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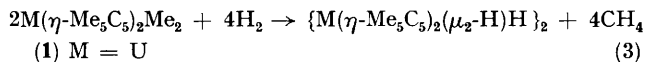
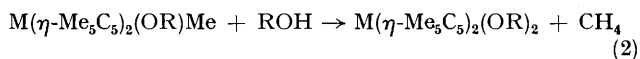
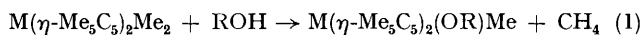
Catalytic Activity of Supported f-Element Organometallic Complexes

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Summary When supported on alumina, the organoactinoids $M(\eta\text{-Me}_5\text{C}_5)_2\text{Me}_2$ ($M = \text{U}$ or Th) exhibit very high catalytic activity for the hydrogenation of propene and the polymerization of ethene.

CURRENTLY there is considerable interest in the properties of organotransition metal complexes (particularly alkyls, allyls, and carbonyls) deposited upon high-area oxides such as γ -alumina and silica gel,¹ in view of the substantial catalytic activity which such systems frequently exhibit (*e.g.*, hydrogenation,^{1a} isomerization,^{1a,2} metathesis,³ and polymerization^{1a,d} of olefins as well as the hydrogenation of CO).⁴ Although organoactinoids⁵ display a variety of distinctive chemical, structural, and electronic properties, and with appropriate ligation can display high reactivity in solution,⁶ no investigations of the chemistry of supported organoactinoids have been reported. We report here the first investigation of thorium and uranium organometallics supported upon γ -alumina.⁷ The complexes, when supported, exhibit much greater activities for the hydrogenation and polymerization of olefins than under homogeneous conditions.

The co-ordinatively unsaturated bis(pentamethylcyclopentadienyl)thorium and uranium dimethyls were studied first. In solution the metal-carbon σ -bonds of these complexes undergo easy alcoholysis (equation 1 and 2) to yield alkoxides, and hydrogenolysis (equation 3) to yield dimeric



(1) $M = \text{U}$

(2) $M = \text{Th}$

hydrides. We have found that in toluene solution at 24 °C and 0.9 atm H_2 pressure, these hydrides catalyse the hydrogenation of hex-1-ene with turnover frequencies N_t (in s^{-1} per actinoid atom) of 1.5×10^{-4} ($M = \text{Th}$) and 1.9×10^{-2} ($M = \text{U}$).⁸ Under comparable homogeneous conditions, the hydrides are marginally active ($M = \text{U}$) or inactive ($M = \text{Th}$) for the catalysis of ethene polymerization.⁸ The effect of binding (1) and (2) to a metal oxide surface was investigated with the possibility of immobilizing the oxophilic organoactinoid centres and stabilizing highly reactive species such as monomeric hydrides.

Hydroxylated γ -alumina (American Cyanamid Company Aerocat 1000) was dehydroxylated in flowing helium at 950–1000 °C or at 475 °C to produce, respectively, a nearly fully dehydroxylated alumina (DA) or one which was about 75% dehydroxylated (PDA) and which contained *ca.* 4 σ -OH, 5.5 σ -O⁻, and 5.5 oxygen vacancies exposing Al^{3+} (cus)^{4a} per nm^2 , where σ -OH represents a surface OH group. Measured amounts (80–160 μmol) of (1) or (2) dissolved in pentane were slurried with 0.5 g of alumina. In the case of the orange uranium compound, the alumina became orange in colour, while the pentane solution was decolourized. The pentane was next evaporated in a stream of helium (0.02 p.p.m. of O_2), and any evolved gases were trapped and measured later.⁹ The supported organoactinoids were then activated in flowing helium or hydrogen at various temperatures and the evolved gases were measured.

The Table shows the reaction products which were measured after sequentially activating (1) supported on DA or PDA for 1.5 h under He (25 °C), 1.0 h under He (100 °C), and then 1.0 h under H_2 (100 °C) (abbreviated as He, 25°, 1.5; He, 100°, 1.0; H_2 , 100°, 1.0). At 25 °C under He, little CH_4 was liberated on DA while large amounts of CH_4 were liberated on PDA. Essentially the same results were obtained on activating (1) under H_2 at 25 °C. It appears

TABLE. Products evolved during activation of $U(\eta\text{-Me}_6\text{C}_6)_2\text{Me}_2$ (1)/ Al_2O_3 in helium.

Alumina Atoms U/nm ² Pretreatment sequence	DA			PDA			PDA		
	He, 25°	He, 100°	H ₂ , 100°	He, 25°	He, 100°	H ₂ , 100°	He, 25°	He, 100°	H ₂ , 100°
Total H ₂ /U	0.001	0.001	—	0.004	0.005	—	0.001	0.002	—
Total CH ₄ /U	0.055	0.42	0.92 ^a	1.2	1.51	1.6 ^b	1.75	1.92	1.95 ^b

^a Small amounts of C₂—C₄ hydrocarbons detected; C₂—C₄/U = 0.01; ^b C₂—C₄ hydrocarbons detected only after H₂ at 150 °C.

likely that activation at low temperatures on PDA largely involves some sequence of protolytic reactions analogous to those in equations (1) and (2). Interestingly, activation in H₂, even at 100 °C on DA, does not readily liberate CH₄, in contrast to the rapid hydrogenolysis in solution.⁵ Methane formation on DA in the absence of H₂ must necessarily involve hydrogen abstraction⁹ from ring or actinoid methyl substituents. Preliminary experiments indicate that the thorium complex (2) behaves in a similar manner.

When pulses of propene (C₃H₆/M = ca. 1) were injected into hydrogen flowing over the supported organoactinoids at 1 atm and 25 °C, hydrogenation was complete for materials of all the activations shown in the Table. Propene hydrogenation was then investigated in a flow reactor at -46 °C using much smaller loadings of (1) and (2) on alumina and H₂/C₃H₆ = 4.68 at a total pressure of 1 atm. A catalyst containing 8 μmol of (1) on DA gave an N_t (turnover frequency per atom of U) of 0.33 s⁻¹ (H₂, 25°), and 0.55 s⁻¹ (H₂, 100°). A similar experiment with (2) on DA gave 0.16 and 0.33 s⁻¹, respectively. An experiment with a higher loading of (1) on PDA (H₂, 120°) gave 100% conversion and established that N_t was greater than 0.1 s⁻¹. These values of N_t compare favourably with those for the same reaction on Pt/SiO₂; at -46 °C N_t is 0.26 s⁻¹ per surface atom of Pt.¹⁰

To determine the fraction of adsorbed uranium species which was catalytically active, pulses of CO were injected into the carrier hydrogen during pulse hydrogenation of propene at 25 °C. For (1) on DA, adsorption of CO corresponded to CO/U = 0.11; however, the conversion of a pulse of propene was reduced from 100 to 13.5%. Since the initial rate of hydrogenation under these conditions must

have been equivalent to several times 100%, values of N_t at -46 °C per effective catalytic site must have been considerably greater than those found per total atoms of uranium.

The polymerization of ethene was investigated by injection of pulses of ethene (C₂H₄/M = ca. 1) into helium flowing over various catalysts at 25 °C. With (1) on PDA, (H₂, 100°; He, 23°, 18), adsorption of ethene corresponded to C₂H₄/U = 4.6 after the sixth pulse, 77% of which was adsorbed. With (1) on DA (H₂, 100°; He, 23°, 18), after 59 pulses C₂H₄/U was 44 and 73% of the final pulse was adsorbed. In a similar experiment with (2) on DA, after 78 pulses C₂H₄/Th was 36 and 76% of the last pulse was adsorbed. Helium was then replaced as the feed gas by hydrogen and rapid catalytic hydrogenation of ethene was observed.

Although complete characterization of the surface actinoid species awaits detailed chemical and spectroscopic investigations which are in progress, the initial results of this study confirm that alumina-supported organoactinoids can exhibit high activity for the hydrogenation of propene and the polymerization of ethene. The activity of the catalytic sites, which represent only a fraction of the supported molecules, is considerably greater than that of homogeneous catalysts prepared from the same precursors. A noteworthy feature of the heterogeneous results is the similar catalytic activity of thorium and uranium which, in view of the known redox properties of these ions,^{5b} suggests that the catalytic cycle involves only the +4 oxidation state.

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