

# Unusual manifestation of benzene radical cations in ESR spectra on sulfated zirconia

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## Abstract

A narrow singlet has been observed in the ESR spectra after benzene adsorption on sulfated zirconia, with its evacuation and freezing leading to the reversible formation of benzene dimer radical cations. The singlet has been proposed to result from the delocalization of the electron density throughout several benzene rings due to fast electron exchange. This distinguishes sulfated zirconia catalysts from zeolites where this effect is not observed because of the small size of channels. © 2000 Elsevier Science B.V. All rights reserved.

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## 1. Introduction

Sulfated zirconia is known to exhibit unique catalytic activity in the low-temperature isomerization of light alkanes [1–3]. Despite intensive investigation by various physicochemical methods, there is no universally accepted theory as what type of sites account for its unique catalytic activity. Some researchers believe that this activity is related to the exceptional strength of its acceptor sites [4]. Even if alkane radical cations are indeed formed on sulfated zirconia, they are too unstable at the reaction temperatures to be observed by ESR. Therefore, benzene seems to be the most suitable test molecule for the investigation of the acceptor sites.

Recently, we have reported the formation of various radical cation species from aromatic

hydrocarbons with high ionization potentials over sulfated zirconia and proved that active sulfated zirconia catalysts possess the strongest one-electron acceptor sites among the known oxide systems [5]. However, the nature of one radical particle — a narrow singlet with  $g \sim g_e$  observed sometimes in ESR spectra after benzene adsorption on sulfated zirconia — was not understood. Similar signals are not observed on zeolites. In the present paper, results of a detailed investigation of transformations of radical particles formed after benzene adsorption on sulfated zirconia and their dependence on the pretreatment conditions are reported.

## 2. Experimental

Zirconium hydroxide was precipitated from aqueous solution of  $Zr(NO_3)_2$  with aqueous ammonia, filtered thoroughly, washed with distilled water and dried at 100°C overnight. The

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solid was treated with 0.2 N  $\text{H}_2\text{SO}_4$  solution ( $5 \text{ cm}^3/\text{g}$ ) for 1 h at room temperature. Then the solid was filtered, dried without washing overnight at  $100^\circ\text{C}$  and calcined at  $550^\circ\text{C}$  for 3 h in air.

Tetragonal zirconia was the only crystalline phase observed in the sample by XRD [5]. With the surface area of  $135 \text{ m}^2/\text{g}$ , the sample contained 4.6 wt.%  $\text{SO}_3$  [5]. This corresponds to the sulfur loading of about 2.5 sulfur atoms/ $\text{nm}^2$ . The sample was active in pentane isomerization at room temperature [5].

ESR experiments were conducted in our ESR in situ installation described elsewhere [6]. One-tenth gram of the catalyst was placed in a quartz ampoule connected to a high-vacuum system. The sample pretreatment included activation in oxygen (10 Torr) at different temperatures in a vacuum line with a trap cooled by liquid nitrogen with subsequent cooling to room temperature and evacuation for 20 min.

Desired amounts of benzene were adsorbed from the gas phase. Prior to the adsorption, benzene (“pure” degree) was purified by a freeze–pump–thaw procedure.

### 3. Results and discussion

If benzene is adsorbed at room temperature on sulfated zirconia activated at  $500^\circ\text{C}$ , which is a typical pretreatment temperature for ESR studies, a superposition of nine-line spectrum with one hyperfine constant of 3.3 G attributable to biphenyl radical cations, which are usually formed from benzene radical cations on catalytic surfaces [5,7], and a narrow very intensive signal with  $g = 2.0026$  occur (Fig. 1, Spectrum 1). The intensity of the latter signal decreases with time until complete disappearance after about 20 min. The former signal grows in intensity for as long as the latter signal is observed. Then, these particles are only subjected to much slower polycondensation processes.

Chen et al. [8], who were the first to observe this picture, assigned the narrow signal to free

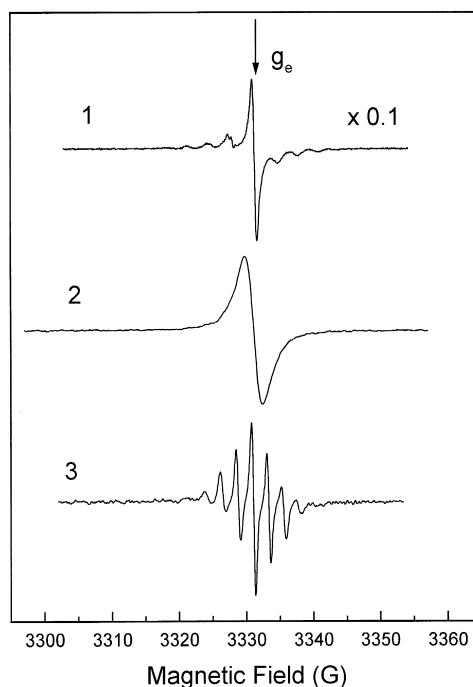


Fig. 1. ESR spectra registered at room temperature after benzene adsorption (10 Torr) on the catalyst activated at  $500^\circ\text{C}$  (1), in 30 min after benzene adsorption (1 Torr) on the catalyst activated at  $300^\circ\text{C}$  (2), and after subsequent evacuation for 30 min (3).

electrons abstracted from benzene molecules, their lifetime being considerably shorter than that of biphenyl radical cations but sufficient to observe them by conventional ESR. To find out what exactly happens with benzene radical cations formed on sulfated zirconia, we have studied this process in our ESR in situ installation.

Sulfated zirconia pores are significantly larger than the channels of ZSM-5 zeolites. Therefore, we were not able to observe thermal benzene monomer radical cations in this system. Benzene dimer radical cations could be formed by adsorbing benzene at temperatures significantly lower than its melting temperature [5]. After heating to room temperature, they quantitatively transformed into biphenyl radical cations with the narrow signal observed as an intermediate. This experiment unambiguously shows that the narrow signal does not correspond to free electrons abstracted from benzene. In the latter case,

it should be observed after benzene ionization at low temperatures and not during its oxidative dimerization yielding biphenyl radical cations.

Its nature was unveiled only by experiments performed on the catalyst activated at 300°C. This is a typical temperature for the catalyst pretreatment prior to its use in the isomerization reactions [9], and it was natural to compare the properties of its acceptor sites after such pretreatment with those exhibited after a standard treatment at 500°C. Unexpectedly, benzene adsorption (1 Torr) on such catalyst at room temperature yielded a singlet with  $g = 2.0026$  and  $\Delta H = 2.5$  G (Fig. 1, Spectrum 2), which was absolutely stable for at least 30 min [10]. The singlet could be simulated by a perfect Lorentzian line with the intensity of  $3.2 \times 10^{15}$  spins/g. Neither benzene dimer nor biphenyl radical cations were observed.

Evacuation of the sample for half an hour led to the formation of the spectrum of benzene dimer radical cations with 12 equivalent lines with  $a = 2.2$  G (Fig. 1, Spectrum 3) resulting from the homogeneous delocalization of the electron density throughout two benzene rings. Benzene re-adsorption on the sample yielded the singlet once more with complete reversible disappearance of the spectrum of benzene dimer radical cations. The linewidth of the singlet appeared to depend on the amount of adsorbed benzene decreasing with its increase and varying from 1 to 3 G.

Moreover, the singlet could be reversibly frozen to benzene dimer radical cations (Fig. 2). The fact that alterations in the apparent concentration of the radical particles obeyed the Curie law proves that the singlet is just another spectroscopic manifestation of the radical cations.

The process leading to the appearance of the singlet in the ESR spectrum must involve fast electron exchange between charged and neutral molecules, which is very typical for aromatic radical cations in solutions. The concentration of the radical cations is not very high. Assuming that the acceptor sites are evenly distributed on the catalyst surface, the average distance

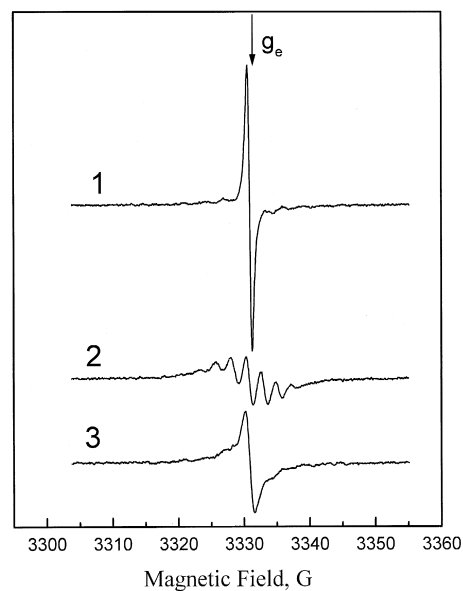


Fig. 2. ESR spectra registered at 248 K (1), 163 K (2) and 218 K (3) after benzene adsorption (10 Torr) at room temperature on the catalyst activated at 300°C.

between the sites on the catalyst activated at 300°C can be evaluated to be about 200 nm. As it seems reasonable to assume that the radical cations should be attached to a surface site, and this distance is too high for direct spin exchange, another important conclusion can be made. The number of sites where the radical cations can be stabilized must be significantly higher than the actual concentration of the radical cations measured by ESR. Therefore, this concentration seems to reflect the energetic properties of the whole system rather than directly reveal some unique extraordinary acceptor sites, which are present on the surface in a very low concentration.

Thus, the singlet seems to represent quasi-free positive charge located in the near-surface liquid rather than free electrons in the sub-surface layer of the catalyst as it was proposed earlier [8]. It seems that the positive charge formed by the abstraction of electron from aromatic molecules can be effectively delocalized throughout relatively large aggregates of the aromatic molecules involving practically all liquid within the catalyst pores, such aggregates

being sufficiently stable to chemical transformations at room temperature.

This effect must be typical for all relatively stable radical cations formed on acidic catalysts from various aromatic molecules. Although it cannot be observed in zeolites due to the small size of their channels, one can expect to observe it on other catalytic systems with sufficiently large pores, which possess strong electron-acceptor sites.

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