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ESCA Studies on Silica- and Alumina-Supported Rhenium Oxide Catalysts

Since it was first reported in 1963 (*1, 2*), catalyst olefin metathesis has been extensively studied (*3*). Because of their high activity and product selectivity at relatively mild reaction conditions (*4–6*), supported rhenium oxide metathesis catalysts have been the subject of numerous physical and spectroscopic investigations (*7–11*).

ESCA examination of a variety of rhenium oxide/γ-alumina or silica catalysts (*12*) has revealed that, in calcined catalysts, the metal is in the +7 oxidation state. These catalysts were completely reduced by hydrogen (1 kPa) at 500–600°C to Re(0). Re(+6) was observed in a NH_4ReO_4/γ-Al_2O_3 sample that had been dried under mild conditions, but the extent of reduction was not quantified. Such quantification might be important since it is known that partial Re reduction, usually by substrate olefin, is a prerequisite for catalytic activity (*13*). This report describes our attempts to apply the ESCA technique to determine (a) the oxidation state or states of rhenium in an active catalyst, and (b) the mode of catalyst deactivation. Determination of the oxidation state or states of the rhenium will not necessarily reveal the catalytically active oxidation state since it is known that only between 0.3 to 20% of the metal is active in catalyzing olefin metathesis (*13–16*). However, one can more readily infer the nature of the active site by studying an active catalyst, rather than a catalyst precursor.

EXPERIMENTAL

Table 1 gives details on the γ-Al_2O_3 and SiO_2 used in these studies.

Catalyst preparation

Rhenium/silica. Silica gel (20 g; previously calcined in air at 650°C) was impregnated using an aqueous ethanol solution of Re_2O_7 (1.43 g). After evaporating away the solvent on a steam bath, the catalyst granules were dried at 100°C overnight, calcined in a dry-air stream at 450°C for 16 h and then in a dry nitrogen stream at 450°C for 3 h. Analyses of the catalyst afforded a 227 m^2/g BET surface area, and a 4.3 wt% Re loading (by plasma emission spectroscopy).

Rhenium/γ-alumina. This catalyst was similarly prepared using activated γ-alumina (25 g) and Re_2O_7 (3.35 g). The catalyst was calcined in an air stream at 600°C for 1 h. Neutron activation analysis showed a 7.9% Re loading.

Reactions of 1-octene with rhenium/SiO_2 or rhenium/Al_2O_3 catalysts. All operations were conducted with vigorous exclusion of air using standard inert-atmosphere techniques. A typical catalytic run is illustrated in the following example. Freshly calcined 4% Re/silica (5 g) was packed on top of a column of glass helices in a vacuum-jacketed, distillation column. The catalyst and glass-packed zones each measured roughly 1.2 × 12 cm. The distillation column was attached to a dry-ice condenser and a 3-neck flask containing 1-octene (25 g). The 1-octene was refluxed through the glass helices and on to the catalyst zone. Liquid (reboiler) and catalyst samples were collected periodically for GLC and ESCA analysis, respectively. GLC and GC/MS analyses were performed using a Hewlett–Packard Model 5710A gas chromatograph

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TABLE 1

Support	Supplier	Mesh	Surface area (m^2/g)	Pore volume (cm^3/g)
γ-Al_2O_3 (T-374)	Girdler	6–8	190	0.36
Silica gel (Grade 57)	Grace	6–8	300	1.00

or a Model 5985 mass spectrometer equipped with 25-m, crosslinked SE30 capillary columns.

ESCA analysis. The samples were analyzed in a Physical Electronic Industries (PHI) Model 555 ESCA/Auger spectrometer equipped with a Mg/Si dual X-ray source. Binding energies were referenced to Si(2*p*) or Al(2*p*) levels at 103.4 and 74.7 eV for SiO_2 or Al_2O_3, respectively.

Alfa $KReO_4$, Re_2O_7, ReO_3, ReO_2, and Re metal standards were used to confirm peak assignments. A Pearson type 7 curve fitting program written by David Hawn was used to analyze overlapping signals.

The catalyst samples were dried at ca. 1×10^{-3} Pa for 1 day and then mounted in a nitrogen dry-box and transferred to the spectrometer without exposure to atmospheric oxygen by means of a high-vacuum-compatible transfer vessel. The atomic ratios were calculated using integrated peak areas for each of the detected elements and ESCA sensitivity factors (*17*). The detection limit is approximately 0.1 at.%.

RESULTS AND DISCUSSION

The reaction of refluxing 1-octene with the Re_2O_7/SiO_2 catalyst produced an 11 mole% yield of hexadecenes and an equilibrium mixture of octenes after 3 h. As expected, no octene metathesis occurred under these conditions (*7, 18*). A cursory kinetic study showed that the 1-octene dimerization rate decreased rapidly suggesting that the catalyst deactivated quickly. This premature catalyst deactivation was probably due to excessive coke formation as the initially white Re_2O_7/SiO_2 catalyst pellets rapidly turned black upon exposure to the refluxing 1-octene vapor. A black powder was washed off the catalyst pellets by the refluxing olefin. Elemental analysis (plasma emission) of the black powder indicated the presence of rhenium, but no rhenium metal was detected by XRD analysis.

In an attempt to determine the nature of this premature catalyst deactivation, the catalyst was analyzed by ESCA and neutron activation at varying reaction times (Table 2). Freshly calcined Re/SiO_2 showed a binding energy characteristic of Re(VII) ($4f_{7/2}$ 46.3 eV, Fig. 1A) consistent with previous findings (*12*).

The high-resolution Re(4*f*) ESCA region showed that after exposure to liquid octene-1 (Figs. 1B–D) a partial change in the Re(+7) oxidation states has occurred to the lower Re(+6) and Re(+4) oxidation states on each surface. Each oxidation state ap-

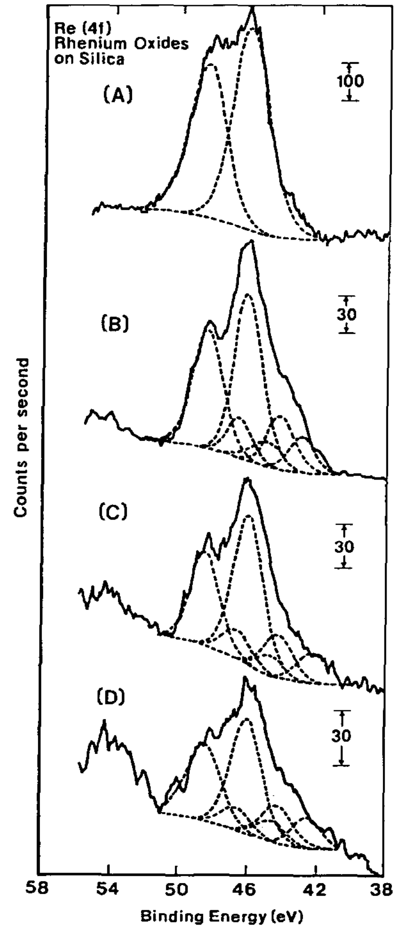

FIG. 1. Rhenium (4*f*) ESCA region of Re/SiO_2 catalysts after exposure to metathesis conditions for (A) 0 min, (B) 10 min, (C) 210 min, and (D) 390 min.

TABLE 2

ESCA Results on Re/SiO$_2$

Reaction time (h)	Relative Re surface conc. (Re/Si atomic ratio)	Surface coke/Re ratio	Surface Re(+6, +4)/Re(+7) atomic ratio	Elemental analysis (neutron activation) (% Re)
0.0	0.081	2.5	0	4.9
0.2	0.074	7.0	0.44	
6.5	0.015	10.1	0.44	4.2

pears as a doublet due to the presence of Re ($4f_{7/2}$) and Re ($4f_{5/2}$) electronic states. The Re ($4f_{7/2}$) peak height is approximately 1.4 times that of Re ($4f_{5/2}$) peak for Re in Re$_2$O$_7$. As carbon was deposited on the catalyst surface some broadening may have occurred in the Re ($4f$) peaks due to an Al*K*α (from Al X-ray window) carbon ghost peak which occurs in this region.

The assignment for Re(+6) and Re(+4) (Re($4f_{7/2}$) is 44.3 and 42.5 eV, respectively) was based on ReO$_3$ and ReO$_2$ standards whose surfaces were partially oxidized *in situ* to Re(+7), then partially reduced to Re(0) metal. This procedure was necessary in order to correctly determine the binding energy position of both Re(+6) and Re(+4). The assignments agree with those previously determined by Cimino *et al.*, while at least two other authors have assigned the Re ($4f_{7/2}$) peak for Re(+4) to occur at a binding energy of 43.2 eV (*19, 20*). The authors assignments are based on ReO$_2$ standard in which the surface is nominally oxidized or based on the sputter reduction of NH$_4$ReO$_4$; both are unreliable without the use of an internal standard. The method we employ used the Re(0) and Re(+7) binding energy position to correctly determine the binding energy position of Re(+4); the details of this procedure will be published separately. The ratio of the Re(+6, +4)/Re(+7) at each exposure period is recorded in Tables 2 and 3.

The ESCA results revealed that the freshly calcined Re/SiO$_2$ contained Re mostly in the +7 oxidation state. Upon exposure to octene-1 vapor, reduction to Re(+6) and Re(+4) has occurred. Catalyst samples withdrawn between 0.2 and 6.5 h revealed a Re(+6, +4)/Re(+7) ratio of 0.44 indicating that significant reduction to Re(+6) and Re(+4) had occurred. In addition, ESCA revealed a buildup of surface coke with time. It is this coke, we feel, that is washed off the catalyst and removes loosely held surface rhenium oxides. In agreement with this coking phenomena there is a decrease in the relative surface rhenium concentration (Re/Si atomic ratio). The fact that the decrease in surface rhenium is much larger than the rhenium loss observed by elemental analysis (neutron activation) suggests that coke formation on the rhenium oxide surface obscures the rhenium from ESCA analysis. This heavy coke buildup is probably responsible for the rapid catalyst deactivation. Consistent with

TABLE 3

ESCA Results on Re/γ-Al$_2$O$_3$

Reaction time (h)	Relative Re surface conc. (Re/Al atomic ratio)	Surface coke/Re ratio	Surface Re(+6, +4)/Re(+7) atomic ratio	Elemental analysis (neutron activation) (% Re)
0.0	0.083	1.8	0.12	7.9
0.2	0.088	2.2	0.34	7.6
8.5	0.079	8.6	0.33	7.3

this conclusion we found that the catalyst can be substantially reactivated by calcination in air.

In a similar fashion the Re/γ-Al_2O_3 catalyst was exposed to octene-1 vapor. After 10 min a liquid sample revealed 12% conversion of the octene-1 with 87% selectivity to tetradecenes (metathesis) and 13% to internal octenes (isomerization). After 1 h one observes a 40% conversion with 97% selectivity to metathesis products. ESCA analysis on these Re/Al_2O_3 samples (Table 3) revealed that the initially calcined catalyst contains Re(+6, +4)/Re(+7) in the ratio of 0.12 indicating that the calcination procedure did not completely oxidize the surface rhenium. Catalyst samples withdrawn between 0.2 and 8.5 h had Re(+6, +4)/Re(+7) ratios of 0.34 indicating that additional reduction had occurred, but less than that observed for the Re/SiO_2 catalysts. The coke formation data for this catalyst is much more intriguing. Although a similar coke buildup was observed the Re/Al ratio remained fairly constant indicating that much less coverage of the rhenium oxide surface had occurred.

CONCLUSIONS

Whereas rhenium oxides supported on γ-Al_2O_3 are catalysts for the metathesis of olefins, we find that rhenium oxides supported on SiO_2 only catalyze the isomerization of olefins under our reaction conditions. While the former reveal a reasonable lifetime and activity the latter deactivate rapidly. ESCA analyses reveal partial reduction to Re(+6) and Re(+4) in both cases. Coking of the catalysts occurred in both systems, but the coke appeared to be much more effective in blocking access to the catalytically active sites in the Re/SiO_2 system.

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