ESR Study on the Nature of Active Site of Silica-supported Chromia in Propane Dehydrogenation Reaction

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ESR spectroscopy was used to investigate the nature of active site of CrO_x/SiO_2 in propane dehydrogenation reaction and Cr^{5+} species was proposed to be the active site for the reaction.

There is considerable interest in the conversion of light alkanes directly to higher value organic chemicals because of the low cost and abundance of the alkanes. The activity and selectivity of chromia-supported catalysts in alkane dehydrogenation have been known for many years.[1-3] Lugo and Lunsford[4] investigated this reaction on the CrO_x/SiO_2, and Slovetskaya, et al.,[5] Van Reijen, et al.[6] and Ashmawy[7] on the CrO_x/γ-Al_2O_3 system, they favored the view that Cr^{2+} species were responsible for the catalytic activity of the above systems in alkane dehydrogenation. Other authors[8,9], however, suggested that Cr^{3+} were active species. Cordischi, et. al.[10] also studied the catalytic behavior of the CrO_x/ZrO_2 for the dehydrogenation of propane by means of pulse reaction, and concluded that Cr^{3+}, arising from the reduction of Cr^{5+}, were the active sites. More recently, carbon dioxide was introduced in the dehydrogenation of propane over the SiO_2-supported chromia catalysts.[11] The promoting effect was found for the reaction because the H_2 produced by the dehydrogenation can be removed via the reversed water-gas shift reaction. In the present work, we investigated the electron-spin resonance (ESR) spectra of Cr^{3+} and Cr^{5+} species in the CrO_x/SiO_2 catalyst under the reaction conditions to determine the active species and found that CO_2 not only played the role in the reversed water-gas shift reaction but also the role of recovering the active chromium species.

CrO_x/SiO_2 catalyst was prepared by the incipient wetness impregnation with chromium nitrate as the starting salt. The sample was dried at 393 K for 12 h and then calcined at 923 K for 6 h in air. The Cr loading was about 5 wt%.

The reactions were carried out in a steady-state microreactor system operating at atmospheric pressure. The typical feed gas consisted of CO_2 (or N_2) and C_3H_8 with the molar ratio of 2.8. About 0.2 g 20-40 mesh catalyst was used in each run, which renders a gas hourly space velocity of 2800 h^{-1}. The reaction effluent was analyzed by the on-line gas chromatography equipped with a thermal conductivity detector and a Chromosorb QS column. The sample was loaded in a quartz flow cell with a side tube for ESR measurement. The treatment was performed as follows: 1) heating in O_2 at 923 K for 1 h, then sweeping by N_2 for 30 min, 2) treating in reactant mixture at 923 K for 5 min and 140 min, respectively. After each treatment, the ESR spectrum was recorded at room temperature on a FE1XG ESR spectrometer operating at the X-band frequency, the microwave power was 1.2 mW. Spin-Hamiltonian parameter g was obtained by computer simulation.

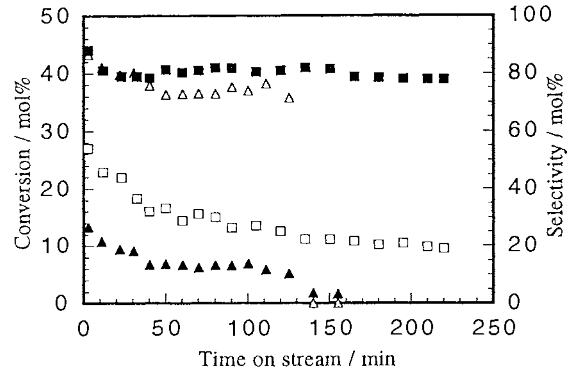

Figure 1. Catalytic behavior as a function of time on stream for 5 wt%Cr/SiO_2 at 923 K. (□) Conversion of propane with CO_2 as carrier gas; (■) Selectivity to propene with CO_2 as carrier gas; (▲) Conversion of propane with N_2 as carrier gas; (△) Selectivity to propene with N_2 as carrier gas.

Figure 1 shows the variations in propane conversion and selectivity to propene over the catalyst as a function of time on stream. When the reaction was conducted in N_2 atmosphere, a deactivation was observed in the first 40 min, followed by a plateau with about 7% propane conversion. After 140 min, the activity was almost lost completely and the products were mainly methane and ethane resulting from the cracking of propane. In contrast, in the atmosphere of carbon dioxide, both the conversions of propane and selectivity to propene were enhanced. For example, the initial conversion of propane was increased from 13% in N_2 atmosphere to 27% in CO_2 atmosphere. In addition, about 12% propane conversion remained even after 200 min in the atmosphere of CO_2 without the decrease of the propene selectivity.

The ESR spectra of the catalyst treated under the reaction conditions were given in Figure 2 to 4. Before oxygen pretreatment, two signals were observed, as seen in Figure 2a. The first weak signal, denoted as β , with g=2.003, is attributed to the cluster-like Cr^{3+}.[12] The other intensive and anisotropic peak, denoted as γ, is assigned to the tetrahedral Cr^{5+} axial species with $g_{\perp}=1.974$ and $g_{\parallel}=1.897$.[13] It was reported that Cr^{5+} and clustered Cr^{3+} were formed in the calcined catalyst.[14] In addition, the existence of Cr^{6+} species in the catalyst was also possible.[15] In fact, we measured the catalysts before and after reactions under both N_2 and CO_2 atmospheres by using the Ultraviolet-Visible Diffuse Reflection (UV-Vis DRS) spectroscopy. It was found that Cr^{6+} species were present in the catalyst before the reaction. After the reactions, the amount of Cr^{6+} species were greatly diminished, but a small amount of Cr^{6+} were still there. Although the activity of the Cr^{6+} can not be exclusively excluded, the coordinatively saturated structure of Cr^{6+} species might lack the activity for the dehydrogenation reaction of ethane as mentioned by Lugo and Lunsford[4]. After O_2 treatment, the β signal disappeared while the γ signal became more intensive as shown in Figure 2b. In addition, the line width of the γ signal was significantly broadened. Very likely, the Cr^{3+} species was oxidized to the Cr^{5+} species by the O_2 treatment. Kazanskii and Pecherskaya[16] attributed the increase of line width to the dipole-dipole

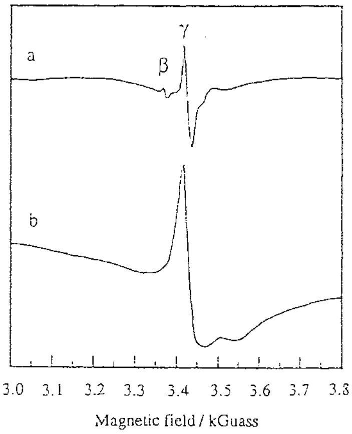

Figure 2. ESR spectra at RT of 5 wt%Cr/SiO_2 sample. Spectrum a: sample calcined in air at 973 K; Spectrum b: sample heated in O_2 at 923 K.

broadening by the paramagnetic oxygen molecules adsorbed on the surface of the catalyst, and concluded that the Cr^{5+} species must locate on the surface of the catalyst. Figure 3 shows the ESR lines recorded after reaction in the CO_2/C_3H_8 mixture for 5 min and 140 min, respectively. The β signal appeared again and its intensity increased with the reaction time whereas the γ signal was decreased with time on stream. In Figure 3b, the β signal becomes predominant. This indicates the transformation between Cr^{3+} and Cr^{5+} in the catalyst under different conditions. Specifically, the Cr^{3+} species was converted into Cr^{5+} species when the catalyst was treated in O_2, and the Cr^{5+} species could be reduced to the Cr^{3+} during the dehydrogenation reaction.

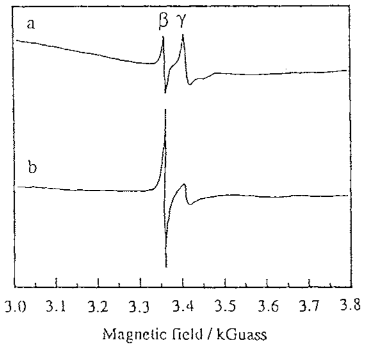

Figure 3. ESR spectra at RT of 5 wt%Cr/SiO_2 sample exposed in CO_2/C_3H_8 mixture flow. Spectrum a: after 5 min; Spectrum b: after 140 min.

The ESR spectra of the catalyst treated under N_2 and C_3H_8 mixtures were shown in Figure 4. It is seen that the spectrum collected for the catalyst after reaction for 5 min consists of γ and β signals. This spectrum is similar to the one in Figure 3a for the catalyst treated in CO_2/C_3H_8 for 5 min. After reaction for 140 min in N_2, the ESR spectrum of the catalyst exhibited only β signal (Figure 4b), indicating that the Cr^{5+} species has been completely reduced to Cr^{3+}.

The starting surface species mainly consisted of Cr^{5+} as evidenced by the ESR spectrum in Figure 2b. However, a great amount of Cr^{5+} has been transformed into Cr^{3+} in 5 min under both CO_2/C_3H_8 and N_2/C_3H_8. This may account for the initial decrease of the activity of the Cr/SiO_2 catalyst for the dehydrogenation of propane under both CO_2 and N_2 atmospheres. After 140 min, the activity was completely lost with the disappearance of Cr^{5+} under N_2. In contrast, the activity remained significantly due to the existence of Cr^{5+} when CO_2 was used.

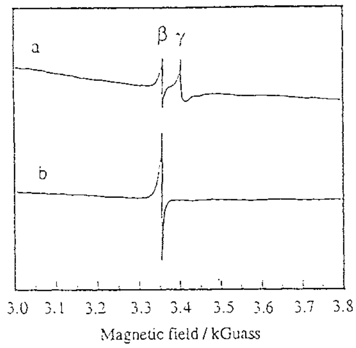

Figure 4. ESR spectra at RT of 5 wt%Cr/SiO_2 sample exposed in N_2/C_3H_8 mixture flow. Spectrum a: after 5 min; Spectrum b: after 140 min.

By correlating the catalytic performance with the ESR results, it appears that the active species over the catalyst for the dehydrogenation of propane are mainly the Cr^{5+} species. The presence of CO_2 in the reactant mixture plays a role in producing the Cr^{5+} species for establishing the active sites. In N_2 atmosphere, however, the catalyst will quickly lose its dehydrogenation activity since the Cr^{5+} species can not be replenished.

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References and Notes

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