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# Selective Lanthanide-catalysed Reactions

Catalytic Properties of Sm and Yb Metal Vapour Deposition Products

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The characteristics of lanthanide catalysts obtained when Sm and Yb were vaporized into a frozen organic (tetrahydrofuran, benzene and methylcyclohexane) matrix (77 K) were investigated. These low-valent, highly dispersed lanthanide particles (indicated as Sm/THF, Sm/benzene, Yb/THF, Yb/benzene etc.) were catalytically active and selective for hydrogenation and isomerization. Samarium usually showed a greater activity than ytterbium. Olefin [ethene, propene, but-1-ene and (z)-but-2ene] hydrogenation obeyed the rate law  $v = kP_{\rm H}$ , suggesting that the reaction is controlled by catalytic activation of hydrogen. The molecular isotopic identity of hydrogen was conserved during the hydrogenation. Yb/THF and Yb/benzene were active for partial hydrogenation of benzene to cyclohexene. For the hydrogenation of olefins and acetylenes the substrate specificity was high; thus C-C double bonds were more readily reduced than triple bonds. The samarium and ytterbium catalysts discriminate between terminal and internal C-C triple bonds, only internal  $C \equiv C$  bonds (but-2-yne and pent-2-yne) being reduced very selectively in contrast to acetylene, methylacetylene and but-1-yne. Solid base character of the lanthanide provides a cause for these differences in catalytic properties.

Homogeneous lanthanide catalysis has developed into a useful procedure in organic synthesis.<sup>1</sup> A less extensive study has been made with heterogeneous lanthanide catalysts.<sup>2</sup> Especially, there have been few catalytic studies published of lanthanide (rareearth) metals compared to oxides, halides *etc*. This is probably because they are not fully reduced by treatment with hydrogen unlike conventional Group VIII metal catalysts. As will appear, we observed that lanthanide metals were used more efficiently when dispersed on a frozen organic matrix (tetrahydrofuran, benzene and methylcyclohexane). The lanthanide metal vapour reaction products thus obtained exhibited unusual activity and selectivity for the hydrogenation of unsaturated hydrocarbons.<sup>3-6</sup> Lanthanide catalysts prepared by metal vapour deposition, possibly best regarded as pseudo-organometallic particles,<sup>7</sup> do exhibit enhanced activity for the reaction.

We have here endeavoured to show the lanthanide-catalysed reactions are of great interest and use. In addition, a great deal of attention has been devoted to defining and better understanding the catalytic behaviour of these low-valent, highly dispersed lanthanide particles by metal vapour techniques.

## Experimental

# **Preparation of Catalysts**

The basic experimental requirements for the preparation of the lanthanide catalysts are a furnace (tungsten wire coil basket; Japan Lamp Industrial) for generating the metal

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catalyst <sup>b</sup>	reaction temp./K	activity $k^c/\min^{-1} g^{-1}$					
		ethene	propene	but-1-ene	(z)-but-2-ene		
Sm/THF*	313	$6.1 \times 10^{-1}$	$3.0 \times 10^{-1}$		$3.2 \times 10^{-1}$		
Sm/THF**	294	$2.1 \times 10^{-2}$	$3.6 \times 10^{-2}$	$7.1  imes 10^{-2}$			
Sm <sup>′</sup> /MCH	293	$2.5 \times 10^{-2}$	$1.5 \times 10^{-2}$	$1.6  imes 10^{-2}$			
Yb/THF	323	$1.6 \times 10^{-3}$	$1.4 \times 10^{-3}$	$4.2 \times 10^{-3}$			

Table 1. Hydrogenation of olefins<sup>a</sup>

<sup>*a*</sup> The reaction was conducted by admitting olefin (47 Torr) and hydrogen (88 Torr). <sup>*b*</sup> The catalyst was outgassed at 473 K for 2 h before use. <sup>*c*</sup> First-order rate constant. Sm/THF\*and Sm/THF\*\* are prepared separately.

vapour inside a Pyrex-glass vacuum system and a cold surface on which the vapour can be deposited. Thus, after evacuation of the reaction system (to *ca.*  $10^{-3}$  Pa), Sm or Yb (*ca.* 0.4–0.5 g; Research Chemicals, purity 99.9 %) was vaporized into an organic solvent matrix (*ca.* 7–8 cm<sup>3</sup>) which had been condensed as a layer on the wall of the cooled (77 K) reactor. Tetrahydrofuran (THF), benzene and methylcyclohexane (MCH), which were distilled over sodium wire immediately prior to reaction, were used as a matrix compound. Upon completion of the low-temperature deposition, the reactor was warmed to room temperature and the excess organic solvent was pumped off. The resulting black, pyrophoric powders are referred to as Sm/THF, Sm/benzene, Sm/MCH, Yb/THF and Yb/benzene.

By scanning electron micrographs of the samarium and ytterbium catalyst grains prepared in this way the gross morphology was described as aggregates of small spheroidal particles with a size of *ca.* 150–500 Å. Their B.E.T. surface areas, which were slightly varied with the preparation batch, were relatively large (Sm/THF = 51–58, Sm/benzene = 38, Yb = 17–23, Yb/benzene = 36 m<sup>2</sup> g<sup>-1</sup>).

# **Reaction Procedures**

Unless otherwise stated, most reactions were carried out with a conventional gas circulation system (ca. 300 cm<sup>3</sup>) in the gas phase. Each catalyst was subjected to evacuation at the prescribed temperatures before the run. The reacting gas in the system was collected by a gas sampler and transferred to a gas chromatograph.

The liquid-phase reaction was conducted in a 30 cm<sup>3</sup> stainless-steel autoclave under 3 MPa of hydrogen. After the autoclave was completely flushed with dry argon, measured amounts of the catalyst, reactant (benzene) or solvent were placed in it. The autoclave was cooled by liquid nitrogen and was degassed *in vacuo*, then pressurized to 3 MPa with hydrogen. All procedures were conducted without exposure to air.

# **Results and Discussion**

# Hydrogenation of Olefinic Bonds

Samarium and ytterbium powders (indicated as Sm/THF, Yb/THF *etc.*) prepared by metal vapour techniques have shown a high ability to catalyse the hydrogenation of a wide variety of unsaturated hydrocarbons.<sup>3-6</sup> The addition rates of hydrogen were represented on coordinates of a first-order equation (substrate: 20–100 Torr;†  $H_2$ : 60–200 Torr). As can be seen in the results of olefin hydrogenation (table 1), the rate

† 1 Torr = 133.322 Pa.

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evacuation temp. <sup>a</sup> /K	surface area/m² g <sup>-1</sup>	activity $k^b/\min^{-1} g^{-1}$
296 333	58	$2.7 \times 10^{-2} (313 \text{ K})$
333 473	72	$6.1 \times 10^{-1} (313 \text{ K})$
333 473	63 70	$\begin{array}{c} 1.6 \times 10^{-1} \ (333 \ \mathrm{K}) \\ 9.7 \times 10^{-1} \ (333 \ \mathrm{K}) \end{array}$
	evacuation temp. <sup><i>a</i></sup> /K 296 333 473 333 473	$\begin{array}{c} \text{evacuation} & \text{surface} \\ \text{area}/\text{m}^2 \text{ g}^{-1} \\ \hline \\ \hline \\ 296 & 58 \\ 333 & 61 \\ 473 & 72 \\ 333 & 63 \\ 473 & 70 \\ \hline \end{array}$

 Table 2. Influence of evacuation temperature on the surface area and activity

<sup>a</sup> For 2 h. <sup>b</sup> The first-order rate constant of ethene hydrogenation is used as an index of activity. Sm/THF\* and Sm/THF\*\*\* are prepared separately.

constants were almost independent of the olefin used [ethene, propene, but-1-ene and (z)-but-2-ene], leading to speculations of hydrogen activation rate-limited hydrogenation. Further, the observed distributions and locations of deuterium in the products of samarium-catalysed deuterogenation indicate that unlike most catalysts of the Group VIII metals the lanthanide catalysts are characterized as those which can conserve the molecular identity of hydrogen during the hydrogenation.<sup>5</sup> For buta-1,3-diene hydrogenation the formation of but-2-ene occurred by 1,4-addition of hydrogen, while a 1,2-addition process was responsible for but-1-ene. But-2-ene was a major product (> 80 %) with a high (e):(z) ratio (2–20).

For all the hydrogenation reactions studied samarium (Sm/THF and Sm/MCH) usually exhibited an activity about an order of magnitude higher than ytterbium (Yb/THF), although the catalytic behaviour of both was essentially similar.<sup>3-6</sup> However, the catalytic activities of lanthanide metal vapour reaction products for homogeneous hydrogenation have been studied, and therein the difference in activity between samarium and ytterbium is less pronounced.<sup>8-10</sup> The activities we observe are not consistent with the results reported on lanthanide metals by Konenko,<sup>11-13</sup> either. The hydrides of samarium and ytterbium showed less activity than the metals, the results being compatible with the study of lanthanide dihydrides and trihydrides.<sup>11,12</sup>

In the reaction the lanthanide catalyst, previously evacuated at high temperatures, was brought into contact with a mixed gas of olefin and hydrogen. Pretreatment of the catalyst by evacuation at the elevated temperature resulted in marked changes in the catalytic properties, especially hydrogenation activity including the reduction of acetylene and benzene. For samarium-catalysed ethene hydrogenation the rate constant of Sm/THF was increased over 10-fold by heating to 473 K (table 2). Since the reactions of metal vapour with solvent molecules accompanied the solvent decomposition reaction in the catalyst preparation,14,15 this thermal treatment in vacuo apparently generates open coordination sites by releasing organic species solvated on the lanthanide clusters. Although an increase in evacuation temperature resulted in a simultaneous increase (1.2–1.3 times) in surface area of Sm/THF or Yb/THF, the specific activity is certainly considerably increased by thermal treatment *in vacuo*. We have found that the degrees of coordinative unsaturation and solvation are important factors in determining the hydrogenation behaviour, especially the catalytic activation of hydrogen. In homogeneous hydrogenation reactions with lanthanide metal vapour reaction products similar characteristics are discussed by Evans et al.9 These are consistent with the fact that the re-adsorption of THF by Sm/THF previously evacuated at 473 K led to a relative reduction in the activity (fig. 1). This poisoning technique is useful for evaluation of the active sites on the lanthanide catalyst. Thus activation and deactivation of the

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**Fig. 1.** Effect of THF re-adsorption on the relative activity (293 K) of ethene hydrogenation. Sm/THF (*ca.* 0.1 g), previously outgassed at 473 K for 2 h, was exposed to various pressures of THF, was briefly evacuated, brought into contact with ethene (20 Torr) and hydrogen (52 Torr) under the same conditions.

catalyst are responsible for the degree of solvation on the catalytically active species. It seems that this reflects reversible changes in the active surface sites.

Besides, the catalyst thus prepared contained some reactive hydrogen species as a result of the solvent decomposition reaction.<sup>14,15</sup> Therefore they are able to hydrogenate olefins even in the absence of gaseous hydrogen. The amount of hydrogen attached corresponds to  $(9.5-15) \times 10^{19}$  H<sub>2</sub> molecules g<sup>-1</sup> – cat. This amount usually decreased with an increase in evacuation temperatures.

## Hydrogenation of Acetylenic Bonds

Our investigations were extended to acetylene hydrogenation over the lanthanide systems.<sup>6</sup> Typical reactions in the range 303–393 K are summarized in table 3. These hydrogenations showed some interesting features which seem additionally to characterize the lanthanide catalysts. In the first place the substrate specificity was high for the hydrogenation of olefins and acetylenes; thus C-C double bonds were more readily reduced than triple bonds. Depending on the acetylenic derivative used (acetylene, methylacetylene and but-1-yne), negligible hydrogenation occurred. The reactivity of but-2-yne was ca. 1% of that of but-2-ene. This is particularly surprising in view of the results obtained when Ceyer and co-workers<sup>16</sup> studied the adsorption of ethene and acetylene on a lanthanide metal surface, Gd(0001), by UPS and AES. A further useful property of the lanthanide catalyst is that it completely discriminates between internal and terminal C-C triple bonds, only internal C=C bonds being reduced very selectively. Thus but-2-yne and pent-2-yne were effectively hydrogenated to (z)-but-2-ene and (z)-pent-2-ene, respectively, in a high selectivity, whereas acetylene, methylacetylene and but-1-yne were not reduced at all under the same conditions. However, the isomerization of these acetylenes rapidly occurred. Methylacetylene was converted into allene at 303 K with equilibrium composition (fig. 2). But-1-yne was isomerized to but-2-yne and buta-1,2-diene, although the conversion into buta-1,3-diene is most thermodynamically favourable. It is accepted that that the isomerization of acetylenic hydrocarbons under alkaline conditions is a much easier process.<sup>17</sup> The base-catalysed rearrangement involves allenes as intermediates. Catalytically, the samarium and

substrate	catalyst <sup>a</sup>	aculvity at 525 K $k/\min^{-1} g^{-1}$	product $(\%)^d$
acetylene	Sm/THF	no reaction	
acetylene	Yb/THF	no reaction	Ι
methylacetylene	Sm/THF	ر ب	allene
methylacetylene	Yb/THF	ر ا	allene
but-l-yne	Sm/THF	c	buta-1,2-diene, but-2-yne
but-2-yne	Sm/THF	$4.4 \times 10^{-4}$	(z)-but-2-ene(65), but-1-ene(35), buta-1,2-diene
but-2-yne	Yb/THF	$1.6 \times 10^{-5}$	(z)-but-2-ene $(70)$ , but-1-ene $(30)$ , buta-1,2-diene
pent-2-yne	Sm/THF	$8.1 \times 10^{-4}$	(z)-pent-2-ene $(91)$ , pent-1-ene $(9)$ , penta-1,3-diene
pent-2-yne	Yb/THF	$9.4 \times 10^{-5}$	(z)-pent-2-ene $(82)$ , pent-1-ene $(18)$ , penta-1,3-diene

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Fig. 2. Isomerization of methylacetylene to allene over Sm/THF (303 K). The reaction was carried out by admitting methylacetylene (44 Torr) over Sm/THF (0.13 g) which had been evacuated at 473 K for 2 h. ●, Methylacetylene; ○, allene.



**Fig. 3.** Hydrogenation of but-2-yne over Sm/THF (353 K). The mixture gas of but-2-yne (31 Torr) and H<sub>2</sub> (87 Torr) was brought into contact with Sm/THF (0.11 g) which had been evacuated at 523 K for 2 h.  $\bigcirc$ , But-2-yne;  $\bigcirc$ , (z)-but-2-ene;  $\bigcirc$ , but-1-ene;  $\bigcirc$ , buta-1,2-diene.

ytterbium employed were found to be similar in action to the base-catalysed isomerizations of acetylenes. It is additionally noted that the presence or absence of hydrogen little affected the isomerization activity and product distribution.

The hydrogenation of but-2-yne and pent-2-yne was the selective conversion to the corresponding olefins. The reaction of but-2-yne (31 Torr) with hydrogen (87 Torr) in the presence of Sm/THF is shown in fig. 3. Rapid hydrogenation occurred initially due to reactive hydrogen attached to the catalyst and then proceeded slowly. As described previously, this is consistent with expectations that the reaction is by a rate-limited hydrogen adsorption process.<sup>5</sup> Samarium was completely selective for olefin formation. (z)-But-2-ene and but-1-ene were formed in 65 and 35% selectivity, respectively, and the yield of (e)-but-2-ene was negligible. The Sm/THF catalyst simultaneously yielded a

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cat. <sup>b</sup>	wt/g	$\rm C_6H_6/cm^3$	solvent	T/K	time/h	conv. (%)	$C_6 H_{10}^{c}$ (%)
Sm/benzene	0.1	2.5		473	5	12	trace
Sm/THF	0.1	2.5		473	5	31	
Sm/THF	1	2.5	diethyl ether	473	5	4.2	12
Yb/THF	1	5		423	20	1.3	11
Yb/THF	1	2.5		473	5	14	5
Yb/benzene	1	5		423	20	6.5	8
Yb/benzene	1	2.5		473	5	12	19

**Table 4.** The results of liquid-phase hydrogenation of benzene<sup> $\alpha$ </sup>

<sup>a</sup> The reaction was conducted at a hydrogen pressure of 3 MPa. <sup>b</sup> Each catalyst was evacuated at 473 K for 2 h before use.  ${}^{c}C_{6}H_{10}/(C_{6}H_{10}+C_{6}H_{12}) \times 100$ .

slight buta-1,2-diene isomer in the very initial stage, the amount of which remained unchanged ever afterward. In hex-3-yne hydrogenation by organolanthanide complexes a Z isomer in hex-3-ene is also a predominant product.<sup>9,10</sup> Evans *et al.*<sup>9</sup> in their homogeneous hydrogenation of hex-3-yne detect > 90% of (*cis*)-hex-3-ene.

Dobson<sup>18</sup> studies the reduction of a diacetylene containing a terminal and an internal triple bond, in which the precedence of reduction is established as terminal and internal  $C \equiv C$  bond. Upon reducing an equimolar mixture of oct-1-yne and oct-4-yne on palladium the preferential hydrogenation of the terminal triple bond over the internal triple bond is substantiated. Petrov and Forost<sup>19</sup> also found that the terminal bonds of hepta-1,5-diyne and octa-1,5-diyne were selectively converted to hept-1-en-5-yne and oct-1-en-5-yne in the presence of palladium. The difference in reducibility is discussed based on the effect of steric hindrance.<sup>20</sup> As shown in a clear example of the hydrogen addition for terminal and internal  $C \equiv C$  bonds by the lanthanide is completely contrary to that of conventional transition-metal catalysts. Mechanistically, the lanthanide catalysts may offer a very different mechanistic situation from the conventional catalysts.

It is generally accepted that lanthanide (rare-earth) catalysts are classified as solid bases,<sup>2</sup> probably not excepting these lanthanide metal vapour deposition products. When the isomerization of but-1-ene was conducted, Sm/THF or Yb/THF exhibited high yields of (z)-but-2-ene [(z):(e) ratio = 2-7]. That the formation of the (z) olefin is favoured over that of the (e) isomer is one of features of base-catalysed isomerization,<sup>21</sup> as well as the results on the isomerization of acetylenes as described above. Preferential formation of (z)-but-2-ene leads to speculations of an abstraction-addition mechanism involving  $\pi$ -allylic intermediates rather than an addition-abstraction mechanism via adsorbed butyl species, where the carbanion formed by the removal of the acidic hydrogen is stabilized in the (z) form. In view of these results the catalysts such as samarium and ytterbium used here are certainly characterized as solid base. Accordingly, the remarkable difference in reactivity of the terminal and internal C=C bonds derives from the low acidity of the C=C-H group. In the reaction of base catalysts with terminal acetylenes, stable species like acetylide may be formed, with the consequent inhibition of hydrogenation.

#### Hydrogenation of Benzene

Catalytic hydrogenation of the benzene ring is more difficult than for most other unsaturated compounds. Interestingly, both the samarium and ytterbium catalysts prepared by vaporizing the metal atoms into a frozen organic matrix also effectively

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catalysed the hydrogenation of the benzene ring. As shown in the results of the liquidphase reaction under 3 MPa of hydrogen (table 4), some catalysts exhibited a marked selectivity for the formation of a partially hydrogenated intermediate; 5–19 mol % yields of cyclohexene were recorded in ytterbium-catalysed reactions at 423 or 473 K. At lower conversions of benzene the selectivity of the ytterbium was high (60–70%), but a gradual decline in selectivity occurred with increased conversion. The formation of cyclohexene by benzene hydrogenation is thermodynamically unfavourable compared with that of cyclohexane<sup>22</sup> and, moreover, the addition rate of hydrogen to cyclohexene is actually much faster than that to benzene.

The most selective systems so far reported are those in which a suitable geometric arrangement of catalytic sites exists or the sites have been coordinatively modified by various additives.<sup>23</sup> It is conceivable that the lanthanide metal vapour deposition process causes similar effects. If the metal aggregates formed in this way behave like pseudo-organometallic particles,<sup>7</sup> they would possess coordinatively high abilities due to the large ionic radius of 4f-elements and hence, would be more active and selective.

Samarium was more active than ytterbium, but no intermediate was produced. The use of appropriate solvents in this system significantly improved the selectivity. Preliminary experiments revealed that diethyl ether was effective for the samarium catalysts at a selectivity of 12 mol% toward cyclohexene.

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