Ultraviolet Raman spectroscopy characterization of sulfated zirconia catalysts: fresh, deactivated and regenerated

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Ultraviolet Raman spectroscopy (UVRS) has been demonstrated to be a powerful new tool for catalysis and surface science studies. UVRS can successfully avoid the surface fluorescence which frequently occurs in normal Raman spectra of many catalysts. Fresh, deactivated and regenerated sulfated-zirconia catalysts have been characterized using this new method. The UV Raman spectrum of the fresh sample is dominated by the tetragonal phase, however, the spectrum of deactivated sulfated zirconia is nearly identical to that of the monoclinic phase of pure zirconia. A regeneration of the deactivated catalyst restores the spectrum back to that of the fresh sample. In addition, a new band at 750 cm⁻¹ associated with the fresh sample attenuates with the deactivation process. This band is tentatively assigned to the surface $[\text{ZrO}_4]^{4-}$ unit which is assumed to bond to the surface sulfate group. The results indicate that the surface phase of sulfated zirconia is reconstructed from tetragonal to monoclinic phase during the deactivation process while the bulk remains in the tetragonal phase after the deactivation. It is proposed that the surface tetragonal phase is stabilized by sulfate groups, and is associated with the catalytic activity.

Keywords: UV Raman spectroscopy; zirconia; sulfated zirconia; deactivation; surface phase transformation

1. Introduction

Raman spectroscopy is potentially one of the most powerful techniques for characterizing catalysts [1,2]. However, conventional Raman spectroscopy using visible laser excitation often suffers from two limitations in catalysis studies, inherently low Raman scattering signals and strong fluorescence which often obscures the weak Raman signal. One technique to avoid interference from fluorescence is to employ ultraviolet excitation because the fluorescence of most molecules and surfaces occurs in the visible region. Asher et al. [3–5] have demonstrated that fluorescence does not interfere with the Raman spectrum for a number of systems when an ultraviolet laser was used as the excitation source. However, there have been no reports to date of catalyst characterization using UV Raman spectroscopy. In principle, UV Raman can not only diminish the fluorescence interference but also greatly increase the Raman signal when the laser frequency falls in an absorbance region of the system giving rise to the resonance Raman phenomenon [6]. Using UV excitation, we have detected the surface Raman signal for several kinds of catalysts, e.g., coked cracking catalysts, sulfated zirconia and even grease-contaminated catalyst samples, all of which are difficult to characterize by normal Raman spectroscopy because of strong fluorescence.

Sulfated zirconia has attracted considerable attention in recent years as a solid acid catalyst [7–12]. Sulfated zirconia shows very high initial activity for alkane isomerization and has been designated as a superacid catalyst. Unfortunately this catalyst deactivates very rapidly. This fact has motivated many researchers to study the nature of the catalytic reactions on sulfated zirconia and extensive catalyst characterization has been made by various techniques in order to understand this deactivation phenomenon [13–18]. Despite this effort the nature of the catalysis is still unclear, and there is no definitive identification of either the active site or the active surface phase. In this contribution we report the UV Raman spectra of sulfated zirconia before and after testing for butane isomerization, together with those of the regenerated catalyst. The UV Raman spectra clearly show a surface phase change associated with the deactivation. This result may shed light into the nature of the catalysis on sulfated zirconia catalysts.

2. Experimental

A previous paper has showed an overview of the UV Raman spectrometer [19]. The frequency doubled output of a 12 W argon ion laser was used as the 257.2 nm excitation source. The power of the 257.2 nm line can be as large as 30 mW, but in this study, the power delivered to the sample was kept below 5 mW to avoid thermal decomposition. The Raman scattering from the sample surface was collected using a backscattering geometry by an AlMgF₂ coated ellipsoidal reflector, and focused
into a single grating spectrograph through a notch filter. The detector is an imaging multichannel photomultiplier tube (IPMT) with a spectral window of 2100 cm\(^{-1}\). The slit width used in fig. 2 is 200 \(\mu\)m and 100 \(\mu\)m in fig. 3. Catalyst samples were formed into pressed discs. The measurements can be performed both in air and in situ in a quartz reactor cell at room temperature. The sample in the quartz cell can be treated over a wide temperature range, r.t.\(-1000^\circ\)C.

Catalyst samples used in this work were kindly provided by Professor Sachtler's group, and a description of the sample preparation has been given elsewhere [10]. Sulfated zirconia, \(\text{SO}_2^-/\text{ZrO}_2\), was prepared from sulfated zirconium hydroxide by calcination at 650\(^\circ\)C in a flow of dry air. The sulfur content was measured to be 1.1 wt\% by inductively coupled plasma (ICP) analysis. Zirconia, \(\text{ZrO}_2\), was prepared by calcining zirconium hydroxide, \(\text{Zr(OH)}_4\), at 650\(^\circ\)C in dry air. The catalyst was tested at 180\(^\circ\)C for isomerization of \(n\)-butane to isobutane. The catalyst after 1 h at reaction conditions is called the used or deactivated catalyst. The deactivated catalyst has an activity less than 10\% of the fresh catalyst. Catalyst regeneration was carried out by oxidizing the used sample disc at 500\(^\circ\)C in a flow of dry air for the data shown in fig. 2 and pure \(\text{O}_2\) for fig. 3 respectively. X-ray diffraction (XRD) patterns show that the sulfated zirconia is mainly tetragonal phase and pure zirconia is mainly monoclinic phase. This is in good agreement with that reported in ref. [20].

As shown in fig. 1, the Raman spectrum of pure zirconia recorded using normal visible excitation (\(\lambda = 514.5\) nm) is characteristic of the monoclinic phase [21], while there is no detectable Raman signal for fresh and used sulfated zirconia because of strong background of fluorescence. The resolution of the normal Raman spectrum is superior to the UV Raman at present because the resolving power of the spectrograph in the UV region is less than in the visible region. Therefore the bands in the UV Raman spectra are relatively broad.

3. Results and discussion

Fig. 2 displays four UV Raman spectra recorded in the 300–1700 cm\(^{-1}\) region for zirconia, fresh sulfated zirconia, used sulfated zirconia and regenerated sulfated zirconia as indicated. Apparently, the fluorescence background is successfully avoided in these UV Raman spectra, so that structural characterization of the catalyst can be performed whether the catalyst is fresh or used. The UV Raman spectrum of pure zirconia gives strong bands at 475, 630, and 750 cm\(^{-1}\), and weak bands at 560 and 690 cm\(^{-1}\). The main bands in this region are very similar to those in fig. 1 except for the lower resolution. The band at 475 cm\(^{-1}\) is fairly narrow but the bands at 630 and 750 cm\(^{-1}\) are actually composed of several overlapping bands. There are at least two bands near 630 cm\(^{-1}\), i.e., 610 and 630 cm\(^{-1}\). The intensities of the lower frequency bands should be stronger than shown in fig. 2 because the notch filter attenuates the Raman signal close to the exciting line. In the region exhibited above,