

## Structural Investigation of $\text{Re}_2\text{O}_7/\gamma\text{-Al}_2\text{O}_3$ Catalysts for Olefin Disproportionation<sup>1</sup>

It is known that  $\text{Re}_2\text{O}_7/\gamma\text{-Al}_2\text{O}_3$  is an active catalyst for olefin disproportionation reactions (1); however, despite a number of papers dealing with the catalytic properties of this system (e.g., 2, 3), the structure of this catalyst has not yet been investigated in detail (4, 5). In addition, the promoting effect of small amounts of various  $\text{SnR}_4$  compounds (where R = alkyl group) is of current interest (6). Thus, this short note deals with our preliminary structural studies of nonpromoted and  $\text{SnBu}_4$  (Bu = butyl) promoted  $\text{Re}_2\text{O}_7/\gamma\text{-Al}_2\text{O}_3$  catalysts using methods of differential thermal analysis (DTG, DTA), X-ray diffraction, and Mössbauer spectroscopy.

### EXPERIMENTAL

A typical catalyst containing 10–20 wt%  $\text{Re}_2\text{O}_7$  was prepared by impregnation of  $\gamma\text{-Al}_2\text{O}_3$  (surface area  $\sim 180 \text{ m}^2\text{g}^{-1}$ ) with an aqueous solution of ammonium perchlorate, followed by drying at 380 K and calcining in dry air at 870 K for 2-h periods. Promoted catalysts were prepared by subsequent addition of  $\text{SnBu}_4$  from a pentane solution, followed by drying at 295 K in a flowing inert gas stream; the  $\text{SnBu}_4$  content of these promoted catalysts was ca. 6 wt%.

The DTA and DTG data were obtained using a MOM (Hungary) instrument; 200-mg samples were studied in flowing air at a heating rate of  $4.5 \text{ K min}^{-1}$ . X-ray diffraction measurements were made with a

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URS-55 apparatus using filtered  $\text{CuK}\alpha$  radiation. Mössbauer spectra were recorded using an electrodynamic spectrometer with  $^{119\text{m}}\text{SnO}_2$  and  $\text{Ca}^{119\text{m}}\text{SnO}_3$  sources; isomer shifts were measured relative to  $\text{SnO}_2$ .

### RESULTS AND DISCUSSION

#### DTG and DTA

The DTG and DTA scans, between 380 and 1270 K, for ammonium perchlorate,  $\gamma\text{-Al}_2\text{O}_3$ , and for  $\gamma\text{-Al}_2\text{O}_3$  after  $\text{NH}_4\text{ReO}_4$  impregnation and drying at 380 K are shown in Fig. 1 as curves 1-1', 2-2', and 3-3', respectively. It is seen therein that ammonium perchlorate decomposes in the temperature interval 580–750 K (curves 1-1'), and this process includes two steps. The DTG scan of  $\gamma\text{-Al}_2\text{O}_3$  (curve 2) shows no visible peaks, while the DTA scan (curve 2') indicates a small endothermic process at ca. 570–690 K corresponding to one of the phase transitions of  $\gamma\text{-Al}_2\text{O}_3$  (?). During these experiments, a gradual weight decrease for the  $\gamma\text{-Al}_2\text{O}_3$  was noted, amounting to a 15% change from the beginning to the end of the scan. Finally, it can be seen in curves 3-3' that the impregnated  $\gamma\text{-Al}_2\text{O}_3$  sample does not show to any great extent the peaks characteristic of  $\text{NH}_4\text{ReO}_4$  at 580–750 K; instead, a new peak appears at temperatures higher than 1120 K. (The small peak at ca. 600 K in curve 3 might indicate that several percent of the rhenium present on the dried sample is in the  $\text{NH}_4\text{ReO}_4$  state.)

From the above data, one may conclude that a strong interaction between the

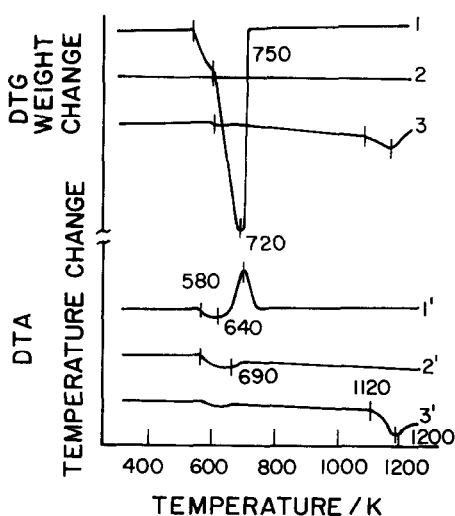


Fig. 1. DTG (curves 1-3) and DTA (curves 1'-3') scans for: 1, 1'  $\text{NH}_4\text{ReO}_4$ ; 2, 2'  $\gamma\text{-Al}_2\text{O}_3$ ; 3, 3'  $\text{Re}_2\text{O}_7/\gamma\text{-Al}_2\text{O}_3$ .

rhenium and the support takes place after impregnation and drying at 380 K. It is important to also report that the DTG and DTA scans of the calcined (at 870 K)  $\text{Re}_2\text{O}_7/\gamma\text{-Al}_2\text{O}_3$  sample were identical to curves 3-3'. From this it follows that the rhenium does not exist in the form of  $\text{Re}_2\text{O}_7$  particles on the  $\gamma\text{-Al}_2\text{O}_3$  surface, since the sublimation temperature of  $\text{Re}_2\text{O}_7$  is ca. 630 K (8); instead, the rhenium must be present as a tightly bound surface compound that is thermally stable in air up to 1120 K. This is in agreement with the results of Freel (4) and Johnson and LeRoy (5).

#### X-ray Diffraction

A sample of massive ammonium perchlorate treated in air at 380 K gave rise to an X-ray diffraction pattern characteristic of its tetragonal crystal structure with  $a = 5.87 \pm 0.02 \text{ \AA}$  and  $c = 12.94 \pm 0.02 \text{ \AA}$ ; hence, the  $\text{NH}_4\text{ReO}_4$  is thermally stable up to 380 K. The X-ray pattern for the  $\gamma\text{-Al}_2\text{O}_3$  alone consisted of two broad peaks from the (400) and (440) planes of the pseudo-spinel structure with lattice parameter  $a \cong 7.93 \text{ \AA}$ . For the calcined (at 870 K) 10%  $\text{Re}_2\text{O}_7/\gamma\text{-Al}_2\text{O}_3$

$\gamma\text{-Al}_2\text{O}_3$  sample, five broad peaks were observed in the diffraction pattern. The most intense reflections were again from the pseudo-spinel (400) and (440) planes, and the three new, and less intense, peaks were from the pseudo-spinel (113), (222), and (115) planes. None of the reflections characteristic of either  $\text{Re}_2\text{O}_7$  (9) or  $\text{NH}_4\text{ReO}_4$  were detected in the diffraction pattern of the calcined  $\text{Re}_2\text{O}_7/\gamma\text{-Al}_2\text{O}_3$  sample. As expected, a mechanical mixture of 10 wt%  $\text{NH}_4\text{ReO}_4$  and  $\gamma\text{-Al}_2\text{O}_3$  showed diffraction peaks characteristic of both of the individual components of the mixture.

From the X-ray data one may again conclude that the rhenium is present on the surface of  $\gamma\text{-Al}_2\text{O}_3$  not in the form of  $\text{Re}_2\text{O}_7$  particles, but in the form of a tightly bound surface compound. For example, this surface compound could be formed epitaxially on the predominant surface planes of  $\gamma\text{-Al}_2\text{O}_3$  in accord with the monolayer model of Schuit and Gates (10). In fact, the addition of rhenium to the  $\gamma\text{-Al}_2\text{O}_3$  changes the relative intensities of the pseudo-spinel diffraction peaks, suggesting a relation between the structures of the  $\gamma\text{-Al}_2\text{O}_3$  and the surface compound. In addition, the X-ray data do not exclude the possibility of partial  $\text{Al}^{3+}$  replacement by  $\text{Re}^{7+}$  ( $\text{Re}^{7+}$  is the expected oxidation state for the calcined sample, in view of

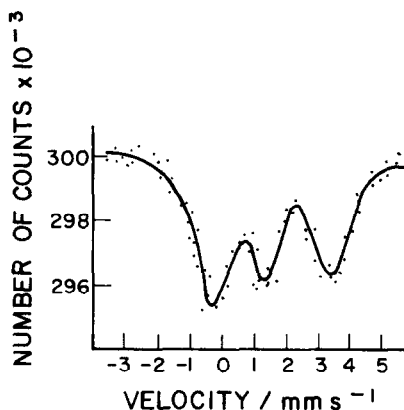


Fig. 2. Mössbauer spectrum at 77 K of  $\text{SnBu}_4$  promoted  $\text{Re}_2\text{O}_7/\gamma\text{-Al}_2\text{O}_3$ .

the work by Johnson and LeRoy (5) in a "presurface layer"; indeed, the ionic radii of these cations are similar (0.57 and 0.52 Å for  $\text{Al}^{3+}$  and  $\text{Re}^{7+}$ , respectively (11)).

### Mössbauer Spectroscopy

A typical Mössbauer spectrum at 77 K of a  $\text{SnBu}_4$ -promoted  $\text{Re}_2\text{O}_7/\gamma\text{-Al}_2\text{O}_3$  catalyst is shown in Fig. 2. This spectrum consists of three resolved lines, and it can be interpreted in the following manner. The central line (isomer shift of  $1.3 \pm 0.1$  mm  $\text{s}^{-1}$ ) is due to  $\text{SnBu}_4$  molecules either weakly adsorbed on the surface or in a state of capillary condensation (12); the remaining two peaks can be assigned to an asymmetric doublet (isomer shift =  $1.5 \pm 0.1$  mm  $\text{s}^{-1}$ , quadrupole splitting =  $3.5 \pm 0.1$  mm  $\text{s}^{-1}$ ) arising from chemisorbed tin compounds of the type  $\text{R}_{4-n}\text{Sn}(\text{OMe})_n$ , where  $n$  may be between 1 and 3, and Me is a metal ion (e.g., Me could be a tin or rhenium cation). Similar spectra were obtained earlier for the initial stages of adsorption of  $\text{SnR}_4$  (R = methyl, ethyl) on  $\gamma\text{-Al}_2\text{O}_3$  at 298 K (12). The intensity asymmetry of the doublet may be caused by either the Goldanskii-Karyagin effect (13), or the presence of  $\text{Sn}(\text{OMe})_4$  which would produce a spectral peak in the region of the left component of the doublet.

Of interest in the present discussion is the fact that the Mössbauer spectrum of the tin species present on the surface of  $\gamma\text{-Al}_2\text{O}_3$  is qualitatively the same as that for the tin species on  $\text{Re}_2\text{O}_7/\gamma\text{-Al}_2\text{O}_3$ . It then follows that the adsorption sites on these two surfaces are similar. These sites, that lead to the formation of  $\text{R}_{4-n}\text{Sn}(\text{OMe})_n$ , may be surface hydroxyl groups or Lewis acid sites. In the first case, the process of chemisorption will be accompanied by the removal of butane, and in the second case the acid sites (e.g., anion vacancies) will act as acceptors of butyl radicals formed by the Sn-R bond cleavage. The

formation of anion vacancies usually takes place during the thermal dehydroxylation of the support; however, in the presence of rhenium, anion vacancies may also be formed by removal of oxygen from the surface capping layer (in the monolayer model (10)) accompanied by the partial reduction of  $\text{Re}^{7+}$ .

At present, the exact nature of the surface sites for  $\text{R}_{4-n}\text{Sn}(\text{OMe})_n$  formation, and the mechanism of tin promotion of  $\text{Re}_2\text{O}_7/\gamma\text{-Al}_2\text{O}_3$  catalysts are open for further investigation. Studies of this type will continue in our laboratories.

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