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Article (Special Issue of the International Symposium on Single-Atom Catalysis (ISSAC-2016))

Identification of active sites for hydrogenation over Ru/SBA-15 using *in situ* Fourier-transform infrared spectroscopy

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ARTICLE INFO

Article history:

Received 25 November 2016

Accepted 30 December 2016

Published 5 September 2017

Keywords:

Ru/SBA-15 catalyst

In-situ Fourier-transform infrared spectroscopy

Hydrogenation

Active site

Hydrogen spillover

ABSTRACT

The active sites for hydrogenation over Ru/SBA-15 catalysts were identified using *in situ* Fourier-transform infrared spectroscopy. The amount of active sites was proportional to the interfacial circumference of the Ru particles. In contrast, the rate of hydrogen spillover from Ru to the support was inversely proportional to the size of the Ru metal particles. Consequently, a catalyst with small Ru metal particles has a high rate of hydrogen spillover but a low density of active sites, whereas one with large Ru particles has a low rate of hydrogen spillover but a high density of active sites. The formation of these active sites is probably an intermediate step in hydrogen spillover.

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1. Introduction

The use of SBA-15-supported Ru catalysts in reactions such as hydrogenation [1,2] and hydrogenolysis [3,4] is becoming increasingly important because of the good performance of such catalysts in H₂ activation. The surface area of SBA-15 is higher than those of previously reported supports for Ru catalysts [5,6], and it has an ordered mesoporous structure, which favors high dispersion of Ru. SBA-15 has few acidic or basic sites and did not affect the studied reactions. The high reactivity of Ru/SBA-15 is therefore normally attributed to high dispersion of small Ru particles [7]. However, strong binding of spillover hydrogen to SiO₂ has been detected on SiO₂-supported Ru catalysts [8]. Moreover, the addition of Ru as a promoter in SiO₂-supported catalysts improves the reducibilities and activities of the catalysts; this is also ascribed to hydrogen spillover

[9]. These findings emphasize the importance of hydrogen spillover in reactions involving hydrogen, and raise the following issues in understanding of catalysts under working conditions. (1) Are the active sites for hydrogenation on Ru/SBA-15 catalysts Ru metal particles or the support? (2) How does hydrogen spill over from Ru to SBA-15? However, to the best of our knowledge, such a fundamental understanding of reaction mechanisms and the nature of active sites is still lacking.

In situ or *in operando* experimental methods need to be used to address these issues of real working catalysts [10]. *In situ* infrared (IR) spectroscopy is a powerful non-destructive technique, and is particularly used to probe surface sites and reaction mechanisms at the molecular level during catalytic reactions [11]. For example, IR spectroscopy has shown that benzene adsorption increases back-bonding of Pt *d* electrons to CO antibonding orbitals, based on the shift in the $\nu(\text{CO})$ vibration

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This work was supported by the National Natural Science Foundation of China (21303163), the Natural Science Foundation of Zhejiang Province (LY13B030006, LY17B060006), the Qianjiang Talent Project in Zhejiang Province (QJD1302011), and the Scientific Research Fund of Zhejiang Provincial Education Department (Y201328681).

DOI: 10.1016/S1872-2067(16)62571-8 | http://www.sciencedirect.com/science/journal/18722067 | Chin. J. Catal., Vol. 38, No. 9, September 2017

to lower frequencies. This indicates that benzene is adsorbed on a single Pt atom (as in π arene complexes) with global transfer of electrons to Pt [12]. *In situ* IR spectroscopy has also shown that during the catalytic cycle in Baeyer-Villiger oxidation on Sn-zeolite beta, a ketone is coordinated to the Lewis acid center, resulting in carbonyl group activation [13].

Here, we report that the active sites for hydrogenation reactions over Ru/SAB-15 can be identified using *in situ* Fourier-transform IR (FTIR) spectroscopy. The formation of these active sites is probably the intermediate step in hydrogen spillover.

2. Experimental

2.1. Catalyst preparation

SBA-15 was synthesized using a previously reported method [14]. P123 (2 g) was completely dissolved in 1.6 mol/L HCl (75 mL), and tetramethyl orthosilicate (3.3 g) was added under vigorous stirring; stirring was continued for about 20 h. The temperature was kept at 40 °C. The resultant white mixture was transferred to a Teflon-lined autoclave and aged at 100 °C for 24 h without stirring. The white powder was recovered, washed, and dried at 110 °C for 6 h. Calcination at 550 °C for 10 h in air gave mesoporous SBA-15.

Supported Ru catalysts with specific Ru loadings were prepared using a two-solvents method [15,16]. Typically, an aqueous solution of RuCl_3 (3.0 mL) was added gradually to cyclohexane (25.0 mL) containing a support material (SBA-15 or Al_2O_3 , 1.0 g) at 25 °C. After vigorous stirring for 15 min, the dark-brown solution became colorless and the originally white support became black. The black powder was separated by centrifugation and dried at 100 °C for 6 h; the product is denoted by Ru/support (wt%). Pd/SBA-15 (4%) was prepared by impregnation with PdCl_2 .

2.2. Catalyst characterization

In situ FTIR spectroscopy was performed using a Thermo Nicolet NEXUS 6700 spectrometer equipped with a mercury cadmium telluride (MCT) detector. A custom-made IR cell enabled spectra to be recorded at ambient temperature and at catalyst activation temperatures (up to 500 °C). Self-supporting disks (9.0 mg) were prepared for IR studies and physisorbed molecules were removed using a He flow. FTIR spectra were collected with 32 scans at a resolution of 4 cm^{-1} at different time intervals until a steady state was reached. The catalyst was reduced *in situ* with H_2 at 400 °C for 30 min at a ramping rate of 20 °C/min, swept with He for 30 min, and cooled to 110 °C under He. These spectra were used as background for obtaining differential FTIR spectra.

The catalyst was subsequently treated using the following procedures; the gas flow rate was kept at 30 mL/min, unless otherwise stated. (a) H_2 adsorption. The sample was treated in a H_2 flow at 110 °C until a stable FTIR spectrum was obtained. Blank SBA-15 was treated in the same way for comparison. (b) H-D exchange. After procedure (a), the gas was switched to D_2

to achieve H-D exchange. Spectra were collected until no change in the OH vibration peak was detected. The sample was then swept with He to expel D_2 until a clean spectrum was obtained. The sample was then retreated with D_2 and IR spectra of the sample without any interference from H_2 were obtained. (c) CO adsorption. After the catalyst had been activated and cooled to 110 °C under He, CO was pulsed into the He stream three times using a six-way valve. After each pulse, the sample was swept with He for more than 10 min and spectra were recorded. After three pulses, the sample was swept with He for more than 8 h.

Transmission electron microscopy (TEM) was performed using a Tecnai G2 F30 S-Twin instrument (Philips-FEI Company) operated at 300 kV. After H_2 adsorption, the samples were dispersed in ethanol and then supported on a Cu grid for TEM measurements.

3. Results and discussion

The *in situ* FTIR spectra in the range 2250–1850 cm^{-1} of the reduced samples after adsorption of H_2 at 110 °C are shown in Fig. 1. No vibration bands from Pd/SBA-15 (4%), Ru/ Al_2O_3 (4%), and SBA-15 were detected in this range, but a peak at 1996 cm^{-1} was observed for Ru/SBA-15 (4%). These results imply that formation of this band is associated with the presence of both Ru and SBA-15, but is not related to the Ru–H bonds in Ru metallic clusters, which would be detected for Ru/ Al_2O_3 . It has been reported that Ru–H species cannot be observed using IR, although adsorbed hydrogen species on various supported metals, e.g., Pt/ Al_2O_3 , Ir/ Al_2O_3 , Ni/ Al_2O_3 , Rh/ Al_2O_3 , and Ni/ SiO_2 have been observed [17,18]. In addition, the intensity of the band arising from the combination tone vibration [19] of Si–O on Ru/SBA-15 at 1866 cm^{-1} did not change after exposure to H_2 , thus the intensity of the Si–O overtone band at 1985 cm^{-1} was constant. The possibility that the band at 1996 cm^{-1} can be ascribed to the Si–O overtone can therefore be ruled out.

CO was adsorbed on Ru/SBA-15 (4%) to enable the band at 1996 cm^{-1} to be distinguished from those for adsorbed CO species. Fig. 2(a) shows that at low coverage of the Ru surface with

Fig. 1. Differential FTIR spectra of catalysts exposed to H_2 flow for 30 min at 110 °C.

Fig. 2. *In situ* FTIR spectra of CO adsorbed on reduced Ru/SBA-15 (4%) as a function of increasing CO coverage (a) and swept with a He flow at various times (b) at 110 °C. CO was introduced using a six-way valve (about 2 μ L) with He as the carrier gas.

CO, a band at 2068 cm⁻¹ ascribed to CO linearly adsorbed on Ru^{δ+} appeared [20]. This band developed together with a band at 2132 cm⁻¹, both related to Ru^{III}(CO)_x multi-carbonyls [21], as coverage with CO increased until a band at 2177 cm⁻¹ indicating physisorbed CO appeared. Few of these chemisorbed CO molecules were removed when the system was flushed with He at 110 °C, even after 8 h (Fig. 2(b)). In addition, the intensity of the carbonyl band at 2068 cm⁻¹ created by the first CO pulse (Fig. 2(a)) was lower than that of the band at 1996 cm⁻¹ shown in Fig. 1. The wavenumber difference is therefore not caused by a surface coverage effect because carbonyl bands with wavenumbers higher than 2068 cm⁻¹ are expected to appear with increasing CO coverage. The CO pulse adsorption results prove that the band at 1996 cm⁻¹ does not arise from any carbonyl species formed on Ru.

Formation of the band at 1996 cm⁻¹ was reversible in the case of Ru/SBA-15 (4%). The band developed gradually when the catalyst was exposed to H₂ and reached its maximum intensity after 60 min (Fig. 3(a)). Subsequent flushing with He led to the disappearance of this band, as shown in Fig. 3(b). This band therefore cannot be assigned to spillover hydrogen on SBA-15 because the migration of hydrogen from Ru to SiO₂ is irreversible [8]. The slow growth of this band during exposure for 1 h also indicates that it cannot be attributed to hydrogen chemi-

sorbed on Ru because hydrogen saturates the Ru particle surfaces in a shorter time (less than a few minutes) [8].

Based on the above discussion, we conclude that the band at 1996 cm⁻¹ cannot be ascribed to adsorbed H species on either Ru metal particles or the SBA-15 support. We postulate that the adsorbed H species are located at the interface between the Ru metal particles and the support. To confirm this hypothesis, we performed experiments using Ru with various interfacial circumferences on SBA-15 by tuning the Ru metal particle size. If the amount of H species is proportional to the interfacial circumference of Ru, these species reside along the Ru-SiO₂ interface on the periphery of the exposed Ru particles. Fig. 4 shows TEM images of Ru/SBA-15 catalysts with various Ru contents. The mean Ru particle sizes calculated from 100 to 150 Ru particles in these TEM images are listed in Table 1. Based on a spherical model (equations (1) and (2)), the Ru particle circumferences were calculated using equation (3); they are presented in Table 1.

$$N \cdot \frac{4}{3} \pi r^3 \cdot \rho = m_{\text{cat}} \cdot \omega \quad (1)$$

$$N \cdot 2\pi r = C \quad (2)$$

$$C = 3m_{\text{cat}} \cdot \omega / (2r^2 \cdot \rho) \quad (3)$$

where ρ is the density of Ru (12.37 g/cm³), N is the number of Ru particles, r is the Ru particle radius, ω is the Ru loading, and

Fig. 3. Evolution of *in situ* FTIR spectra of reduced Ru/SBA-15 (4%) in H₂ at 110 °C. (a) During exposure to H₂ after reduction; (b) During flushing with He after exposure to H₂.

Fig. 4. TEM images and size distributions of Ru particles of (a) Ru/SBA-15 (1%), (b) Ru/SBA-15 (4%), and (c) Ru/SBA-15 (10%).

Table 1

Textural properties of catalysts.

Catalyst	D_{Ru} (nm)	C_{Ru} (10^7 m)	S
Ru/SBA-15 (1%)	1.6	1.7	0.578
Ru/SBA-15 (4%)	1.8	5.4	3.01
Ru/SBA-15 (10%)	2.6	6.5	3.83

D_{Ru} : Ru particle size; C_{Ru} : Total circumference of Ru particles; S : Band area in the range of 2100–1800 cm^{-1} at saturation in H_2 .

C is the total circumference of the Ru particles.

Fig. 5 shows the evolution of the *in situ* FTIR spectra of reduced Ru/SBA-15 with various Ru loadings at 110 °C. The IR spectra of Ru/SBA-15 (4%) are shown in Fig. 3(a). The band areas at surface saturation with H_2 were calculated to be 0.578, 3.01, and 3.83 for Ru/SBA-15 (1%), Ru/SBA-15 (4%), and Ru/SBA-15 (10%), respectively (Table 1). It can be seen from Table 1 that the band area at saturation increased linearly with increasing Ru particle circumference, indicating that the species corresponding to the bands in the range 2100–1800 cm^{-1} reside at the interfacial sites between Ru particles and the support. For the sake of convenience, we denote these sites by S_x . A precondition of the formation of special species is the presence of both Ru metal and SiO_2 in the hydrogen atmosphere, therefore the process can be represented by the proposed model shown in Scheme 1. Molecular H_2 dissociates on active Ru metal sites and saturates the Ru surface within a few minutes. The dissociated hydrogen atoms then migrate from the Ru metal sites to the S_x sites between Ru and SiO_2 ; this pro-

Scheme 1. Hydrogen spillover to active sites on periphery of Ru on SBA-15 in H_2 .

cess takes a longer time. The migration is also dependent on the Ru particle size; the smaller the Ru particle size is, the faster the migration of H atoms from Ru metal sites to S_x is, as shown in Figs. 3 and 5.

The reactivities of these H species were evaluated using H-D exchange experiments. When D_2 was introduced, the intensities of the hydroxyl bands at 3740 and 3660 cm^{-1} decreased, whereas the intensities of the deuterioxyl bands at 2760 and 2630 cm^{-1} increased, as shown in Fig. 6(a). Some of the hydroxyl groups corresponding to the band at 3660 cm^{-1} remained even after a few hours in D_2 . No changes in the bands at 2100–1800 cm^{-1} were observed. After flushing with a He flow for more than 1 h, the adsorbed deuterium had been completely swept away, as in the case of adsorbed hydrogen in He. We then introduced D_2 again to investigate the nature of the bands in the range 2100–1800 cm^{-1} . As shown in Fig. 6(b), a band centered at 1987 cm^{-1} was formed in D_2 but it was red shifted relative to the band at 1994 cm^{-1} in Fig. 5(b), and of much lower intensity than that in H_2 ; the former change can be ascribed

Fig. 5. Evolution of *in situ* FTIR spectra of reduced catalysts in H_2 at 110 °C. (a) Ru/SBA-15 (1%); (b) Ru/SBA-15 (10%).

Fig. 6. *In situ* FTIR spectra of Ru/SBA-15 (10%) during H-D exchange (a) and on exposure to D₂ at 110 °C after complete removal of any adsorbed H species (b).

to the deuterium isotope effect [22]. No replacement of H species by D species occurred during H-D exchange (Fig. 6(a)), therefore the much weaker band for D species cannot be attributed to the deuterium isotope effect alone. It mainly arises because D species are less stable than H species.

Based on the above analysis, we propose a possible structure in which an H atom is coordinated to both Ru and Si, as shown in Scheme 2. The formation of this structure is probably the intermediate step in the hydrogen spillover process. The red shift in the Si-H stretching band [23] from 2100 to 1996 cm⁻¹ is probably caused by the presence of Ru-H bonds from which electrons can be transferred to Si-H species. This electron transfer is responsible for the higher reactivity of Ru-H-Si species compared with those of isolated Si-H species reported in the literature [24–26]. It should be noted that hydrogenation

Scheme 2. Proposed structure of active sites on Ru/SBA-15.

may also take place on the Ru metal particle surfaces, but these active sites are more important when high selectivity toward targeted products is desired, especially when multi-bond hydrogenation is required [27].

4. Conclusions

In situ FTIR spectroscopy showed the presence of special adsorbed H species on reduced Ru/SBA-15 catalysts but not on Pd/SBA-15, Ru/Al₂O₃, or SBA-15. These H species were differentiated from adsorbed CO species and were reproducible in H₂. The formation rate of these H species depended on the Ru metal particle size, with small Ru particles giving faster formation of these H species. The amount of these H species was proportional to the Ru interfacial circumference, indicating that these species reside along the Ru-SiO₂ interface on the periphery of exposed Ru particles. H-D exchange experiments suggested that these H species were active in hydrogenation. A possible structure for these active sites was proposed.

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Graphical Abstract

Chin. J. Catal., 2017, 38: 1597–1602 doi: 10.1016/S1872-2067(16)62571-8

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利用原位红外光谱确证Ru/SBA-15的加氢活性位点

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摘要: Ru/SBA-15催化剂具有高的氢气活化能力, 因此被广泛应用在加氢和氢解反应中。一般认为Ru/SBA-15催化剂的高活性与金属Ru的高分散有关, 然而有研究发现在氧化硅载体上还存在溢流的氢, 这部分溢流氢也很可能参与加氢和氢解反应。这就产生了两个关键性的问题: (1) Ru/SBA-15的催化加氢活性中心是什么, 是金属Ru还是载体SBA-15; (2) 在金属Ru上解离的H是如何迁移到载体上的。因此, 加氢活性位点及其形成机理的确认对理解Ru/SBA-15催化剂的高活性至关重要。

原位红外光谱可从分子层面研究在工作状态的催化剂表面活性位点的状态, 进而推测可能的反应机理。通过与催化剂Pd/SBA-15, Ru/Al₂O₃和SBA-15比较发现, 在氢气氛围中Ru/SBA-15催化剂的原位红外谱图中存在一个独特的位于1996 cm⁻¹的峰。由于在Pd/SBA-15, Ru/Al₂O₃和SBA-15上都不存在这个峰, 因此该峰的形成是金属Ru和SBA-15相互作用的结果。此外, Si–O键在位于1866 cm⁻¹的合频峰不随氢气氛围变化而变化, 因此可排除这个峰属于Si–O键振动的倍频峰。为了排除该峰的产生是由于CO的吸附, 我们采用脉冲引入CO的方法, 发现在低的CO覆盖率下, 红外谱图中位于2068 cm⁻¹处出现了一个CO在Ru^{δ+}上的线性吸附峰。随着CO覆盖率增加, 该峰逐渐蓝移至2075 cm⁻¹, 同时位于2132 cm⁻¹处的峰强度增强了, 这两个峰都归属于Ru⁺(CO)_x物种的振动峰。这些CO的化学吸附强度都很高, 即使在He气中吹扫1 h后仍然存在, 而1996 cm⁻¹峰的形成是可逆的。此外, 低CO覆盖率下生成的吸附峰(2068 cm⁻¹)的强度低于1996 cm⁻¹峰的强度, 因此可以排除1996 cm⁻¹峰属于CO吸附峰的可能。既然1996 cm⁻¹峰的形成是可逆的, 将这个峰归属于载体上氢的可能性也可排除, 因为形成载体上氢的过程是不可逆的。另外, 形成1996 cm⁻¹峰的速率还证明了这个峰不属于金属Ru上吸附的氢, 因为金属Ru上氢的吸附是很快的。通过以上分析, 我们推断1996 cm⁻¹峰应该指认为在Ru和SBA-15界面处位点的红外峰。

为了证明这一点, 我们制备了不同Ru负载量的Ru/SBA-15催化剂, 发现这个界面处位点峰的峰面积与金属Ru颗粒在载体上形成交界面的周长成正比, 而峰达到稳态所需时间与Ru颗粒大小成反比。这说明H₂在金属Ru上发生解离吸附后迁移到Ru和SBA-15界面处, 形成了Ru–H–Si物种。当金属Ru的颗粒比较小时, 与载体形成交界面的周长小, Ru–H–Si物种的数量少, 体现在红外谱图上峰的峰面积小, 但解离的氢迁移到该界面所需时间变短了。当金属Ru的颗粒比较大时, 与载体形成交界面的周长变大, Ru–H–Si物种的数量多, 1996 cm⁻¹峰的峰面积大, 但解离氢的迁移慢了。此外, H–D交换实验还证明这个界面处的位点具有加氢活性。与文献报道的孤立Si–H物种的红外峰位置比较发现, Ru–H–Si物种具有明显的峰红移现象, 说明该物种中的Si–H键活性很高, 这可能是由于金属Ru将电子转移至Si–H键的结果。总之, 以上结果清晰地表明这个1996 cm⁻¹峰归属为结构是Ru–H–Si的活性位点。

关键词: Ru/SBA-15催化剂; 原位红外光谱; 加氢反应; 活性位点; 氢溢流

收稿日期: 2016-11-25. 接受日期: 2016-12-30. 出版日期: 2017-09-05.

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基金来源: 国家自然科学基金(21303163); 浙江省自然科学基金(LY13B030006, LY17B060006); 浙江省“钱江人才计划”(QJD1302011); 浙江省教育厅科研项目(Y201328681).

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