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The surface sites of sulfated zirconia studied in situ by laser-induced fluorescence spectroscopy

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Abstract

The surface sites of sulfated zirconia were investigated in situ by laser-induced fluorescence spectroscopy using aniline as the probe molecule. Different from the cases for many other oxides, the aniline adsorbed on the unique active sites of sulfated zirconia at r.t. is changed into another species, which emits a characteristic fluorescence band at 422 nm. The results illustrate that the sulfate groups in sulfated zirconia are favorable for the generation of these unique active sites, which also rarely exist on pure zirconia composed of tetragonal and monoclinic phases but do not exist on pure zirconia composed of monoclinic phase.

1. Introduction

Sulfated zirconia catalyst has attracted considerable attention since it was claimed as a solid superacid which can catalyze the skeletal isomerization of *n*-butane to isobutane at r.t. and change the color of Hammet indicator at $\mathrm{p}K_a < -11.9$ [1,2]. Furthermore, it shows remarkable activity in many catalytic reactions [3–5]. Lots of papers suggested that the superacidity is responsible for its unique catalytic properties. However, many authors gave different opinions that sulfate zirconia is not a superacid [6–8], and its acidity is even weaker than the zeolite HZSM-5 [9]. Numerous characterization techniques have been used to study this catalyst, unfortunately, it cannot detect the active sites of this catalyst [10,11]. On the other hand, Hino and Arata [12,13] reported that tungsten oxide or molybdenum oxide supported on zirconia also behaves as solid superacid in several catalytic reactions. Now, the nature of the catalytic behavior of sulfated zirconia is still a matter of controversy and the understanding of the active sites of this catalyst is ambiguous. As we known, laser-induced fluorescence (LIF) spectroscopy is a very sensitive characterization technique, and it provides not only the electronic state information of the luminescent species but also the information of the microenvironment around these species [14]. During recent years, LIF spectroscopy received increasing attention in heterogeneous catalysis, especially in the surface properties of solid catalysts [15,16]. In this work, we developed a LIF spectroscopy approach for the first time to study in situ the surface sites of sulfated zirconia catalysts using aniline as the probe molecule, which is a weak organic base. The results sensitively show the characteristic fluorescence band of the adsorption species on the unique active sites of sulfated zirconia.

2. Experimental

The fluorescence measurements were performed in situ using a home-built LIF spectroscopy setup [17,18].

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A continuous wave 244 nm laser (Coherent Innova 300 Fred) was used as the excitation source; a home-made quartz sample cell was placed around a focal point of an ellipsoidal mirror; the fluorescence signal from the sample was collected with the ellipsoidal mirror and focused onto a 32 cm monochromator (Jobin-Yvon Triax 320) by passing through a filter with cut-off wavelength below 280 nm; CCD (ISA Spectrum One CCD 3000) was mounted at the focal plane in the exit of the monochromator to detect the fluorescence signal. The wavelength calibration of this setup had been carried out with a mercury lamp, and the detected fluorescence spectrum of standard compound, quinine sulfate in 0.5 M H_2SO_4, is the same as the standard spectrum [19].

IR spectra measurements were recorded on a Thermo Nicolet 470 FT-IR spectrometer with resolution of 4 cm^{-1} and scan numbers of 64. Raman spectra were collected on ACTON SpectraPro 300i Raman spectrometer. The excitation wavelength was 532 nm, and the resolution was 4 cm^{-1}.

Sulfated zirconia was prepared according to the literature [20]. The zirconium precursors, sulfate-doped $Zr(OH)_4$ and $Zr(OH)_4$, were from MEI. Two sulfated zirconia catalysts were prepared by calcining sulfate-doped $Zr(OH)_4$ at 400 °C for 2 h (denoted as SO_4^{2-}–ZrO_2-400) and at 700 °C for 2 h (denoted as SO_4^{2-}–ZrO_2-700), respectively. And two ZrO_2 samples, that were investigated as comparison with sulfated zirconia, were prepared by calcining $Zr(OH)_4$ at 400 °C for 2 h (denoted as ZrO_2-400) and at 700 °C for 2 h (denoted as ZrO_2-700), respectively. Aniline (AR grade) was further purified by distillation under vacuum. These SO_4^{2-}–ZrO_2-400, SO_4^{2-}–ZrO_2-700, ZrO_2-400 and ZrO_2-700 samples were individually pressed into thin disk which was fixed in the sample cell and placed in a focal point of the ellipsoidal mirror. Before introduction of aniline, the sample was calcined in the sample cell at 450 °C for 1 h in O_2 flow and subsequently at 450 °C for 1 h in N_2 flow. After the sample was cooled down to r.t., N_2 flow was passed through the aniline saturator at r.t. to bring aniline vapour into the sample cell for 30 min. Then, the sample was purged by N_2 flow at r.t. Subsequently, the sample was increased its temperature under N_2 flow step by step for studying the changes of adsorbates on the catalyst. At the same time, the LIF spectra of the sample were collected in situ following above process. On the other hand, IR characterization was also carried out under the same treatment process and conditions for these samples as the LIF spectra measurements.

3. Results and discussion

Fig. 1 shows the in situ LIF spectra of the fresh catalysts and after aniline adsorption onto the catalysts at r.t. These fresh catalysts: SO_4^{2-}–ZrO_2-400, SO_4^{2-}–ZrO_2-700, ZrO_2-400 and ZrO_2-700 after calcination at 450 °C for 1 h in O_2 flow and subsequently at 450 °C for 1 h in N_2 flow, all exhibit a similarly broad emission band centered at ca. 510 nm. This band is attributed to the coordinatively unsaturated surface sites, $(Zr^{4+}–O^{2-})_{\text{Low Coordination}}$, of the zirconia [21]. Similar luminescence behavior and assignment were also reported on MgO and SrO [21,22]. After simulating these spectra based on Gaussian curve for a fluorescence band [23], as shown in Table 1, the emission band at ca. 510 nm consists of three sub-bands with peak positions at ca. 470, 535 and 615 nm. Comparing the catalysts SO_4^{2-}–ZrO_2-700 and ZrO_2-700 with the catalysts SO_4^{2-}–ZrO_2-400 and ZrO_2-400, the full width at half maximum (FWHM) of these sub-bands becomes narrower, and the relative areas of these sub-bands change. Therefore, it is suggested that these three sub-bands likely result from the different types of coordinatively unsaturated sites on the zirconia surface for these four catalysts.

After introduction of aniline to the fresh SO_4^{2-}–ZrO_2-400 at r.t., the fluorescence spectrum obviously exhibits a weak band at 350 nm and a strong band at 422 nm, while the intensity of the band at 510 nm decreases dramatically. For the fresh SO_4^{2-}–ZrO_2-700 adsorbing aniline, the fluorescence spectrum shows the

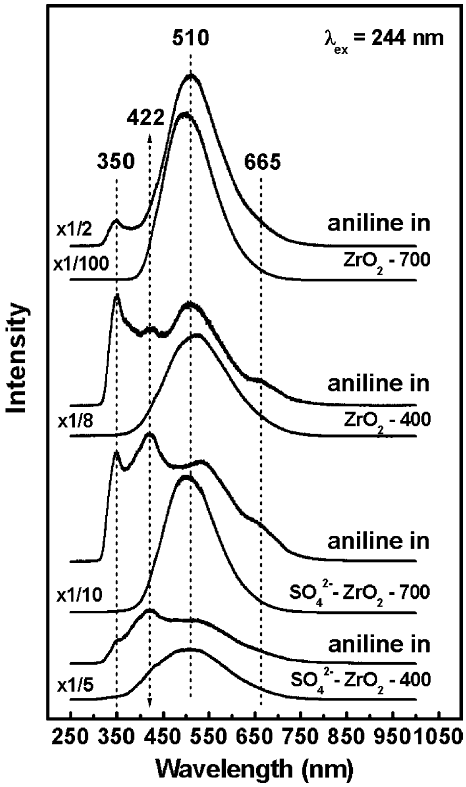

Fig. 1. In situ LIF spectra of the fresh catalysts and after aniline adsorption onto the catalysts at r.t.

Table 1
Simulation of the fluorescence spectra shown in Fig. 1, based on Gaussian curve

	Peak position/nm (FWHM/nm, relative area of the sub-band)						
SO_4^{2-}–ZrO_2-400				462 (118.0, 1.20)	542 (115.9, 1.00)	619 (147.2, 0.50)	
Aniline in	347 (29.7, 0.08)	377 (55.4, 0.06)	411 (82.1, 0.78)	483 (117.1, 0.42)	530 (147.4, 1.00)	627 (174.3, 0.43)	
SO_4^{2-}–ZrO_2-700				477.0 (89.8, 0.82)	533.7 (108.4, 1.00)	613.1 (126.6, 0.21)	
Aniline in	344.6 (29.3, 0.21)	371.2 (30.4, 0.07)	415.4 (85.3, 0.86)	487.0 (55.3, 0.09)	540.4 (125, 1.00)	653.8 (98.4, 0.20)	687.8 (93.5, 0.06)
ZrO_2-400				480.5 (107.7, 0.58)	534.5 (127, 1.00)	611.2 (150.3, 0.42)	
Aniline in	346.9 (29, 0.35)	374.0 (32.4, 0.19)	412.5 (66, 0.54)	485.1 (80.5, 0.38)	527.6 (115.4, 1.00)	608.5 (160.4, 0.39)	678.5 (88.0, 0.09)
ZrO_2-700				473.7 (77.7, 0.80)	530.6 (96.8, 1.00)	608.2 (112.9, 0.21)	
Aniline in	345.9 (34.2, 0.05)	378.0 (54.2, 0.05)		476.2 (91.8, 0.60)	531.0 (103.7, 1.00)	622.6 (125.7, 0.32)	

$\sum\chi^2$ is in the range of 0.60–6.3 for the fluorescence intensity with the magnitude of 10000 a.u. The area of the sub-band at ca. 535 nm is assumed to be 1.00 for the calculation of the relative areas of the sub-bands.

bands at 350, 422 and 665 nm besides the band at ca. 510 nm. The band at 665 nm is the superposition of the band at ca. 510 nm and the second diffraction of the band at 350 nm. However, compared SO_4^{2-}–ZrO_2-700 with SO_4^{2-}–ZrO_2-400, the intensity ratio of the band at 422 nm to that at 350 nm decreases. Interestingly, after aniline admission onto the fresh ZrO_2-400, the fluorescence band at 422 nm appears; however, its intensity is very weak. Whereas, this band at 422 nm does not emerge for the case of the fresh ZrO_2-700.

Simulation shows that the band at 350 nm is the superposition of two bands at 345 and 375 nm. These two bands correspond to the fluorescence band and the phosphorescence band of aniline adsorbed on the catalyst, respectively [24]. For the band at 422 nm, we have not found a paper reporting that this band is related to aniline. Same experiments have been done for other oxides: SiO_2, Al_2O_3, MgO, TiO_2, ZnO, and zeolite HZSM-5, NaZSM-5, HY, and NaY, the band at ca. 350 nm exhibits, but the band at 422 nm does not appear. This indicates that a part of aniline, which is adsorbed on the unique active sites of sulfated zirconia at r.t., has changed into another species which emits a characteristic fluorescence band at 422 nm. Based on the intensity ratio of the band at 422 nm to that at 350 nm, it is suggested that the sulfate groups in sulfated zirconia are favorable for the generation of these unique active sites, and that the proportion of these unique active sites to the all adsorption sites on sulfated zirconia surface decreases with increasing the calcination temperature of catalyst.

One feature of sulfated zirconia catalyst is the catalyst deactivation in short time [25,26]. In this case, after the sulfated zirconia catalysts adsorbing aniline were purged by N_2 flow, the LIF spectra showed that the intensity of the band at 422 nm remained unchanged. Then, increasing the temperature of catalyst in N_2 flow up to 450 °C step by step, it was observed that the color of these two sulfated zirconia catalysts became black. This indicates that the species is strongly adsorbed on the active sites, and that high temperature leads to the coke formation on the catalyst surface. After these two catalysts were regenerated by calcining at 450 °C in O_2 flow for 30 min and subsequently in N_2 flow for 30 min, the color of the catalysts became dark yellow. This means that most of coke was burned off. Subsequently, after the catalysts were cooled down to r.t., aniline was again admitted into the sample cell. Shown in Fig. 2, the LIF spectra cannot completely recover, just exhibiting a quite weak emission band at 422 nm. This suggests that most active sites were still covered by coke.

On the other hand, in situ IR characterization, shown in Fig. 3, was carried out under the same treatment process and conditions as the in situ LIF characterization for the fresh catalysts. For sulfated zirconia, the IR spectra just show the vibration bands of aniline besides

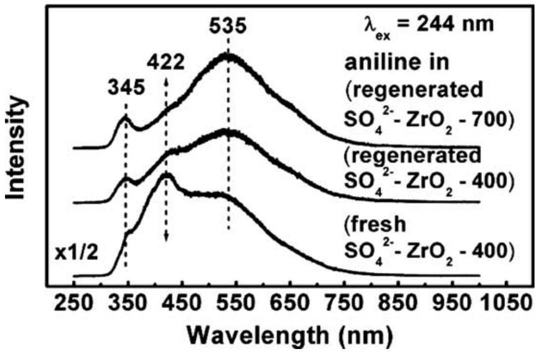

Fig. 2. In situ LIF spectra after aniline adsorption onto the regenerated catalysts at r.t.

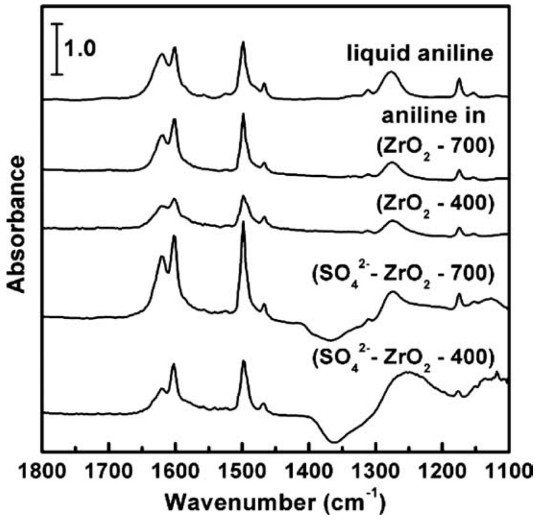

Fig. 3. In situ IR difference spectra after aniline adsorption onto the fresh catalysts at r.t. The IR spectrum of liquid aniline is added for comparison, and it is the same as that from Aldrich library of IR spectra.

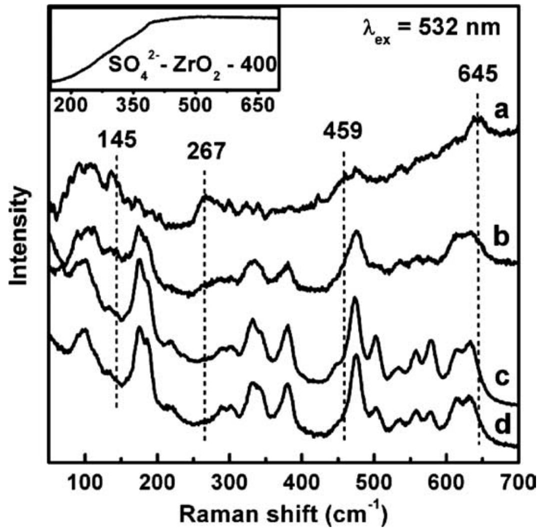

Fig. 4. Raman spectra of (a) ZrO_2-400 uncalcined in the sample cell; (b) ZrO_2-400, (c) ZrO_2-700, (d) SO_4^{2-}–ZrO_2-700, and (inset) SO_4^{2-}–ZrO_2-400 after calcination in the sample cell at 450 °C for 1 h in O_2 flow and subsequently at 450 °C for 1 h in N_2 flow.

the vibration bands of sulfate groups in the range 1400–1250 cm^{-1} [27]. Thus, these results demonstrate that the amount of the species responsible for the fluorescence band at 422 nm is very small, and that its fluorescence quantum efficiency is much higher than that of aniline. According to the peak position, single peak and high fluorescence quantum efficiency, this species is similar to the aniline oligomer [28]. Therefore, it is suggested that the electrons of aniline are delocalized due to the interaction between aniline and the unique active sites, which act as the Lewis acid sites. On the other hand, this means that the proportion of the unique active sites to the all adsorption sites on sulfated zirconia surface is very small. This may be why numerous characterization techniques cannot detect these unique active sites.

Fig. 4 shows the Raman spectra of these catalysts. It is observed that fresh ZrO_2-400 contains not only monoclinic phase zirconia but also tetragonal phase zirconia with Raman bands at 145, 267, 459 and 645 cm^{-1} [29]. Whereas, fresh ZrO_2-700 and SO_4^{2-}–ZrO_2-700 just contain monoclinic phase zirconia. The Raman bands of SO_4^{2-}–ZrO_2-400 cannot be obtained because of strong luminescence interference. In connection with the LIF characterization results shown in Fig. 1, this indicates that the existence of the unique active sites is related to the crystallographic form for pure zirconia. These unique active sites rarely exist on pure zirconia composed of tetragonal and monoclinic phases but do not exist on pure zirconia composed of monoclinic phase. Whereas, sulfate groups are favorable for the generation of these unique active sites on sulfated zirconia surface. Similarly, Ecormier et al. [30] also found that the pure zirconia composed of tetragonal and monoclinic phases possesses poor activity in α-pinene isomerization reaction, and that sulphation of zirconia greatly enhances the catalytic activity. The relationship between the unique active sites, which are detected by LIF spectroscopy using aniline as the probe molecule, with the alkane isomerization reactions on sulfated zirconia catalyst is unclear; and further investigations are underway.

4. Conclusions

By in situ laser-induced fluorescence spectroscopy using aniline as the probe molecule, it is sensitively detected that there are a very small amount of unique active sites on the surface of sulfated zirconia. These unique active sites also rarely exist on the pure zirconia composed of tetragonal and monoclinic phases. The sulphation of zirconia evidently increases the amount of these unique active sites on sulfated zirconia surface, even for the monoclinic phase zirconia which does not possess these unique active sites. The strong interaction between the unique active sites and adsorbate may be one reason of the catalyst deactivation in short time.

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