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Low Valent Actinides as Hydrogenation Catalysts

INTRODUCTION

As part of an ongoing effort toward exploring the nonaqueous chemistry of uranium(III) (*1*), we have observed that reduction of UCl_4 with excess lithium aluminum hydride in tetrahydrofuran (THF) produces $UCl_3(THF)_x$ as a transient species and ultimately precipitates a black pyrophoric solid. The solid is an active olefin hydrogenation catalyst of variable activity and is different from either uranium metal or UH_3. We find that adsorption of the $UCl_3(THF)_x$ onto γ-alumina prior to reduction with $LiAlH_4$ provides a reproducible catalyst for olefin hydrogenation at room temperature and these studies are described herein.

EXPERIMENTAL

UCl_3–Al_2O_3 + xs $LiAlH_4$. A purple solution containing 0.9 mmol $UCl_3(THF)_x$ in 90 ml tetrahydrofuran was prepared (*1*) and filtered onto 30 g γ-Al_2O_3 ($\frac{1}{8}$-in. pellets, Strem Chemicals, Inc., 100 m^2/g, dehydroxylated at 900°C under vacuum for 12 h). The THF solution above the γ-Al_2O_3 was colorless after 6 h and dark purple pellets of UCl_3–Al_2O_3 (~1% loading) were obtained. To this reaction mixture was added 50 ml of a 1 *M* solution of $LiAlH_4$ in THF (Alfa Chemicals) and immediate vigorous hydrogen evolution was observed. After 24 h the solution was decanted from the pellets, which were subsequently washed with 100 ml THF and vacuum dried for 12 h. The resulting grey pellets (**I**) were observed to react violently with nitrogen, air, or water but could be handled safely under a dry argon atmosphere.

As a control experiment 30 g of dehydroxylated γ-Al_2O_3 was treated with $LiAlH_4$ in the manner previously described for the preparation of **I** and slightly gray–white pellets (**II**) were obtained.

Catalytic hydrogenation. Catalyst **I** (1.0 g) was loaded into a 100-ml flask and connected to a 50-ml manifold with inlet for vacuum, olefin, hydrogen, and equipped with a Validyne pressure gauge. It was observed that pretreatment with 1 atm H_2 at 150°C for 12 h afforded a stable catalyst with no appreciable decrease in activity observed for ~200 turnovers with C_2H_4/H_2. The experimental conditions for a variety of runs are presented in Table 1. Untreated catalyst **I** gave approximately the same initial activity but the rate eventually slowed to 10% of that observed for a pretreated catalyst.

Catalyst **II** was also activated for 12 h at 150°C and 1 atm H_2 pressure. No catalytic activity was observed for ethylene hydrogenation at room temperature (Table 1) and only at temperatures in excess of 150°C was the reduction to ethane observed. In all cases product identification was afforded by mass spectral analysis.

RESULTS AND DISCUSSION

While this study was in progress a report (*2*) appeared suggesting that catalytic uranium(III) solutions could be generated from UCl_4 and excess $LiAlH_4$ in THF. We have observed only limited stability of such solutions and have instead observed further reduction which yielded a black pyrophoric solid containing both uranium and aluminum. X-Ray powder diffraction data suggest a different species from uranium metal or UH_3 but because of its extreme reactivity, even with molecular nitrogen, characterization of this material has been difficult. This material is a room-temperature olefin

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TABLE 1

Effect of Different Catalysts on Hydrogenation

Catalyst (wt)	Temp (°C)	Olefin (Torr)	H_2 (Torr)	Turnover[b]	Products
I (1.0 g)	25	Ethylene (300)	(300)	8–10	Ethane
UH_3 (1.0 g)	25	Ethylene (200)	(400)	N.R.	—
U (1.0 g)	25	Ethylene (200)	(400)	N.R.	—
I (1.1 g)	25	Cyclohexene (60)	(140)	[c]	Cyclohexane
II (1.0 g)	25	Ethylene (300)	(300)	N.R.	—
I (3.0 g)	25	Benzene (25)	(450)	N.R.	—

[a] Volume 150 ml, static conditions.

[b] Expressed as (mmol olefin/mmol uranium · h) and estimated from pressure drop which approximated H_2 consumed. The number was determined during the first hour of repeated runs, with no decrease in rate observed for ~200 turnovers.

[c] Due to adsorption of the cyclohexene by the alumina an accurate turnover could not be obtained from pressure drop, but mass spectral analysis at various time intervals suggested a similar rate to that observed with ethylene.

hydrogenation catalyst, but it is probably not a simple uranium(III) species.

A more convenient catalyst (**I**) has been obtained by first adsorbing the $UCl_3(THF)_x$ onto γ-Al_2O_3 followed by reduction with excess $LiAlH_4$. This species is still difficult to handle, but it is more reproducible and somewhat less reactive than the unsupported species described above. Further studies are planned in order to examine hydrogenation selectivity, but the present work clearly demonstrates a moderate activity with respect to ethylene and cyclohexene hydrogenation to ethane and cyclohexane, respectively (Table 1). This is particularly interesting since neither uranium metal nor UH_3, even as high surface area powders (~0.8 m^2/g) (*3*), show appreciable catalytic activity of this sort until 180–200°C. No hydrogenation of benzene was found to occur at room temperature and even at 250°C only a trace of cyclohexane was detected.

Although **I** appears to be less active than a recently reported (*4*) uranium(IV) catalyst derived from an organometallic complex supported on alumina, the selectivity of **I** has yet to be examined and it is unlikely that catalyst activity has been optimized in the present study. For these reasons we are quite interested in further characterization of **I** and in other studies of low valent actinides as catalysts, in general.

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