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Article

Effect of Pt cocatalyst in Pt/TiO₂ studied by in situ FTIR of CO adsorption

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ABSTRACT

In situ transmission infrared spectroscopy was used to study the role of Pt cocatalyst in Pt/TiO₂ using CO as a probe molecule. An 11 cm⁻¹ redshift of CO adsorbed on Pt/TiO₂ was observed under irradiation in the absence of changes in the CO coverage or sample temperature. In contrast, no CO shift was detected on Pt/Al₂O₃. This indicates that the redshift of the CO adsorption peak is due to the photogenerated electron transfer from TiO₂ to Pt, and this accounts for the increased photocatalytic activity by the loaded Pt cocatalyst.

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1. Introduction

As a typical photocatalyst, TiO₂ has attracted much interest in recent decades [1–4]. In the TiO₂ photocatalytic system, facile electron-hole recombination is the main factor for the low quantum efficiency [5–7]. Efficient charge separation and migration is highly demanded to improve photocatalytic performances.

Noble metals, such as Pt, are used as cocatalysts, because noble metals not only serve as electron sinks, but also provide effective proton reduction sites, which considerably accelerate the proton reduction reactions. In the process of photocatalytic H₂ production, proton reduction by photoinduced electrons is regarded to take place on the cocatalyst under irradiation. Therefore, electron transfer from the photocatalyst to the co-

catalyst is very important. Kamat et al. determined the apparent Fermi level of the TiO₂-Au composite system, and found that the shift of Fermi level TiO₂-Au relative to TiO₂ increases with the particle size of Au nanoparticles decreasing, reflecting more electrons transferred to Au for higher photocatalytic performances [8].

In situ Fourier transform infrared (FTIR) spectroscopy is a powerful method to obtain vibrational information of surface molecules. The direction of electron transfer can be directly estimated by monitoring the CO vibrational frequency on the cocatalyst [9–11]. Domen and co-workers demonstrated the first successful direct probing of the Fermi level of the cocatalyst (Pt) supported on the photocatalyst (GaN) during UV irradiation by in situ ATR-SEIRAS measurement through monitoring the frequency of the adsorbed CO vibrational [12]. Subse-

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quently, they investigated the visible light-induced changes in Pt/(Ga_{1-x}Zn_x)(Ni_{1-x}O_x), Pt/TaON, and Pt/LaTiO₂N powder photocatalysts using infrared spectroscopy with adsorbed CO probe molecules on Pt cocatalysts [13].

In this work, in situ transmission infrared spectroscopy was applied to study electron transfer between photocatalyst and cocatalyst in Pt/TiO₂ using CO as a probe molecule. The results certify that a redshift of the infrared CO peaks under irradiation reflecting electron transfer from TiO₂ to Pt particles.

2. Experimental section

2.1. Synthesis of materials

Pt-loaded TiO₂ catalyst, Pt/TiO₂, was prepared by the impregnation method. Commercially available TiO₂ (Degussa P25) was used as the support. Briefly, 1 g P25 was dispersed into 30 mL H₂PtCl₆ aqueous solution at a given concentration and stirred for 6 h. After evaporation, the obtained dry powder was oxidized with O₂ at 300 °C for 2 h, then reduced with H₂ at 300 °C for 2 h. The final products are referred as 0.1% Pt/TiO₂. Pt/Al₂O₃ was prepared using the same method as Pt/TiO₂.

2.2. Characterizations of materials

All infrared spectra were collected with a resolution of 4 cm⁻¹ and 64 scans by a Fourier transform infrared spectrometer (Nicolet NEXUS 470) with an MCT detector. All of the spectra shown here are in the absorbance mode, and their backgrounds were recorded before admitting the adsorbed gas under corresponding experimental conditions of the spectra. All samples were pressed into self-supporting wafers (ca. 25 mg) and mounted inside an IR cell with BaF₂ windows for FTIR spectroscopy.

Transmission electron microscope (TEM) images of the samples were examined by a Tecnai G2 F30 S-Twin (FEI) microscope with an acceleration voltage of 300 kV. High resolution scanning electron microscopy (HRSEM) images were obtained on a Hitachi S-5500 Ultra-high Resolution SEM with an acceleration voltage of 30.0 kV.

2.3. Photocatalytic reactions

The photocatalytic reaction was performed in a Pyrex reaction cell connected to a closed gas circulation and evacuation system. Typically, 0.1 g powder of catalyst was dispersed in the reaction cell containing 200 mL methanol aqueous solution. A Pyrex glass filter, filled with water, was placed between the Xe lamp and the reaction cell to remove the IR light illumination from the Xe lamp. Prior to the reaction, the suspension was deaerated by evacuation. A 300W Xe lamp irradiated the reaction cell from the top. The gaseous products were periodically analyzed by an on-line gas chromatograph (Shanghai GC-920, TDX-01 carbon molecular sieve packed column, Ar carrier gas). The chromatograph was equipped with a thermal conductivity detector, a flame ionization detector, and a methanizer. H₂ was measured by the thermal conductivity detector.

3. Results and discussion

3.1. Materials characterization

TEM images shown in Fig. 1 reveal that P25 TiO₂ particles have a particle size of about 20 nm, and Pt nanoparticles with particle sizes of about 1.5 nm were deposited onto the P25 TiO₂. HRSEM images show the deposited Pt nanoparticles were quite uniform on the P25 TiO₂ surface.

3.2. Photocatalytic reaction

Figure 2 shows the effect of deposited Pt nanoparticles on H₂ production in the photocatalytic reforming of methanol. No H₂ was produced without Pt deposited on P25 TiO₂ in this investigation. As mentioned in the literature [14], photocatalytic activity is obviously enhanced after Pt deposition on P25 TiO₂, which demonstrated the important role of the Pt cocatalyst in photocatalytic reforming of methanol. Pt cocatalysts loaded on P25 TiO₂ could promote or accelerate the photocatalytic processes.

3.3. FTIR spectra of CO adsorbed on Pt/TiO₂

Figure 3 displays the FTIR spectra of adsorbed CO at room

Fig. 1. TEM (A,C) and HRSEM (B,D) images of P25 TiO₂ (A and B) and Pt/TiO₂ (C and D).

Fig. 2. H₂ production in the photocatalytic reforming of methanol.

Fig. 3. FTIR spectra of CO adsorbed on Pt/TiO₂ after pretreatment with O₂ and H₂.

temperature on Pt/TiO₂. It shows that CO adsorption gives strong bands at 2119 and 2079 cm⁻¹ attributed to CO adsorbed on Pt/TiO₂ pretreated with O₂ and H₂, respectively. According to the literature, the CO peak is attributed to the linear adsorption [15–17], $\nu_{\text{CO}} > 2100$ cm⁻¹ suggesting CO adsorbed on Ptⁿ⁺, while $\nu_{\text{CO}} < 2100$ cm⁻¹ suggests CO adsorbed on Pt⁰ [18]. The redshift of CO peaks on Pt⁰ relative to Ptⁿ⁺ indicate that Pt with more electrons shows the redshift of the CO peaks.

3.4. FTIR spectra of CO adsorbed on Pt/TiO₂ under irradiation

Figure 4 displays the FTIR spectra of adsorbed CO on Pt/TiO₂ at different irradiation time. A band at 2079 cm⁻¹ was observed with CO adsorbed on Pt/TiO₂. After irradiation for 1–60 s, the peak shifted to 2068 cm⁻¹. According to the integrated areas of the CO peaks, the CO coverage was not altered during irradiation.

3.5. FTIR spectra of CO adsorbed on Pt/TiO₂ at different temperatures

As shown in Fig. 5, when the sample temperature increased from 25 to 200 °C, the CO peak shifted from 2079 to 2071 cm⁻¹.

Fig. 4. IR spectra of CO adsorbed on Pt/TiO₂ after different irradiation time.

Fig. 5. IR spectra of CO adsorbed on Pt/TiO₂ at different temperatures.

According to the integrated area of the CO peaks, the CO coverage did not change, suggesting that the CO peak shift is mainly attributed to the increasing temperature.

3.6. FTIR spectra of CO adsorbed on Pt/Al₂O₃ under irradiation

Figure 6 displays the FTIR spectra of CO adsorbed on Pt/Al₂O₃ at different irradiation times. A band at 2053 cm⁻¹ is observed when CO is adsorbed on Pt/TiO₂. After irradiation for 1–60 s, the peak remained at 2053 cm⁻¹.

When CO adsorbs on a metal, the electrons are partially transferred from a *d*-orbital of the metal to the anti-bonding CO molecular orbitals. This electron-transfer strengthens the metal–C bond and weakens the C–O bond. The strengthening of the M–CO bond is reflected in the increase of the vibrational frequencies for the M–C bond.

There are many factors that influence CO vibrational frequencies, such as CO coverage [9,19], sample temperature, and adsorbates. As shown in Fig. 4, the intensity of the band due to CO adsorbed on Pt did not change under irradiation, indicating that CO coverage is not the reason for the redshift of the CO peak in this work. Figure 5 indicates that the sample tempera-

Fig. 6. FTIR spectra of CO adsorbed on Pt/Al₂O₃ at different irradiation time.

ture influences the CO vibrational frequencies, but to obtain a 11 cm^{-1} redshift of the CO peak, the sample temperature would need to be greater than $200\text{ }^{\circ}\text{C}$. However, the temperature of the in situ cell is maintained below $30\text{ }^{\circ}\text{C}$ with water cooling, which indicates that temperature increases from irradiation are not the reason for the redshift of the CO peak.

Under irradiation by a Hg-Xe lamp, electrons in the valance band of TiO_2 could be excited to the conduction band, while holes remain in the valance band. Photogenerated electrons can transfer to the Pt particles, which makes more electrons in the Pt particles transfer into the two π^* anti-bonding molecular orbitals of CO. This electron transfer weakens the C–O bond, shifting the CO peaks to lower wavenumbers. The CO peak redshift reflects the photogenerated electron transfer process from TiO_2 to Pt particles. Because Al_2O_3 is an insulator, no photogenerated electrons and holes will be generated under Hg-Xe lamp irradiation. Without electron transfer to the Pt particles, the peak for CO peak adsorbed on $\text{Pt}/\text{Al}_2\text{O}_3$ does not shift, which further illustrates that the peak redshift of the CO adsorbed on Pt/TiO_2 comes from the photogenerated electrons on TiO_2 transferring to the Pt particles.

4. Conclusions

Electron transfer in Pt/TiO_2 photocatalyst during UV irradiation has been studied by in situ transmission infrared spectroscopy using CO as a probe molecule. The results reveal that an 11 cm^{-1} redshift of the CO peak is indicative of photogenerated electron transfer from TiO_2 to Pt particles. Pt nanoparticles can promote charge separation and enhance the H_2 production. The shift direction of the CO peak can be used as an effective reporter of the interaction between photocatalyst and cocatalyst.

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Graphical Abstract

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Effect of Pt cocatalyst in Pt/TiO_2 studied by in situ FTIR of CO adsorption

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A band at 2079 cm^{-1} was attributed to CO adsorbed on Pt nanoparticle, while the peak shifted to 2068 cm^{-1} after UV irradiation. CO peak redshift indicates photogenerated electron transfer from TiO_2 to Pt particles.

采用CO吸附原位红外光谱研究Pt/TiO₂光催化体系中助催化剂作用

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摘要: 采用CO作为探针分子, 将原位透射红外光谱应用于研究助催化剂Pt在Pt/TiO₂光催化体系中的作用. 实验发现, 光照条件下, CO的覆盖度及样品温度没有明显变化, CO在Pt/TiO₂上的吸附峰红移11 cm⁻¹, 在Pt/Al₂O₃上的吸附峰没有位移, 表明CO在Pt/TiO₂上的红移来源于TiO₂上的光生电子转移到Pt上, 这解释了为什么加入Pt助催化剂可提高光催化产氢活性.

关键词: 一氧化碳吸附; 二氧化钛; 助催化剂; 光催化; 原位红外光谱

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1. 前言

TiO₂作为最典型的光催化剂在最近几十年吸引了众多研究者的兴趣^[1-4]. 在TiO₂光催化过程中, TiO₂自身的光生电子空穴复合是限制其光催化反应的量子效率提高的主要因素^[5-7]. 如何提高光生电子空穴的分离效率, 抑制电子空穴复合, 提高光生载流子氧化还原表面吸附物种的几率, 是提高TiO₂光催化反应效率的关键.

Pt等贵金属催化剂以其优良的活化氢分子和质子还原能力在光催化分解水制氢领域中, 常作为还原助催化剂和质子还原放氢催化剂, 可以显著提高光催化制氢反应的活性. 光催化制氢过程中, 半导体催化剂经光照产生的光生电子在Pt等助催化剂的作用下, 与H⁺进行反应产生氢气. 因此, 研究光催化剂和助催化剂之间的相互作用和电子转移过程是非常重要的. Kamat等^[8]使用C₆₀/C₆₀⁻氧化还原电对作为探针研究了Au/TiO₂体系的电子转移情况, 发现Au纳米粒子越小, Au/TiO₂体系的费米能级越负, 越有利于光催化产氢.

吸附探针分子的傅里叶变换红外光谱(FTIR)是对表面结构非常敏感的谱学方法, 经常用于从分子水平上研究催化剂表面和界面的性质, 根据CO吸附在催化剂上的吸附峰位置可有效地判别反应过程中电子的转移方向和程度^[9-11]. Yoshida等^[12]使用电化学与红外衰减全反射相结合的方法, 以CO作为探针分子研究了模型催化剂Pt/GaN体系CO的红外吸附峰位移与Pt/GaN费米能级间的关系, 说明CO吸附红外光谱可以研究光催化剂和助催化剂之间的电子转移过程. Lu等^[13]进一步将此技术用于研究氮氧化物光催化剂(Ga_{1-x}Zn_x)(N_{1-x}O_x),

TaON和LaTiO₂N与负载的Pt助催化剂之间的电子转移过程.

本文使用CO作为探针分子, 将原位透射FTIR谱应用于研究光照条件下Pt/TiO₂体系中光催化剂和助催化剂之间的电子转移过程. 实验发现, CO在Pt上的IR吸附峰在光照条件下明显红移, 反映出TiO₂上的光生电子可以转移到Pt粒子上.

2. 实验部分

2.1. 催化剂的制备

Pt/TiO₂催化剂采用浸渍法制得: 将TiO₂ (Degussa P25)分散在计算好浓度的H₂PtCl₆水溶液中浸渍并搅拌6 h, 然后将其水浴蒸干, 所得固体粉末经研磨后在O₂气氛中300 °C下氧化2 h, 然后在H₂气氛中300 °C下还原2 h得到最终样品, Pt的负载量为0.1 wt%. Pt/Al₂O₃ (国药集团, 99.0%)催化剂的制备方法和负载量与Pt/TiO₂相同.

2.2. 催化剂的表征

CO吸附的原位FTIR谱实验在配有MCT-检测器的Nicolet Nexus型傅里叶变换红外光谱仪上进行. 仪器分辨率4 cm⁻¹, 扫描范围4000–650 cm⁻¹, 扫描次数32次. 采用的原位池为自制的装有BaF₂窗片的石英高温透射红外样品池. 催化剂样品压成自支撑薄片(约25 mg)置于池体中部, 首先抽真空除去样品池中的空气, 然后在0.1 MPa的H₂气流中以10 °C/min的速率升至300 °C还原2 h. 还原结束后, 样品在300 °C抽真空10 min, 在真空中降至室温并采集本底. 引入饱和CO, 吸附平衡后, 抽真空, 样品谱与背景谱的差谱即为CO在Pt/TiO₂上的吸附谱图. 实验中使用的光源型号为200W Hamamatsu LC8双光纤

头的Hg-Xe灯,光谱范围为 $\lambda < 420$ nm.

透射电子显微镜(TEM)测试是在Tecnai G2 F30 S-Twin (FEI公司)型透射电子显微镜(TEM)上进行,加速电压为300 kV. 高分辨扫描电子显微镜(HRSEM)测试是在HITACHI S-5500型SEM上进行,加速电压为30.0 kV.

2.3. 催化剂产氢性能的评价

催化剂的光催化产氢性能的评价在密闭的真空玻璃系统内进行,催化剂的用量为0.1 g,反应溶液为160 mL二次水和40 mL甲醇的混合溶液,催化剂在磁力搅拌下悬浮在甲醇水溶液中. 光照前,将体系内的空气排空,反应在15 °C条件下进行. 反应池由Pyrex反应器构成,上部为一夹层水套,用于减少红外辐射产生的热量. 光照采用顶式照法,光源为日本生产的300 W氙灯,工作电压为110 V,电流为20 A. 气体产物在上海海欣公司生产的GC-920型色谱仪上进行. 气体产物从取样器中被载气Ar带出,进入色谱的碳分子筛TDX-01填充柱分离,然后进入热导检测器,测量H₂的含量.

3. 结果与讨论

3.1. 催化剂的TEM和HRSEM结果

图1为TiO₂和Pt/TiO₂催化剂的TEM和HRSEM照片. 由TEM结果可知,载体P25 TiO₂粒子大小为20 nm左右,沉积在P25上面的为Pt粒子,大小约为1.5 nm. 与透射电镜结果相一致,HRSEM表明,1.5 nm左右的Pt纳米粒子均匀沉积在20 nm左右的P25粒子的表面.

3.2. 催化剂TiO₂和Pt/TiO₂的光催化产氢活性结果

图2是催化剂TiO₂和Pt/TiO₂的光催化重整甲醇制氢活性. 如图所示,在我们的实验条件下,未负载Pt的TiO₂催化剂基本检测不到H₂的产生;与文献[14]报道类似,负载贵金属Pt后,产氢活性大大提高,产氢速率达到约570 $\mu\text{mol/h}$,说明Pt助催化剂的负载是TiO₂光催化产氢性能的关键,Pt的负载使光催化产氢成为可能.

3.3. CO吸附在Pt/TiO₂上的FTIR谱

图3是CO吸附在Pt/TiO₂上的FTIR谱. 如图所示,CO吸附在经过O₂氧化处理后的Pt/TiO₂上时,吸附峰在2119 cm^{-1} ;CO吸附在经过H₂还原处理后的Pt/TiO₂上时,吸附峰在2079 cm^{-1} . 根据文献[15–17]报道,上述吸收峰来自吸附在Pt上的CO线式吸附, $\nu_{\text{co}} > 2100$ cm^{-1} 归属为正价Pt上的CO吸附, $\nu_{\text{co}} < 2100$ cm^{-1} 归属为零价Pt上的CO吸附^[18]. 不同价态的Pt上的CO吸附峰的位置说明Pt粒子上的电子越多,CO吸附峰位置越红移.

3.4. 光照条件下CO在Pt/TiO₂上的FTIR谱

图4是CO在Pt/TiO₂上,光照0, 10, 20, 30, 60 s时的FTIR谱. 光照前,CO的吸附峰位于2079 cm^{-1} . 在Hg-Xe灯照射条件下,60 s内CO在Pt上的吸附峰由2079 cm^{-1} 逐渐红移到2068 cm^{-1} . 从红外峰的积分面积来分析,CO在样品表面的覆盖度基本没有变化.

3.5. 不同温度条件下CO在Pt/TiO₂上的FTIR谱

图5是不同温度条件下CO在Pt/TiO₂上的FTIR谱. 如图所示,随着样品温度的升高,CO的吸附峰逐渐红移,由室温25 °C时的2079 cm^{-1} ,逐渐红移到200 °C时的2071 cm^{-1} ,且根据红外吸附峰积分面积估算,在样品温度从25 °C升高到200 °C过程中,CO在样品表面的覆盖度变化不大. 因此CO吸附峰的红移应主要来源于样品温度的提高.

3.6. 光照条件下CO在Pt/Al₂O₃上的FTIR谱

图6是光照0, 10, 30和60 s条件下,CO吸附在Pt/Al₂O₃上的FTIR谱. 可以看出,随着光照时间的延长,CO吸附峰置未发生变化,一直位于2053 cm^{-1} 处,该峰强度也未随着光照时间的变化而发生明显的变化.

CO吸附在Pt粒子表面时,存在 $d-\pi$ 反馈,Pt的 d 电子进入CO分子的 $2\pi^*$ 反键分子轨道,导致C=O键减弱,使得CO吸附特征峰移向低波数(红移),其位移程度同 $d-\pi$ 反馈程度有密切的关系. 导致CO吸附峰红移的因素有很多,比如CO覆盖度的变化^[9,19]、样品温度的变化和共吸附物的影响等. 然而,如图4所示,光照条件下,CO的吸附强度没有明显的减少,说明CO红移并不是CO覆盖度的变化引起的. 图5说明温度同样是影响CO吸附峰位移的重要因素,但要使CO吸附峰红移11 cm^{-1} ,样品温度必然要达到200 °C以上. 但在光照条件下,原位池热偶显示样品的温度一直在30 °C以下,所以光照条件下,CO吸附峰的红移并非来源于光照导致的样品温度升高.

在Hg-Xe灯照射下,TiO₂作为带隙为3.0 eV的半导体,能够产生光生电子和空穴,TiO₂上产生的光生电子转移到Pt粒子上,可以使Pt上的电子密度提高,从而有更多的Pt的 d 电子进入CO的 $2\pi^*$ 反键分子轨道,从而导致C=O键减弱,使得CO在Pt上的吸附峰红移^[12]. 光照过程中,CO吸附峰的红移过程反映了光生电子从TiO₂向Pt粒子的转移过程,光照60 s后,CO的红移基本结束,谱峰位置固定在2068 cm^{-1} ,表明光生电子从TiO₂向Pt粒子的转移达到平衡. 由于Al₂O₃是绝缘体,在Hg-Xe灯照射下不会产生光生电子和空穴,所以没有电子转移到Pt上,CO在Pt/Al₂O₃上的吸附峰没有发生位移,进一步说明了在

光照条件下, CO吸附在Pt/TiO₂样品上的红移来源于TiO₂上的光生电子转移到Pt上.

4. 结论

本文以CO为探针分子, 采用透射原位FTIR谱研究了光照条件下, Pt/TiO₂体系中的电子转移情况. 实验发

现, 光照条件下, CO在Pt上的IR吸附峰红移11 cm⁻¹, 说明光生电子从TiO₂转移到Pt上, Pt可以作为助催化剂分离光生电子和空穴, 提高光催化产氢活性. 在助催化剂上红外吸附CO的IR峰的位移方向和程度, 可以有效地反映助催化剂和半导体催化剂间的相互作用和电子转移情况.