO_2 was 150 °C. The corresponding catalyst offers a CO conversion of 87% at a reaction temperature of 240 °C, which is significantly higher than that of the previously reported Au/ Fe_2O_3 , Au/ CeO_2 , and Au/ $CeZrO_4$ catalysts. The Au/ ZrO_2 catalysts were characterized by X-ray diffraction, atomic absorption spectrometry, N_2 -physisorption, and scanning electron microscopy. The results indicate that the catalytic performance of the Au/ ZrO_2 catalysts is mainly influenced by the morphology and pore structure of the ZrO_2 that was hydrothermally synthesized at different temperatures. A uniform nanodisk morphology and increase in the pore volume and pore diameter of the ZrO_2 particles lead to a higher catalytic activity of the Au/ ZrO_2 catalyst.

Key words: hydrothermal method; hydrothermal synthesis temperature; gold; zirconia; supported catalyst; water-gas shift reaction

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水煤气变换 (WGS) 反应主要用于净化合成气, 为合成氨等反应过程提供洁净的 H_2 来源. 近年来,

由于以纯氢为燃料的车载质子交换膜燃料电池 (PEMFC) 技术的兴起, 使得这一经典反应再次引起

研究者的极大兴趣^[1,2]. 负载 Au 催化剂具有较高的低温活性、较宽的活性温区、较好的抗氧化性能及抗水性能, 因而被认为是最适合用于 PEMFC 苛刻操作环境的 WGS 催化剂之一^[3,4].

目前, 具有较好 WGS 催化活性的负载 Au 催化体系包括 $\text{Au/Fe}_2\text{O}_3$ ^[5-7], Au/CeO_2 ^[8-11], Au/TiO_2 ^[12], Au/ThO_2 ^[13], $\text{Au/Cu}_x\text{Mn}_y\text{O}_z$ ^[14], Au/CeZrO_4 ^[15-17] 及 Au/ZrO_2 ^[5,18-23] 等. 其中, Au/ZrO_2 因性能优异而成为近年来的研究热点. 研究发现, ZrO_2 的晶型^[18]、颗粒及晶粒大小^[19]、表面羟基的浓度^[19]以及比表面积^[20]等性质对 Au/ZrO_2 催化剂的性能有显著影响. 例如, Au 负载在单斜相 ZrO_2 (m- ZrO_2) 上比负载在四方相 ZrO_2 (t- ZrO_2) 上具有更高的低温 WGS 催化活性^[18]; ZrO_2 晶粒尺寸增大会减少催化剂的活性中心, 即 Au- ZrO_2 接触边界的浓度^[19]等. 而这些性质又直接由 ZrO_2 的制备方法所决定, 因此选择合适的 ZrO_2 制备方法对于提高催化剂性能、研究催化剂结构-性能之间的关系以及进一步指导催化剂的优化具有重要的意义. 目前, 文献所报道的 Au/ZrO_2 催化剂中 ZrO_2 载体主要采用回流法^[18,19]、沉淀法^[5,20-22]及水热模板法^[23]制备, 而以无需模板剂的简单水热法合成的 ZrO_2 为载体制备的 Au/ZrO_2 催化剂尚未见报道. 本文在水热条件下采用直接水解 ZrOCl_2 水溶液的方法合成了一系列纳米 ZrO_2 载体, 着重考察了 ZrO_2 的水热合成温度对 Au/ZrO_2 催化剂的结构及其 WGS 催化性能的影响.

ZrO_2 的水热合成步骤如下. 取 60 ml 0.40 mol/L 的 $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ (AR, 国药集团化学试剂有限公司) 水溶液装入 100 ml 水热釜中, 在不同温度下水热处理 6 h. 然后对水热产物进行离心洗涤数次, 以 AgNO_3 溶液 (0.20 mol/L) 检测至无 Cl^- 为止. 所得沉淀于 120 °C 干燥 8 h, 450 °C 焙烧 4 h 后, 制得 ZrO_2 载体, 标记为 ZrO_2-t (t 代表水热合成温度). Au/ZrO_2 催化剂采用沉积-沉淀法制备, 以 KOH 为沉淀剂, 理论 Au 含量为 1.0%, 标记为 Au/ZrO_2-t . 使用 X'Pert Pro 粉末衍射仪 (荷兰 PANalytical 公司) 对样品进行 X 射线粉末衍射 (XRD) 分析, Co K_α 射线源 ($\lambda = 0.1790$ nm), 扫描速率 0.25°/s. 利用 Varian SpectraAA-220 型原子吸收分光光度计 (美国 Varian 公司) 分析催化剂中 Au 的实际含量. 使用 ASAP 2020 型全自动比表面及孔隙度分析仪 (美国

Micromeritics 公司), 以 N_2 为吸附质, 在液氮温度 (-196 °C) 下测定催化剂样品的比表面积和孔结构. 样品的形貌使用日立 S-4800 型扫描电子显微镜 (SEM) 进行观察.

WGS 反应在 CO-CMAT9001 型变换催化剂活性评价装置上进行. 活性测试前, Au/ZrO_2 催化剂先用 H_2 于 300 °C 还原 2 h, 在 H_2 保护下降至室温后, 迅速将催化剂放入反应管中开始活性测试. 反应条件为: 常压, 150~300 °C, 汽气比为 1:1, 催化剂用量为 0.5 g, 空速为 10000 $\text{cm}^3/(\text{g}\cdot\text{h})$. 原料气为模拟甲醇重整气, 组成为 10% CO , 60% H_2 , 12% CO_2 , N_2 为平衡气. 出口气体中 CO 含量通过日本 Shimadzu GC-8A 型气相色谱仪分析检测.

图 1 为各 Au/ZrO_2 催化剂上的 WGS 反应活性. 由图可知, 在所考察的反应温区内, 催化剂的活性顺序为 $\text{Au/ZrO}_2-150 > \text{Au/ZrO}_2-170 > \text{Au/ZrO}_2-190 > \text{Au/ZrO}_2-130$, 即随着 ZrO_2 水热合成温度的升高, Au/ZrO_2 催化剂活性呈先升高后降低的“火山形”趋势变化. 这可能与 ZrO_2 及 Au/ZrO_2 催化剂的物理化学性质相关. 此外, 尽管 Au/ZrO_2-150 的实际 Au 负载量仅为 0.88% (见表 1), 但在 240 °C 反应时 CO 转化率高达 87%, 明显高于相同反应温度下本课题组先前所报道的 8.0% $\text{Au/Fe}_2\text{O}_3$ ^[7], 3.0% Au/CeO_2 ^[11] 及 3.0% Au/CeZrO_4 ^[17] 催化剂 (分别为 64%, 15% 和 69%). 可见, 以水热法制备的 ZrO_2 为载体所制得的

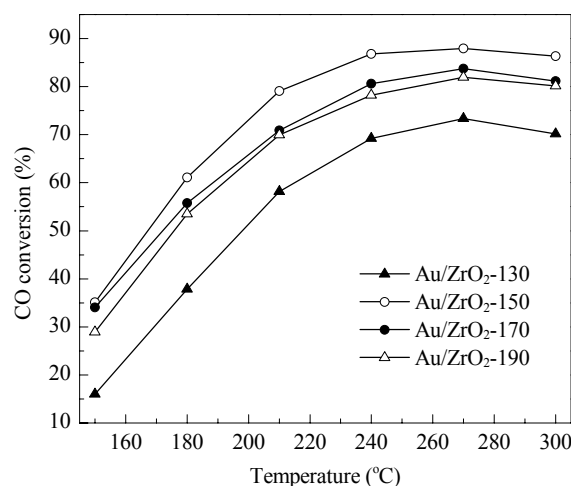


图 1 不同 Au/ZrO_2 催化剂的 WGS 反应催化活性

Fig. 1. Catalytic activity of Au/ZrO_2 catalysts for water-gas shift reaction. Reaction conditions: catalyst 0.5 g, feed 10% CO -60% H_2 -12% CO_2 -18% N_2 , space velocity = 10000 $\text{cm}^3/(\text{g}\cdot\text{h})$, steam/gas volume ratio = 1.

Au/ZrO₂ 催化剂在保持高活性的同时, 大大降低了 Au 负载量, 因此具有可观的商业应用价值.

为了探明 ZrO₂ 水热合成温度影响催化剂 WGS 性能的原因, 我们首先考察了 Au/ZrO₂ 催化剂的晶相结构. 图 2 为系列 Au/ZrO₂ 催化剂在 H₂ 气氛下于 300 °C 还原 2 h 后的 XRD 谱. 由图可见, 各催化剂样品均出现单斜相 ZrO₂ 的特征衍射峰 (JCPDS 01-089-9066), 且未发现单质 Au 的特征衍射峰 ($2\theta = 44.7^\circ$, JCPDS 01-089-3697), 这可能是由于样品中 Au 负载量较低 (见表 1) 或者 Au 以高分散状态存在所致. 不同的是, 随着水热温度的升高, ZrO₂ 的晶化程度逐渐提高, 通过 Scherrer 公式对 $2\theta = 32.9^\circ$ 的衍射峰进行计算发现 ZrO₂ 的晶粒尺寸从 3.0 nm 增至 7.4 nm (见表 1). 结合图 1 可知, 样品 Au/ZrO₂-150, Au/ZrO₂-170 和 Au/ZrO₂-190 中 ZrO₂ 晶粒尺寸与其催化 WGS 活性关联得很好, 即催化剂中 ZrO₂ 晶粒尺寸越小, 其活性越高, 这与文献 [19,24] 结果一致. 这可能是由于随着 ZrO₂ 晶粒尺寸的减小, Au-ZrO₂ 接触边界 (即 WGS 催化活性位) 的浓度增大所致 [19,24]. 值得注意的是, 尽管样品 Au/ZrO₂-130 晶粒尺寸最小, 但活性却最低. 这说明除载体晶粒尺寸外, 还有其他更为重要的因素制约着 Au/ZrO₂ 催化剂的 WGS 性能.

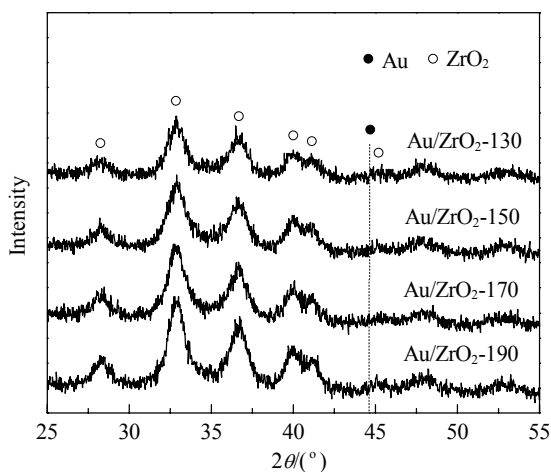


图 2 不同 Au/ZrO₂ 催化剂经 H₂ 还原后的 XRD 谱
Fig. 2. XRD patterns of the reduced Au/ZrO₂ samples.

表 1 列出了系列 Au/ZrO₂ 催化剂的 Au 负载量、ZrO₂ 晶粒尺寸、比表面积和孔结构参数. 可以看出, 各催化剂的 Au 负载量差别不大, 且比表面积与其催化活性不能较好的关联, 因此这两者不应该是

决定该系列催化剂性能差异的关键因素. 还可以看出, 随着水热温度的升高, 催化剂的总孔体积及平均孔径先增大后减小, 这与其活性的变化趋势完全一致, 即总孔体积越大或者平均孔径越大, 催化剂活性越高. 水热温度为 150 °C 时, 催化剂具有最大的平均孔径及总孔体积, 对应最佳的催化活性; 而 ZrO₂ 水热温度为 130 °C 的催化剂具有最小的平均孔径 (仅为 5.7 nm) 和最小的总孔体积, 其活性最低. 廖卫平等 [16] 在研究 Au/Ce_{1-x}Zr_xO₂ 水煤气变换催化剂时也得到相同结论, 并认为这是大孔径促进了 Au 在载体表面的分散所致. Tabakova 等 [5] 发现, Au/ZrO₂ 水煤气变换催化剂发生失活主要是由于活性测试过程中催化剂总孔体积明显减小所致, 这同样说明较大的孔体积有利于保持 Au/ZrO₂ 水煤气变换催化剂的高催化活性. 实际上, 较大的孔径和孔体积有利于反应物分子快速进入孔道, 生成的产物也可以快速脱出, 降低了分子的扩散阻力, 从而提高了催化反应速率.

表 1 不同 Au/ZrO₂ 催化剂的物理性质

Table 1 Physical properties of Au/ZrO₂ catalysts

Sample	Au loading ^a (%)	Particle size of ZrO ₂ ^b (nm)	BET surface area (m ² /g)	Pore volume (cm ³ /g)	Average pore diameter (nm)
Au/ZrO ₂ -130	0.89	3.0	61	0.195	5.7
Au/ZrO ₂ -150	0.88	3.7	58	0.367	20.9
Au/ZrO ₂ -170	0.91	5.1	58	0.295	16.3
Au/ZrO ₂ -190	0.91	7.4	50	0.280	9.1

^aMeasured by atomic absorption spectroscopy.

^bCalculated from the FWHM of ZrO₂(111) using the Scherrer equation.

图 3 为不同 Au/ZrO₂ 催化剂的 SEM 照片. 可以看出, 水热温度对 ZrO₂ 颗粒的形貌及尺寸都有较大的影响, ZrO₂ 颗粒由诸多一次晶粒通过一定的方式构筑而成. 水热温度为 130 °C 时, ZrO₂ 小晶粒排列较为无序, 颗粒不具有特定的形貌, 且颗粒与颗粒之间相互粘附, 形成较大的团聚颗粒. 水热温度为 150 °C 时, ZrO₂ 以厚度约为 50 nm、直径约为 150 nm 的规则圆形片状结构存在, 颗粒之间未发生明显的团聚现象. 当水热温度升高到 170 °C 时, 大部分 ZrO₂ 颗粒保持了圆形片状结构, 但该部分 ZrO₂ 颗粒的厚度及直径均明显减小; 另有部分 ZrO₂ 颗粒失去了特定的形貌, 且颗粒之间发生明显的团聚现象.

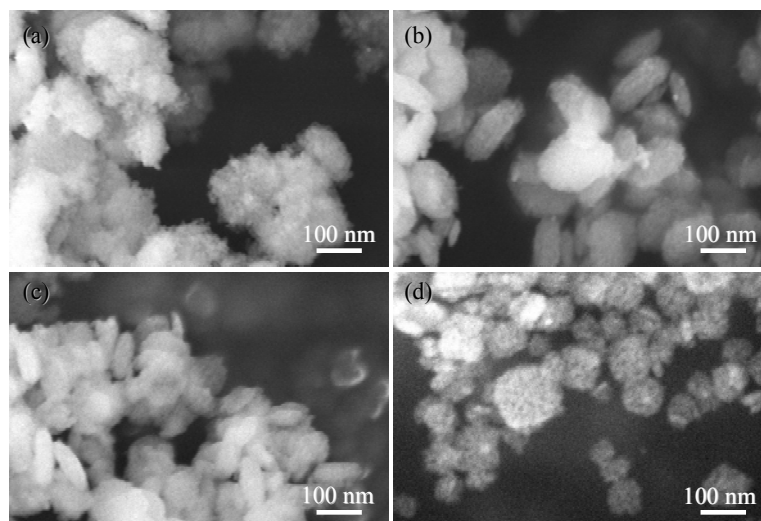


图3 不同 Au/ZrO_2 催化剂的 SEM 照片

Fig. 3. SEM images of Au/ZrO_2 catalysts. (a) Au/ZrO_2 -130; (b) Au/ZrO_2 -150; (c) Au/ZrO_2 -170; (d) Au/ZrO_2 -190.

对于水热温度为 $190\text{ }^\circ\text{C}$ 的样品, 其 ZrO_2 颗粒具有不太规则的片状结构, 片状结构的直径为 $50\sim 150\text{ nm}$, 在这些颗粒的表面可清楚地看到由 ZrO_2 晶粒堆积而成的 10 nm 左右的孔道, 说明此时 ZrO_2 晶粒明显长大, 与 XRD 结果一致. 总体上, 随着水热温度的升高, ZrO_2 晶粒的排布从无序到有序再到无序, 表现在颗粒形貌上即经历了一个从无特定形貌到规则圆形片状结构, 再到不规则片状结构的变化过程. 这可能是因为在水热条件下钨盐水解缩聚, ZrO_2 以“均匀溶液饱和析出”机制^[25]从溶液中析出结晶, 当温度较低时析出缓慢, 短时间内不能长成较好的形貌; 当温度太高时, 析出速度太快, ZrO_2 晶粒生长杂乱而没有固定形貌; 而温度适宜时, ZrO_2 晶粒析出速度合适, 形貌较为规整. 结合催化剂活性数据分析, 认为水热温度为 $150\text{ }^\circ\text{C}$ 合成的 ZrO_2 负载的 Au 催化剂表现出较佳催化活性可能与 ZrO_2 晶粒排布规整形成圆形片状结构有关. 因为载体晶粒排布规整时, 载体颗粒间的堆垛有利于形成较大的二次孔道; 另一方面, 载体表面存在着择优暴露晶面, 此晶面可能为活性晶面, 这两者均有助于 Au/ZrO_2 活性的提高. 关于催化剂暴露晶面对活性的影响已有很多报道^[26,27].

综上所述, 以水热法制备的 ZrO_2 负载的 Au 催化剂具有优越的 WGS 催化性能, 在 Au 负载量较低的情况下, Au/ZrO_2 -150 样品表现出比 $\text{Au/Fe}_2\text{O}_3$, Au/CeO_2 及 Au/CeZrO_4 更高的催化活性. 不同水热

温度下合成的 ZrO_2 具有不同的孔结构和形貌特征, 而总孔体积及平均孔径越大、形貌越规整的催化剂具有越高的 WGS 催化活性.

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英 译 文

English Text

The water-gas shift reaction ($\text{CO} + \text{H}_2\text{O} \leftrightarrow \text{CO}_2 + \text{H}_2$, $\Delta H = -41.2 \text{ kJ/mol}$, $\Delta G = -28.6 \text{ kJ/mol}$, WGS) is mainly used to purify the reformed gas and to supply pure H_2 for ammonia and other chemical synthesis processes. Recently, this reaction has attracted renewed attention because of its application in on-line H_2 production to fuel proton exchange membrane fuel cells (PEMFCs) [1,2]. Gold supported catalysts are regarded as the most promising low-temperature WGS catalysts for use under the harsh operating conditions of PEMFCs because of their superior low-temperature catalytic efficiency, wide operating temperature range, and excellent oxidation-tolerant and water-tolerant properties [3,4].

It has been established that gold supported catalysts such as Au/ Fe_2O_3 [5–7], Au/ CeO_2 [8–11], Au/ TiO_2 [12], Au/ ThO_2 [13], Au/ $\text{Cu}_x\text{Mn}_y\text{O}_z$ [14], Au/ CeZrO_4 [15–17], and Au/ ZrO_2 [5,18–23] give high catalytic activity in the low-temperature WGS reaction. The Au/ ZrO_2 system has been of great interest because of its excellent catalytic performance. The physical properties of ZrO_2 such as its crystal phase [18], particle/crystallite size [19], density of surface hydroxyl groups [19], and specific surface area [20] were found to strongly influence the catalytic performance of Au/ ZrO_2 catalysts for the low-temperature WGS reaction. For in-

stance, Au nanoparticles supported on monoclinic zirconia exhibited higher WGS activity than that on tetragonal zirconia [18] and the increase in the particle size of ZrO_2 caused a significant decrease in Au- ZrO_2 contact boundaries i.e. active sites for the WGS reaction [19]. Considering that the physical properties of ZrO_2 are directly affected by the preparation method, it is critical to choose a suitable ZrO_2 preparation method to improve the catalytic efficiency of the Au/ ZrO_2 catalyst to investigate the structure-property relation of the catalysts and to further guide the design of new catalysts. ZrO_2 supports for Au/ ZrO_2 catalysts have been mainly synthesized by a reflux method [18,19], a precipitation method [5,20–22], and a template-directed hydrothermal method [23] while no reports have focused on the preparation of Au/ ZrO_2 catalysts with ZrO_2 synthesized by a template-free hydrothermal method. In this paper, a series of ZrO_2 samples were prepared from a ZrOCl_2 aqueous solution by hydrolysis under hydrothermal conditions and used as supports for Au/ ZrO_2 catalysts. The effects of hydrothermal synthesis temperature of zirconia on the structural properties and low-temperature WGS catalytic activity of Au/ ZrO_2 were investigated.

A typical ZrO_2 hydrothermal synthesis was carried out as follows. $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ aqueous solution (60 ml, 0.40 mol/L) was transferred into a 100 ml Teflon-lined stainless steel autoclave and this was maintained at different hydrothermal temperatures for 6 h. The resultant precipitate was then washed thoroughly with deionized water, dried at 120 °C for 8 h, and calcined at 450 °C in static air for 4 h. The support is denoted ZrO_2-t , where t refers to the hydrothermal temperature of ZrO_2 . The Au/ ZrO_2 catalysts with a nominal Au loading of 1.0% were prepared by a deposition-precipitation method using KOH as the precipitating agent. The catalyst samples are denoted Au/ ZrO_2-t . X-ray diffraction (XRD) measurements for the structure determination were carried out with a PANalytical X'Pert Pro diffractometer using $\text{Co } K_\alpha$ radiation ($\lambda = 0.1790 \text{ nm}$) and the scanning speed was 0.25°/s. The actual loading of gold in each catalyst was measured by atomic absorption spectroscopy (AAS) on a Varian SpectrAA-220 atomic absorption spectrometer. The specific surface area and pore structure of the samples were measured at -196 °C on a Micromeritics ASAP 2020 physical adsorption analyzer. A Hitachi S-4800 scanning electron microscope (SEM) was used to study the morphology of the catalysts.

The catalytic activity of the samples for the WGS reaction was measured from 150 to 300 °C on a CO-CMAT9001 apparatus that was equipped with a flow reactor. The preliminarily pretreatment of the samples was performed under a H_2 atmosphere at 300 °C over 2 h in a tubular-furnace and then the samples were quickly transferred to the reactor tube after cooling to ambient temperature under the H_2 flow. The

following testing conditions were applied: atmospheric pressure; catalyst 0.5 g; space velocity = $10000 \text{ cm}^3/(\text{g}\cdot\text{h})$; feed gas was a model reformed methanol gas containing 10% CO, 60% H_2 , 12% CO_2 , and balance was N_2 ; the ratio of vapor to feed gas was 1. The concentration of CO in the effluent was analyzed on-line using a gas chromatograph (Shimadzu GC-8A) equipped with a thermal conductivity detector (TCD).

The catalytic activity of the gold-zirconia catalysts for the low-temperature WGS reaction is shown in Fig. 1. As shown in this figure, significant differences in CO conversion were found for the samples over the whole testing temperature region. The catalytic activity decreased as follows: $\text{Au/ZrO}_2\text{-150} > \text{Au/ZrO}_2\text{-170} > \text{Au/ZrO}_2\text{-190} > \text{Au/ZrO}_2\text{-130}$, i.e. with an increase in the hydrothermal synthesis temperature of ZrO_2 , the catalytic activity of the resultant Au/ZrO_2 catalysts increased initially and then decreased and gave a maximum at the hydrothermal temperature of $150 \text{ }^\circ\text{C}$. The influence of the hydrothermal temperature of ZrO_2 on the catalytic performance of the Au/ZrO_2 catalysts may be related to differences in the physical properties of the catalysts. Although the real gold loading is just 0.88% (Table 1), the $\text{Au/ZrO}_2\text{-150}$ sample gives a CO conversion of 87% at the reaction temperature of $240 \text{ }^\circ\text{C}$, which is significantly higher than that of the reported 8.0% $\text{Au/Fe}_2\text{O}_3$ [7], 3.0% Au/CeO_2 [11], and 3.0% Au/CeZrO_4 [17] catalysts (conversion is 64%, 15%, and 69%, respectively). In other words, the Au/ZrO_2 catalysts with the ZrO_2 support prepared by the hydrothermal method can maintain high catalytic activity even though the gold content is very low, which is of great commercial value.

To investigate the reason for the difference in catalytic activity of the samples, several characterization methods were used. XRD patterns for the gold-based samples pretreated in hydrogen are shown in Fig. 2. All the diffraction peaks are related to the monoclinic phase of zirconia (JCPDS 01-089-9066) and no characteristic peaks of metallic gold are present (typical 2θ of 44.7° , JCPDS 01-089-3697), suggesting a high dispersion of gold particles on the support surface. With an increase in the hydrothermal temperature the XRD peaks of ZrO_2 become sharp and intense, indicating that the crystallization process is very effective. The corresponding crystallite size of the ZrO_2 particles calculated using the Scherrer equation increases from 3.0 to 7.4 nm (Table 1). Based on the catalytic activity results, the catalytic behavior of the catalysts correlates well with the crystallite size of the ZrO_2 particles for $\text{Au/ZrO}_2\text{-150}$, $\text{Au/ZrO}_2\text{-170}$, and $\text{Au/ZrO}_2\text{-190}$, i.e. smaller zirconia nanoparticles lead to a higher catalytic activity for the Au/ZrO_2 catalyst, which is consistent with the results reported by Li et al. [19] and Zhang et al. [24]. The improvement in activity upon reducing the ZrO_2 crystallite size is attributed to the increased

Au-ZrO_2 contact boundaries in the catalysts [19,24], which are regarded as active sites in the WGS reaction. However, the $\text{Au/ZrO}_2\text{-130}$ sample is an exception because it has the lowest CO conversion even though it has the smallest ZrO_2 crystallite size. Therefore, other important factors determine the catalytic activities of these catalysts in addition to the crystal structure.

The actual gold loading and structural and textural properties of the Au/ZrO_2 catalysts are shown in Table 1. All the samples have a very similar gold loading of about 0.90% and there is no correlation between the BET surface area and the resulting catalytic activity, indicating that these two parameters are not crucial factors that affect the catalytic performance of the samples. As shown in Table 1, the pore structure of the catalysts is significantly affected by the hydrothermal synthesis temperature. The pore volume and average pore diameter of the samples increased initially and then decreased with an increase in the hydrothermal temperature and they reached a maximum at $150 \text{ }^\circ\text{C}$, which coincides with the change in catalytic activity. In other words, a larger pore volume and a larger average pore diameter lead to a higher catalytic activity of the Au/ZrO_2 catalyst. The $\text{Au/ZrO}_2\text{-150}$ sample with the largest pore volume and average pore diameter gave the highest WGS catalytic activity. In contrast, the $\text{Au/ZrO}_2\text{-130}$ sample with the smallest pore volume and average pore diameter gave the lowest WGS catalytic activity. A similar relationship between the pore diameter and the catalytic activity with respect to the $\text{Au/Ce}_{1-x}\text{Zr}_x\text{O}_2$ WGS catalysts was reported by Liao et al. [16], who suggested that a benefit of the large pore diameter was the promotion of gold dispersion on the surface of the supports. In addition, Tabakova et al. [5] showed that the deactivation of the Au/ZrO_2 catalysts for the low-temperature WGS reaction was mainly attributed to a reduction in pore volume, suggesting the importance of a large pore volume for high catalytic activity. Actually, a large pore diameter and a large pore volume greatly benefit the transfer of reactant/product molecules into or out of the pores in the catalysts and, therefore, they contribute to a higher reaction rate.

Figure 3 shows SEM images of the Au/ZrO_2 catalysts. We observe that the ZrO_2 particles synthesized at various hydrothermal temperatures give different morphologies and particle size distributions and are composed of many primary crystal grains with different arrangements. The ZrO_2 particles synthesized at $130 \text{ }^\circ\text{C}$ do not have a specific morphology and they agglomerate into larger clumps wherein the primary crystal grains are arranged in a disorderly manner. As the hydrothermal temperature reaches $150 \text{ }^\circ\text{C}$, the ZrO_2 particles have a well-developed nanodisk shape with a diameter of about 150 nm and a thickness of about 50 nm. No agglomeration is observed in this sample. For the $\text{Au/ZrO}_2\text{-170}$

sample the majority of the ZrO_2 particles maintain their nanodisk morphology with a smaller particle size compared to the Au/ ZrO_2 -150 sample. This is accompanied by a small proportion of the particles losing their specific morphological features. In addition, agglomeration occurs in this sample as well. For the Au/ ZrO_2 -190 sample the ZrO_2 particles have an irregular nanodisk shape with a diameter of 50–150 nm and pores with a diameter of 10 nm are clearly observed on the surface of these ZrO_2 particles indicating that the ZrO_2 crystallite size increases greatly, which is in agreement with the XRD result. The arrangement of the ZrO_2 primary crystal grains changes from being disordered to ordered and then disordered again with an increase in the hydrothermal temperature. Correspondingly, the ZrO_2 particles change from a state without specific morphology to a state with uniform nanodisk morphology and finally to a state with an irregular nanodisk morphology. A possible reason is that under hydrothermal conditions the ZrO_2 separates from the precursor aqueous solution by a precipitation mechanism from the supersaturated solution [25]. At a lower hydrothermal temperature (130 °C), the precipitation or crystallization of ZrO_2 is too slow to give rise to a specific morphology within a relatively short period of time. However, if the hydrothermal temperature is too high (such as 170 and 190 °C), the crystallization will be so fast that ZrO_2 can not form a regular morphology. On the contrary, at a suitable temperature (150 °C) the ZrO_2 primary crystal grains separate out at a moderate rate and are thus ready to develop a specific regular morphology of ZrO_2 secondary particles.

Combined with the catalytic activity results it is clear that the best WGS catalytic activity of Au/ ZrO_2 -150 is related to the uniform nanodisk morphology of the ZrO_2 support that was constructed by the regularly arranged ZrO_2 crystal grains. The packing of particles with uniform nanodisk shape is favorable for the formation of larger secondary pores. In addition, the surface of ZrO_2 -150 may preferentially expose certain crystallographic planes that act as the catalytically active planes for the WGS reaction. Both of these factors enhance the catalytic activity of the Au/ ZrO_2 -150 sample. A number of papers concerned with the active crystallographic plane of the catalysts have been published [26,27].

In summary, a series of ZrO_2 samples were prepared by a facile hydrothermal route and were used as supports for low-content (< 1.0%) Au/ ZrO_2 catalysts. These catalysts exhibit promising catalytic efficiency for the low-temperature WGS reaction. The Au/ ZrO_2 -150 sample showed significantly higher activity than that of the reported Au/ Fe_2O_3 , Au/ CeO_2 , and Au/ CeZrO_4 catalysts. The ZrO_2 samples that were synthesized at different hydrothermal temperatures gave various pore structures and morphologies, which are shown to be decisive factors that influence the catalytic performance of the Au/ ZrO_2 catalysts. The uniform nanodisk morphology and the increases in pore volume and pore diameter of the ZrO_2 support are responsible for the high catalytic activity of the Au/ ZrO_2 catalyst.

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