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Actinide heterobimetallic oxides (Th, U): reduction studies

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Abstract

In our laboratories we have been studying the synthesis and reactivity of binary actinide and lanthanide intermetallic compounds. In this work, the air-oxidation of $ThCu_2$ and $AnNi_2$ (An = Th, U) was followed by thermogravimetry (TG) and the products were characterized by X-ray powder diffraction (XRD). The heterobimetallic oxides obtained are described by the formulas $2MO·ThO_2$ (M = Cu, Ni) and $2NiO·UO_3$. The thermogravimetric analysis under hydrogen of these heterobimetallic oxides show one mass loss for $2MO·ThO_2$ and two mass losses for $2NiO·UO_3$ over a wide range of temperature (293–1273 K). The characterization by XRD shows that the reduction products are $2M·ThO_2$ (M = Cu, Ni) and $2Ni·UO_2$, with all the actinides in the 4+ oxidation state. The actinide heterobimetallic oxides were described as copper or nickel supported catalysts.
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1. Introduction

Binary intermetallic compounds of lanthanide or actinide metals combined with *d* metals (usually Ni, Co, Mn, or Fe) have drawn the attention of many authors and have been found to be catalytically active in many reactions [1–8]. However, the starting compounds decompose under the reaction conditions into rare earth oxides or nitrides, leaving at their surface the *d* metal to which the catalytic activity was attributed [6,7]. This new type of catalysts are more active and selective than those obtained by conventional routes. Examples are the copper-rare earth or thorium intermetallic compounds [9,10] that are more active than $Cu/ZnO/Al_2O_3$ for the methanol synthesis.

We have previously reported the oxidation of $LnCu_2$ (Ln = La, Ce, Pr, Nd) intermetallic compounds [11], the products were described as $2CuO·CeO_2$ and $3CuO·Ln_2CuO_4$. The reduction study under hydrogen of the oxidized intermetallics was also undertaken [12]. In this work, the oxidation of $ThCu_2$ and $AnNi_2$ (An = Th, U) and the

reduction of the oxidized actinide intermetallic compounds, using thermo gravimetric analysis, are reported.

2. Experimental

2.1. Materials

$ThCu_2$ and $AnNi_2$ (An = Th, U), were prepared by arc melting ingots of stoichiometric amounts of Cu (Goodfellow, 99.99%), Th (Goodfellow, 99.9%) and U (Goodfellow, 99.9%) on a water-cooled copper crucible under Ti-gettered high-purity argon (AirLiquide, N45) atmosphere. The compounds solidify congruently. However, to ensure homogeneous ingots, remelting was performed at least three times. The weight losses were <0.5 wt.%. After melting, the 5 g ingots were kept under nitrogen inside of a glove box (H_2O and O_2 contents <5 ppm). For oxidation and reduction studies purpose, typically a 0.1 g ingot and particle size <200 mesh were used.

2.2. Oxidation and reduction

The experiments were carried out under dry (AirLiquide, K) air or hydrogen (AirLiquide, N57) by recording mass uptakes during temperature-programmed oxidation us-

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ing a TAInstruments 951 thermogravimetric analyser (Pt crucibles), with a flow rate of $50 \, cm^3/min$ at $10 \, K/min$ heating rate up to $1273 \, K$.

2.3. Powder X-ray diffraction

Powder X-ray diffraction patterns (XRD) were obtained in reflection geometry with a Philips PW1710 based diffractometer using Cu Kα monochromatic radiation (λ = 1.5406 Å). The operational settings for all the XRD scans were: voltage, $40 \, kV$; current, $30 \, mA$; scan range, $10-90° \, 2\theta$ using a step size of $0.02°$ at $1 \, s$ per step. For identification purposes, the relative intensities (I/I_0) and the d-spacing (Å) was compared with standard diffraction patterns in the ASTM and JCPDS powder diffraction files [13,14].

3. Results and discussion

3.1. Starting materials

Fig. 1 shows the XRD patterns obtained for the actinide intermetallic compounds. The diffraction patterns for $ThCu_2$ (hexagonal structure, $P6/mmm$), $ThNi_2$ (hexagonal structure, $P6/mmm$) and UNi_2 (hexagonal structure, $P6_3/mmc$) indicate pure crystalline phases and show lattice parameters ($ThCu_2$: $a = 4.387$ Å, $c = 3.472$ Å; $ThNi_2$: $a = 3.96$ Å, $c = 3.844$ Å; UNi_2: $a = 4.966$ Å, $c = 8.252$ Å) that agree with the published values [13,14].
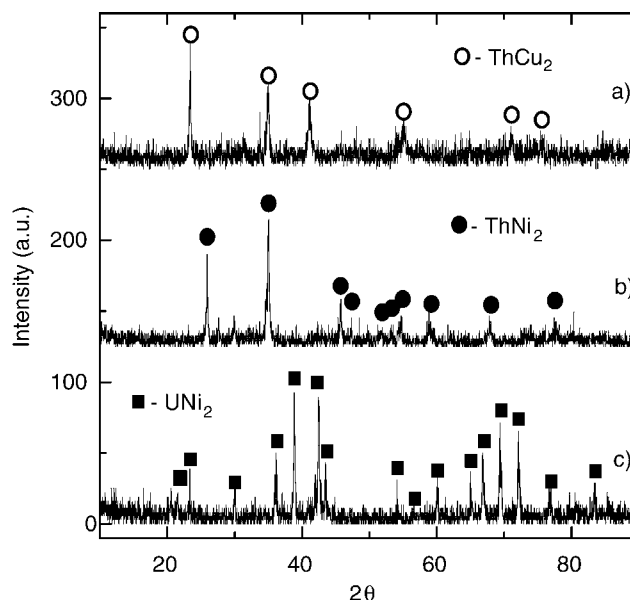

Fig. 1. XRD patterns of (a) $ThCu_2$, (b) $ThNi_2$ and (c) UNi_2.

3.2. High temperature oxidation of ThCu$_2$ and AnNi$_2$ (An = Th, U)

The temperature-programmed oxidation under air of the actinide intermetallic compounds, $ThCu_2$ and $AnNi_2$ (An = Th, U), was studied. The TG curves reported in Fig. 2 shows a progressive mass uptake over a wide range of
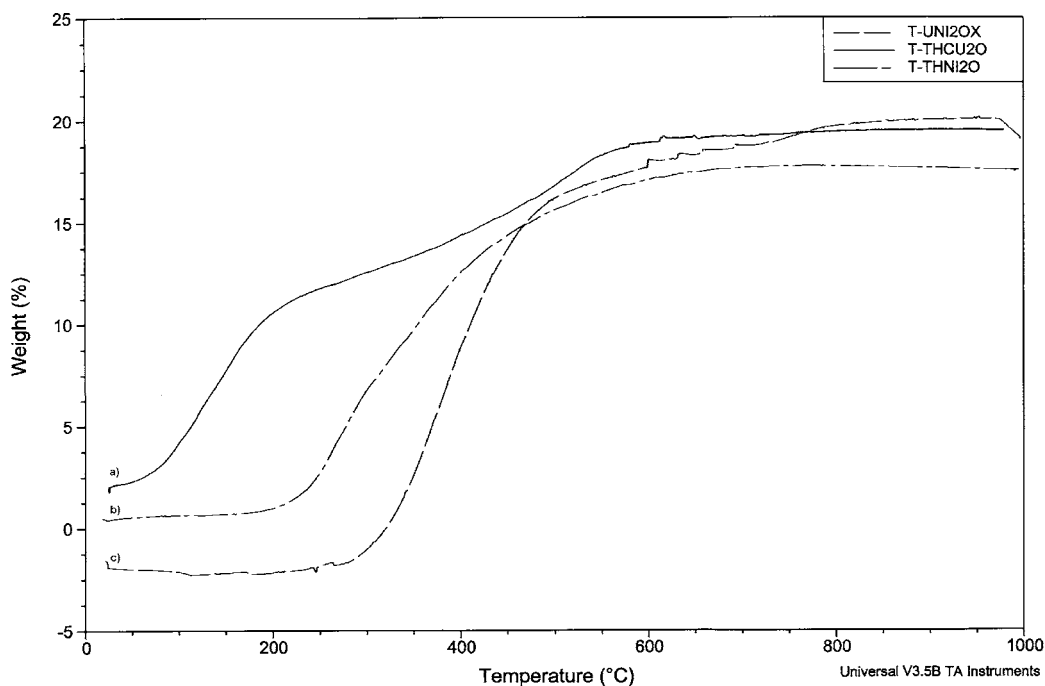

Fig. 2. TG profiles under dry air ($PO_2 = 0.2 \, bar$, $\beta = 10 \, K/min$): (a) $ThCu_2$ (18.4 mg), (b) $ThNi_2$ (20.1 mg) and (c) UNi_2 (23.9 mg).
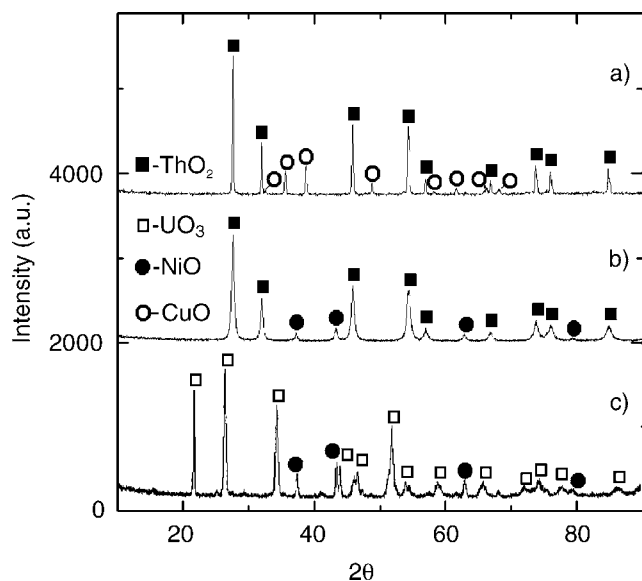
Fig. 3. XRD patterns after oxidation: (a) 2CuO·ThO$_2$, (b) 2NiO·ThO$_2$ and (c) 2NiO·UO$_3$.

Table 1
TG mass uptakes under dry air

| Compound	Δm (%), expt.	Δm (%), theor.	T_m (K)	Product stoichiometry
ThCu$_2$	17.4 ± 0.5	17.8	423, 748	ThCu$_2$O$_4$
ThNi$_2$	18.2 ± 0.5	18.3	673	ThNi$_2$O$_4$
Uni$_2$	21.9 ± 0.5	22.5	673	UNi$_2$O$_5$

temperature, the onset occurring at 298 K for ThCu$_2$, at 473 K for ThNi$_2$ and at 548 K for UNi$_2$. The oxidation is completed at approximately 973 K for all compounds. From the total oxygen uptake, stoichiometries were calculated. They correspond to the formulas ThCu$_2$O$_4$, ThNi$_2$O$_4$ and UNi$_2$O$_5$ (Table 1). The XRD patterns of the oxidized actinide intermetallics present no more diffraction lines of the starting materials (Fig. 3). New diffraction lines appear, corresponding to a mixture of phases. From the precursors ThCu$_2$ and ThNi$_2$, CuO and NiO accompany ThO$_2$,

respectively, whereas, for the precursor UNi$_2$, NiO is accompanied by UO$_3$. This implies complete oxidation of copper, nickel, thorium and uranium into Cu^{2+}, Ni^{2+}, Th^{4+} and U^{6+}, respectively.

On the basis of these results, the stoichiometries of the total oxidation are illustrated by the following equations:

$$ThM_2 + xO_2 \rightarrow 2MO \cdot ThO_2 \quad (M = Ni, Cu) \tag{1}$$

$$UNi_2 + yO_2 \rightarrow 2NiO \cdot UO_3 \tag{2}$$
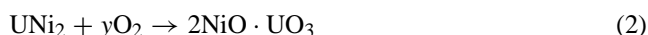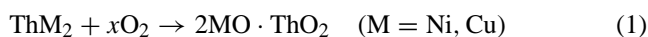
In the present investigation, no distinct mass uptake corresponding to successive oxidation of the two components of the intermetallics could be detected for AnNi$_2$ (An = Th, U). For ThCu$_2$, two distinct mass uptake were recorded (Fig. 2a): first, $\Delta m = 9.6 \pm 0.5\%$ (298–523 K); second, $\Delta m = 7.8 \pm 0.5\%$ (523–973 K).

It is known that the standard Gibbs free energy for actinide oxide formation is by far more negative than that of copper or nickel oxides (e.g. −1168.77 kJ/mol for ThO$_2$ versus −129.7 kJ/mol for CuO; −1168.77 kJ/mol for ThO$_2$ versus −211.7 kJ/mol for NiO; −1145.9 kJ/mol for γUO$_3$ versus −211.7 kJ/mol for NiO; 1031.7 kJ/mol for UO$_2$ versus −211.7 kJ/mol for NiO; crystalline solids at 298.15 K
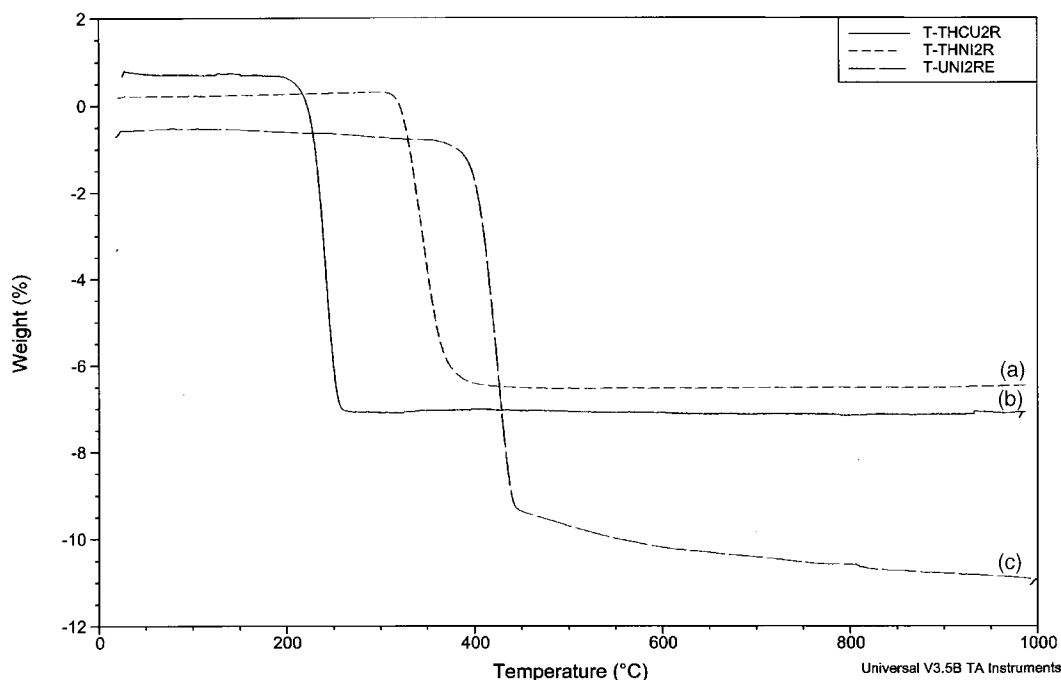

Fig. 4. TG profiles under pure hydrogen (PH_2 = 1 bar, β = 10 K/min): (a) ThNi$_2$O$_4$ (22.5 mg), (b) ThCu$_2$O$_4$ (21.7 mg) and (c) UNi$_2$O$_5$ (28.7 mg).

and 1 bar) [15]. Moreover, the preferential oxidation of the element with the highest Gibbs free energy of formation has been found for Mg_2Cu [16] and $CeCu_x$ [17]. In some cases the heat involved during f block element oxidation promotes the oxidation of the second component, which prevents the observation of successive oxidations [17,18]. Therefore, for $ThCu_2$ the two distinct mass uptakes are consistent with a first step involving the oxidation of thorium (mass uptake for $ThCu_2$ oxidation into $2Cu \cdot ThO_2$, calc.: 8.9%; found: 9.6 ± 0.5%), followed by a second step for the oxidation of copper (mass uptake for $2Cu \cdot ThO_2$ oxidation into $2CuO \cdot ThO_2$, calc.: 8.2%; found: 7.8 ± 0.5%). A second statement that can be made for the nickel based compounds, $AnNi_2$ (An = Th, U), is that the formation of surface oxidized layers can account for the complete oxidation process being governed by oxygen diffusion into the bulk, leading to indiscernible first oxidation of the actinides.

3.3. Reduction studies

The temperature-programmed reduction under hydrogen of the oxidized actinide intermetallic compounds, $2CuO \cdot ThO_2$, $2NiO \cdot ThO_2$ and $2NiO \cdot UO_3$, was also studied by the TG technique. The curves reported in Fig. 4 show a progressive mass loss over a wide range of temperature, the onset occurring at 473, 573 and 623 K for $2CuO \cdot ThO_2$, $2NiO \cdot ThO_2$ and $2NiO \cdot UO_3$, respectively. The reduction is completed at 523, 673 and 1173 K, respectively. From the total mass loss, stoichiometries were calculated leading to the formulas: ThM_2O_2 (M = Cu, Ni) and UNi_2O_2
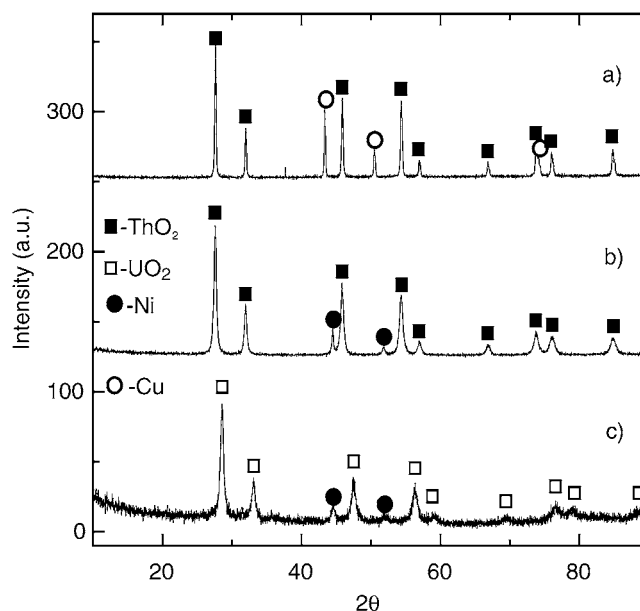

Fig. 5. XRD patterns after reduction: (a) $ThCu_2O_2$, (b) $ThNi_2O_2$ and (c) UNi_2O_3.

(Table 2). The XRD patterns obtained after reduction shows a set of diffraction lines that correspond to a mixture of two phases: Ni or Cu along with ThO_2 and Ni along with UO_2 (Fig. 5); thorium and uranium in the 4+ oxidation state.

On the basis of these results, stoichiometries for the reduction were proposed (Eqs. (3) and (4)) and the products described as new type of supported catalysts, copper or nickel
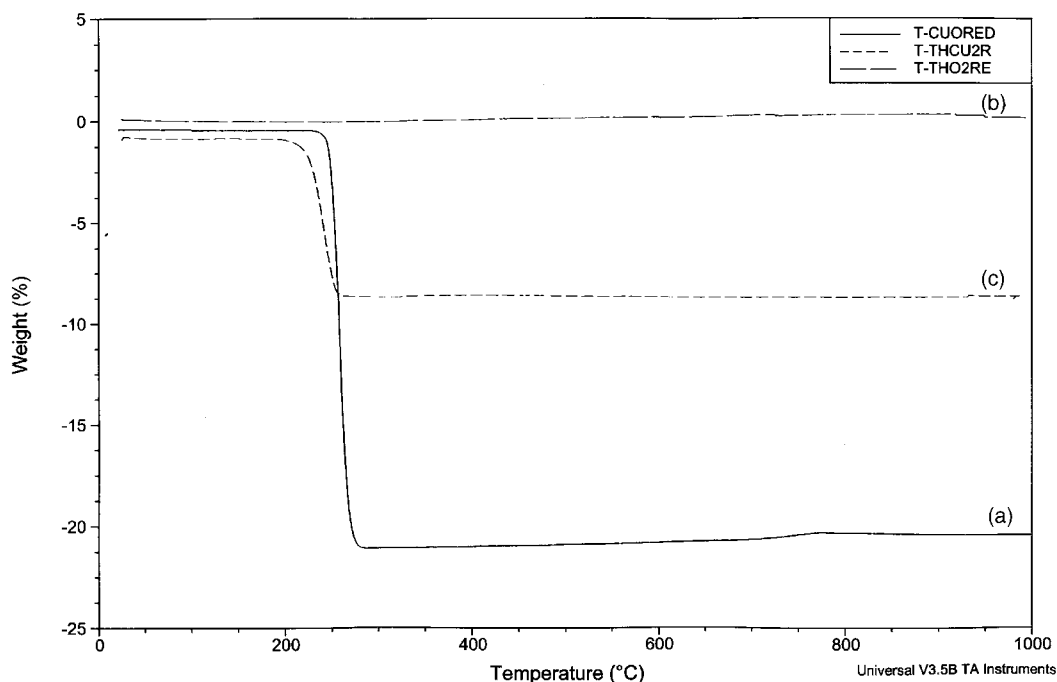

Fig. 6. TG profiles under pure hydrogen (P_{H_2} = 1 bar, β = 10 K/min): (a) CuO (25.1 mg), (b) ThO_2 (22.6 mg) and (c) $2CuO \cdot ThO_2$ (21.7 mg).

Table 2
TG mass losses under hydrogen

Oxide stoichiometry	Δm (%), expt.	Δm (%), theor.	T_m (K)	Product stoichiometry
$ThCu_2O_4$	-7.7 ± 0.5	-7.6	515	$ThCu_2O_2$
$ThNi_2O_4$	-7.2 ± 0.5	-7.7	619	$ThNi_2O_2$
UNi_2O_5	-10.3 ± 0.5	-11.0	698, 798	UNi_2O_2
CuO	-20.3 ± 0.5	-20.1	532	Cu
NiO	-21.0 ± 0.5	-21.4	600	Ni

supported on actinide oxides [11,12]

$$2MO \cdot ThO_2 + xH_2 \rightarrow 2M \cdot ThO_2 + H_2O \quad (M = Ni, Cu) \tag{3}$$

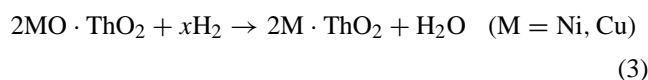$$2NiO \cdot UO_3 + yH_2 \rightarrow 2Ni \cdot UO_2 + H_2O \tag{4}$$

Fig. 4 shows that $2MO \cdot ThO_2$ (M = Cu, Ni) gives only one mass loss, over a wide range of temperature (298–1273 K). No distinct mass loss corresponding to successive reduction of the two-oxide component of the oxidized thorium intermetallic compounds were observed. Therefore, the TG mass loss correlate the XRD results and correspond to CuO or NiO reduction into Cu or Ni. Accordingly, the reduction of CuO and NiO, in the same experimental conditions, exhibited onset of mass loss at 498 and 573 K, respectively. The reduction was completed at 548 and 623 K, respectively. Cu and Ni were quantitatively formed (mass loss for CuO and NiO, calc.: -20.1 and -21.4%; found: -20.3 ± 0.5 and $-21.0 \pm 0.5\%$). The temperatures of maximum reduction rate, T_m, were 532 K for CuO and 600 K for NiO. Concomitantly, the reduction of ThO_2 gives no mass losses over the same range of temperature (298–1273 K). As an example, Fig. 6 shows the TG curves obtained under hydrogen for CuO, ThO_2 and $2CuO \cdot ThO_2$.

$2NiO \cdot UO_3$ gives two distinct mass losses (Fig. 4c): first, $\Delta m = -8.7 \pm 0.5\%$ (623–723 K); second, $\Delta m = -1.6 \pm 0.5\%$ (723–1173 K), attributed to successive reduction of NiO to Ni (mass loss for $2NiO \cdot UO_3$ reduction into $2Ni \cdot UO_3$, calc.: -7.4%; found: $-8.7 \pm 0.5\%$) and UO_3 to UO_2 (mass loss for $2Ni \cdot UO_3$ reduction into $2Ni \cdot UO_2$, calc.: -3.6%; found: $-1.6 \pm 0.5\%$).

4. Conclusions

The temperature-programmed oxidation under air of $ThCu_2$ and $AnNi_2$ (An = Th, U), followed by reduction under hydrogen, was studied by thermogravimetric analysis. The oxidation products were described as actinide heterobimetallic oxides, $2MO \cdot ThO_2$ (M = Ni, Cu) and $2NiO \cdot UO_3$. After reduction, the products are $2M \cdot ThO_2$ (M = Ni, Cu) and $2Ni \cdot UO_2$, with all the actinides in the 4+ oxidation state. These products are better described as a

new type of copper or nickel supported catalysts on actinide oxides. Therefore, binary copper– or nickel–actinide intermetallic compounds are interesting precursors, providing a new method for the synthesis of such a type of catalysts.

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