EPR study of electron-acceptor sites on the surface of solid acid catalysts during catalytic reactions

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Abstract: An original approach was developed for quantitative characterization of electron-acceptor sites on the surface of operating catalysts by EPR. Electron-acceptor sites of different strength can be characterized using a set of spin probes with different ionization potentials. It has been demonstrated that electron-acceptor sites can exist on the surface of operating catalysts using 1-chlorobutane dehydrochlorination over finely dispersed MgO, and Al_2O_3 as a test reaction. The experimentally observed high electron affinity of solid acid catalysts can be explained assuming that acid dissociation to the separated positive and negative ions occurs on their surface.

Keywords: EPR spectroscopy, electron-acceptor sites, operating catalysts.

1. Introduction

Obtaining information on the nature and concentration of active sites on the surface of heterogeneous catalysts for prediction of their catalytic activity is one of the main goals of physical methods used for investigation of catalysts. Particularly important is characterization of operating catalysts when the concentration of the tested sites can be directly compared with the catalytic activity.

Electron-acceptor sites of different strengths can be characterized using aromatic probes with different ionization potentials.[1,2] It was demonstrated that the catalytic activity of doped alumina catalysts in such conventional acid-catalyzed reaction as ethanol dehydration correlated with the concentration of weaker acceptor sites.[3] Weak electron-acceptor sites formed due to the MgO halogenation were shown to be responsible for the solid-state reaction between nanocrystalline MgO and CF_2Cl_2.[4,5]

In this study we characterized weak electron-acceptor sites formed during 1-chlorobutane dehydrochlorination over several oxide catalysts using perylene as a spin probe. Good correlations were observed between their concentrations and the catalytic activity, both substantially changing due to the surface modification with chlorine. The developed approach can be also used for characterization of other types of active sites on the surface of operating catalysts by EPR using appropriate spin probes.

2. Experimental

Nanocrystalline MgO, Al_2O_3 and ZrO_2 were studied in catalytic dehydrochlorination of 1-chlorobutane. The samples were placed in an EPR sample tube, activated in the argon flow for 1 h at the reaction temperature, and subjected to reaction with 1-chlorobutane introduced into the argon flow. 1-Chlorobutane conversion to a mixture of butenes was monitored by gas chromatography. After the reaction was carried out for the desired time, the sample was quickly cooled down to room temperature and filled with a 2×10^{-2} M solution of perylene in toluene. The concentration of electron-acceptor sites was determined by integration of the EPR spectra registered immediately after the spin probe adsorption and after additional heating at 80°C for 18 h. Quantum chemical simulations were carried out by density functional method using Gaussian 09 software, B3LYP hybrid functional and 6-31+G(d,p) basis set.

3. Results and discussion

The catalytic activity of nanocrystalline MgO, Al_2O_3 and ZrO_2 in 1-chlorobutane dehydrochlorination was found to increase significantly during the first ~20-30 minutes on stream accompanied by modification of the oxide surface with chloride ions, before reaching a steady state. For MgO the dehydrochlorination mechanism is also changed from E2 on the pure oxide to E1. No electron-acceptor sites were observed on the surface of initial MgO samples. They appeared only during the reaction. A good correlation was observed between the catalytic activity and the concentration of weak electron-acceptor sites (Fig. 1). Fresh Al_2O_3 and ZrO_2 are characterized by substantial concentrations of electron-acceptor sites. This makes them more active than MgO. The concentration of electron-acceptor sites was also found to grow during initially due to the surface chlorination following the increase of the catalytic activity, and again a good correlation was observed between the catalytic activity and the concentration of the studied electron-acceptor sites.

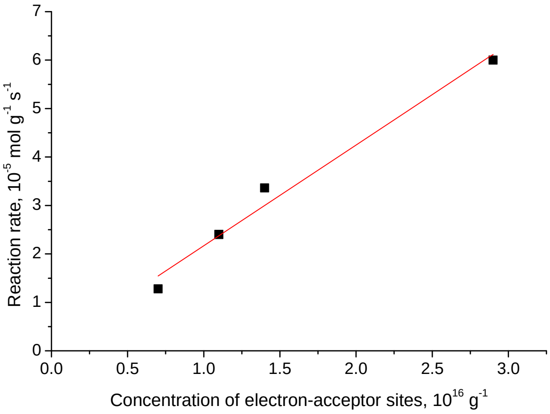

Figure 1. Correlation between the catalytic activity in 1-chlorobutane dehydrochlorination over nanocrystalline MgO at 250°C and intensities of the EPR spectra observed after perylene adsorption.

The electron affinity of conventional Bronsted or Lewis acid sites of chlorine-doped MgO was found to be about 2 eV and is definitely not sufficient to account for their experimentally observed electron-acceptor properties. The electron affinity about 7 eV was observed only for positively charged clusters chlorine-containing clusters. Such sites can be formed by separation of the charged fragments formed by HCl chemisorption to the distance when they no longer feel each other. The acidity of resulting Bronsted acid sites is comparable with those of hydronium ions in conventional strong liquid acids. In fact, our calculations show that the strength of such sites is just right for Cl^- abstraction and initiation of the experimentally observed 1-clorobutane dehydrochlorination following the E1 mechanism.

4. Conclusions

Electron-acceptor sites were shown to exist on the surface of operating catalysts using 1-chlorobutane dehydrochlorination over nanocrystalline MgO, Al_2O_3 and ZrO_2 as an example. The concentration of weak elector-acceptor sites was found to correlate with the catalytic activity. The obtained results indicate that weak electron-acceptor sites tested using perylene may be the active sites accounting for 1-chlorobutane dehydrochlorination in the active state of the catalysts. The developed method can be used to monitor changes in the concentration of electron-acceptor sites as well other types of active sites, which can be characterized by EPR using appropriate spin probes, on the catalyst surface in the course of any catalytic reaction. According to the results of our simulations, the experimentally observed high electron affinity of solid acid catalysts can be explained assuming that HCl dissociation to the positive and negative ions occurs on their surface. The resulting sites are remarkably similar in their properties to the species resulting from the electrolytic dissociation of strong homogeneous acids and superacids and accounting for their reactivity.

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