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Rare Earth Metals as Hydrogenation Catalysts of Unsaturated Hydrocarbons

HAYAO IMAMURA,[1] AKIRA OHMURA, EITETSU HAKU, AND SUSUMU TSUCHIYA

Department of Industrial Chemistry, Faculty of Engineering, Yamaguchi University,
2557 Tokiwadai, Ube 755, Japan

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To elucidate the characteristics of rare earth metallic catalysts the hydrogenation of unsaturated hydrocarbons (ethene, propene, 1-butene, 1,3-butadiene, ethyne, propyne, and benzene) were carried out around ambient temperature using samarium and ytterbium particles formed by clustering metal atoms in frozen organic matrices by metal vapor techniques. In the hydrogenation reactions the rare earth metallic catalysts discriminated between the C–C double bonds and triple bonds; alkenes, dialkenes, and aromatic compounds were readily hydrogenated, whereas alkynes were not hydrogenated at all. However, enhanced isomerization activity of propyne to propadiene was observed. The addition rates of hydrogen to alkenes were represented on coordinates of a first-order equation: $v = kP_{H_2}$. Preliminary kinetic studies suggest that the reaction is controlled by the hydrogen adsorption process. This identification is reinforced by the H_2–D_2 isotope scrambling measurements. The hydrogenation of 1,3-butadiene by the rare earth catalysts was completely selective for alkene formation, and the yield of 2-butene was relatively high (>80%) with a high *trans* : *cis* ratio (2 ~ 20). The mode of hydrogen addition to the diene was examined using isotope techniques, indicating that 1-butene and 2-butene were formed by 1 : 2- and 1 : 4-addition of hydrogen to 1,3-butadiene, respectively. In addition, it was found that the molecular identity of hydrogen was conserved during the hydrogenation of unsaturated hydrocarbons. © 1985 Academic Press, Inc.

INTRODUCTION

Recently, because of growing industrial applications of rare earth materials their chemical and physical properties have been extensively examined. The catalytic characteristics have also been studied, but less extensively. It has been shown that the rare earth compounds exhibit the catalytic ability in a great variety of reactions, of which the cracking in petrochemistry and the gas cleanup in automobiles are practically performed. However, there have been few catalytic studies published of rare earth metals compared to oxides, halides, etc. (*1*, *2*). This is probably because they are not fully reduced by treatment with hydrogen unlike most catalysts of the Group VIII metals.

We have found that catalytically reactive rare earth metal particles are prepared by dispersing metal atoms into frozen organic matrices at −196°C (*3*, *4*). Samarium thus prepared shows enhanced hydrogenation activities of ethene. Thus, this metal vapor deposition should be of general applicability of the preparation of catalysts of rare earth metals difficult to reduce, and it is likely that enhanced activities can be obtained for a variety of reactions. Klabunde (*5*, *6*) has previously reported on metal–solvent codepositions on a cold surface and how this affects the activity of the resultant powders. It seems that metal atom clustering in organic media leads to new materials of fascinating properties, which is turning out to be an important area.

In the present paper, we undertook to study the catalytic properties of rare earth metals, which were formed by clustering of

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[1] To whom correspondence should be addressed.

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metal atoms in frozen organic matrices, as hydrogenation catalysts of various unsaturated hydrocarbons.

EXPERIMENTAL

Materials. Rare earth metals (samarium and ytterbium, >99.9%) were obtained as chips from Research Chemicals. Tetrahydrofuran (THF), benzene, and pentane were used as an organic matrix into which the rare earth metal vapor was dispersed, and were thoroughly dehydrated using sodium wire. Unsaturated hydrocarbons (ethene, propene, 1-butene, ethyne, propyne, 1,3-butadiene, and benzene) were fractionated prior to use and were checked for purity by gas chromatography.

Procedures. The Pyrex glass apparatus for the preparation of the samarium and ytterbium catalysts is modeled after reactors described in the literature (7). It consists of a glass test-tube-shaped bottom, 35 mm in diameter × 350 mm long, fitted with a 32-mm O-ring joint. The reaction vessel which is equipped with an organic vapor inlet tube and two electrodes connected to a tungsten wire coil basket is attached to a high-vacuum line. The two tungsten electrodes (2.0 × 500 mm) are insulated and sealed with Pyrex glass. On the inside of the vessel, the inlet tube descends to within ca. 10 mm of the metal vapor source. The power source is a 0- to 130-V transformer which delivers 7 V at a rating of 30 A under preparative conditions.

The preparation of the catalysts by metal vapor deposition was accomplished in two ways. In a standard procedure for the preparation of Sm–THF, Sm–benzene, and Sm–pentane, the entire reaction system was evacuated to a pressure of about 10^{-6} Torr and then the reaction zone was cooled using liquid nitrogen. The voltage in the electrodes was gradually increased until the metal began to vaporize, and the organic matrix gas was simultaneously introduced through the inlet tube into the system. The high-temperature rare earth species were brought into contact with organic molecules and were simultaneously codeposited on the inner cold surfaces of the reactor. For example, the preparation of Sm–THF was conducted by vaporizing 1 g of samarium with 3 ml of THF. In contrast with the Sm–solvent systems, Sm(Yb)/THF was prepared as follows: about 0.6 g of samarium (or ytterbium) was vaporized onto frozen THF matrices (5 ml) which had been condensed in a state of a layer on the walls of the reactor cooled to −196°C. Upon completion of metal deposition, the reactor was warmed to room temperature and the excess organic solvent was pumped off leaving a black residue. The rare earth catalysts prepared in this way were extremely sensitive to air turning into nonreactive materials by oxidation. Thus, all manipulations were carried out under an atmosphere of dry argon.

The catalytic reactions were studied in a conventional gas circulation system having a reaction space of ca. 300 cm^3. Prior to every measurement of the reaction about 0.07 g of each catalyst was subjected to outgassing at prescribed temperatures, and the mixture of reactant and hydrogen gases was admitted into the reactor. The change in the pressure registered on a mercury manometer was followed during the reaction and the compositions of the gas phase were monitored using gas chromatography.

RESULTS AND DISCUSSION

(I) Characteristics of Rare Earth Catalysts

We studied how the morphology of the rare earth particles developed during clustering metal atoms in low temperature organic matrices. Some SEM micrographs of these particles are shown in Figs. 1a–c. The particles were widely distributed in size and shape. It can be seen that the "as-prepared" Sm–THF sample has a spongy appearance and consists of layer-type flakes, but that the gross morphology of Sm(Yb)/THF is surprisingly different from that of

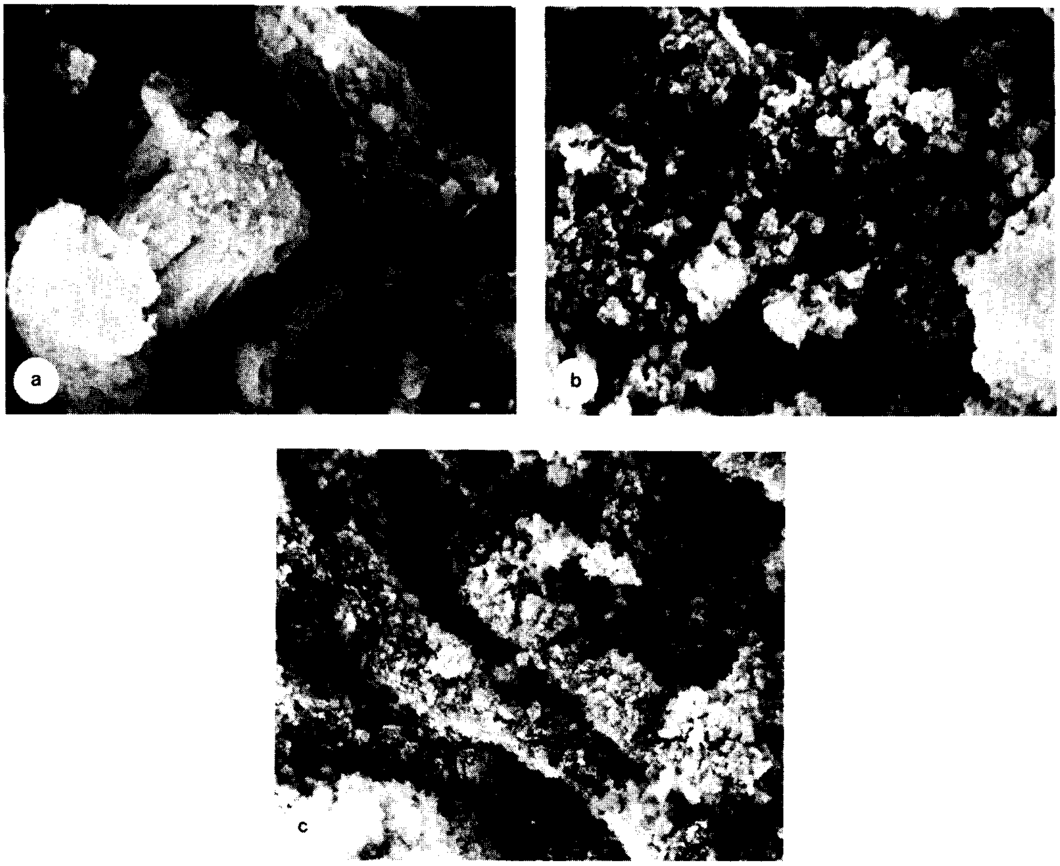

FIG. 1. Scanning electron micrographs of rare earth catalysts. (a) Sm–THF (×11,500), (b) Sm/THF (×24,000), (c) Yb/THF (×8,600).

Sm–THF. Klabunde (*8*) has shown that significantly different clustered forms of nickel are observed when different solvents are employed. It appears that the clustering processes involved in determining the character of metal particles are very dependent upon preparative conditions (metal, solvent, deposition method, quantitative details, temperature, time, etc.). A higher magnification picture of the Sm/THF grains shows that they are made up of small spheroidal particles which are individually <20 nm in size, which are loosely combined without any preferred orientation, resulting in a porous structure as a whole.

Therefore, the specific surface area of the rare earth catalyst was relatively large. An estimate by the BET method using nitrogen adsorption isotherms yielded values ranging from 5.6 to 72.3 m^2/g. However, since the thermal stability of the catalysts with respect to particle and surface area integrity was not very great, the BET surface area of Sm/THF somewhat increased with the preheating temperature *in vacuo*, passed through a maximum around 200°C with an enhancement by a factor of 1.2 and then progressively decreased at higher temperatures, as shown in Table 1. SEM observations of Sm/THF showed that the heat treatment little affected externally the shape of the particles.

(II) Catalytic Hydrogenation of Unsaturated Compounds

We have carried out hydrogenation reac-

TABLE 1

BET Surface Area of Rare Earth Catalysts

Catalyst	Evacuation temp[a] (°C)	Surface area ($m^2 \cdot g^{-1}$)
Sm/THF	60	61.2
Sm/THF	200	72.3
Sm/THF	450	52.4
Yb/THF	200	19.4
Sm–THF	200	5.6

[a] For 2 h.

tions with various unsaturated hydrocarbons, using catalytically active rare earth metal particles which are differently prepared. Unless otherwise stated, the hydrogenation reactions were conducted largely over Sm/THF and Yb/THF. The reactions showed some interesting features which seemed synthetically and industrially useful. In the first place the rare earth catalysts exhibited interesting selectivity characteristics, especially high substrate specificity. They were effective for hydrogenation of the C–C double bond, but the triple bond was not reduced at all under similar conditions. No hydrogenation of ethyne and propyne was detectable up to 100°C but propyne was quickly converted into propadiene at the initial rate of 8.2×10^{-5} mmol/s · g-Sm at 18°C, and the equilibrium composition was reached within several hours. Propyne–propadiene isomerization is known to be effectively catalyzed by some bases (*9*), of which ZnO acts via a 1,3-hydrogen shift (*10*). Homogeneous catalytic activities of alkyne hydrogenation by organolanthanoid complexes have been recently reported by Evans *et al.* (*11*).

The hydrogenation of alkene readily occurred by the samarium catalyst and to a lesser extent by the ytterbium catalyst. The results obtained for all the systems are summarized in Table 2. From preliminary kinetic experiments of alkene hydrogenation it was found that the reaction obeyed first-order kinetics and that its rate conformed to the expression

$$v = kP_{H_2}, \qquad (1)$$

where k is the rate constant and P_{H_2} the pressure of hydrogen. Similar kinetic features have been reported on the hydrogenation processes of propene in the presence of a series of rare earth catalysts elsewhere (*12*). Interestingly we observed that the rate constants of the samarium and ytterbium catalysts were almost unchanged regardless of variation in the alkene although it is generally agreed that the reduction rates de-

TABLE 2

Hydrogenation Results of Alkenes[a]

Catalyst	Evacuation temp[b] (°C)	Reaction temp (°C)	Activity $k(\text{min}^{-1} \cdot g^{-1})$		
			Ethene	Propene	But-1-ene
Sm/THF[c]	200	21	2.1×10^{-2}	3.6×10^{-2}	7.1×10^{-2}
Sm/THF	23	40	2.7×10^{-2}		
Sm/THF	200	40	6.1×10^{-1}		
Sm/THF	400	40	1.2×10^{-1}		
Yb/THF	200	50	1.6×10^{-3}	1.4×10^{-3}	4.2×10^{-3}
Sm–THF	18	82	2.9×10^{-2}		
Sm–THF	200	80	2.8×10^{-1}		
Sm–benzene	400	18	1.6×10^{-2}		

[a] Catalyst = 0.075 g, alkene = 47 Torr, hydrogen = 88 Torr.

[b] For 2 h.

[c] Prepared separately from the other Sm/THF.

crease with increasing the substitution of alkyl groups about the double bond (*13*).

The H_2–D_2 equilibrium reaction rapidly occurred over the Sm/THF catalyst at 18°C, but in the presence of ethene there was no indication of HD formation. Hence the preferential adsorption of ethene by samarium with subsequent blocking of dissociative hydrogen adsorption and retardation of the exchange reaction is expected. The rate equation (1) for the hydrogenation of alkenes can involve different mechanistic interpretations, of which catalytic activation of hydrogen on the catalyst surfaces seems important in this system. This is consistent with the results that the hydrogenation rates were almost independent of the nature of the reactant alkenes employed.

The catalytic activity varied markedly with the evacuation temperature of the catalysts before each run. When the first-order rate constant k is used as an index of catalytic activity, the values of the ethene hydrogenation over Sm–THF and Sm/THF increased by over an order of magnitude with a change in temperature from 18 to 200°C. Precise reasons for this are unknown, but the catalytic properties can be partially explained in terms of the facts that organic molecules solvated on the metal clusters were cleaved upon pyrolysis with an increase in temperature; the dependence of the activity is involved in the extent of exposure of active sites on the rare earth aggregates by evolution of adsorbed organic molecules. Further heating of Sm/THF to 400°C, however, led to 80% reduction in activity. This deactivation of the catalyst probably results from the decrease in surface area due to grain growth as described previously (Table 1).

In the hydrogenation of 1-butene there was a simultaneous isomerization, and the *cis* : *trans* ratio of the butene by Sm/THF and Yb/THF was about 2 and 7, respectively. In marked contrast to the case of hydrogenation, the isomerization activity was essentially independent of the evacuation temperatures of the catalyst. This is reasonable if one considers that the influence of the outgassing temperature on the hydrogenation activity is closely related to the activation abilities of hydrogen of the rare earth catalyst. In addition, both isomerization activities and isomeric compositions were almost unchanged irrespective of the presence or absence of hydrogen as well. Accordingly, preferential formation of *cis*-2-butene leads to speculations of an abstraction–addition mechanism involving π-allylic intermediates rather than an addition–abstraction mechanism via adsorbed butyl species.

The hydrogenation of ethene over Sm–THF, Sm–benzene, and Sm–pentane was accompanied by slow hydrogen absorption, but Sm(Yb)/THF exhibited negligible indication throughout the reaction. It was found that the catalytic activity of the Sm–solvent systems was markedly reduced by hydrogen uptake in the catalyst. This indicates that the reaction may have been catalyzed by the samarium hydride (SmH_2) as shown by the X-ray diffractogram of the catalyst after the run. The catalytic activity of rare earths in several forms (metal, dihydride, and trihydride) have been systematically investigated by Konenko (*14, 15*). It is known that the reactivity sequence for the *para–ortho* hydrogen conversion and propene hydrogenation conducted around 200°C is generally metal > dihydride > trihydride. This is consistent with our observations. However, the specific activity of the catalyst formed by metal vapor deposition as described here was quite superior to that reported in Refs. (*12, 14, 15*).

The catalytic characteristics were a function of the nature of the organic matrices into which the rare earth atoms were dispersed. This functional dependence suggests that the interaction between the rare earth species and organic molecules during clustering of metal atoms at low temperatures plays an important role in this system.

The hydrogenation over Sm(Yb)/THF was further extended to include conjugated systems: 1,3-butadiene and benzene. Al-

TABLE 3

Hydrogenation Results of Buta-1,3-diene[a]

Catalyst	Evacuation temp[b] (°C)	Reaction temp (°C)	Conversion[c] (%)	Selectivity (%)		
				But-1-ene	*trans*-But-2-ene	*cis*-But-2-ene
Sm/THF	24	24	4.0	13	77	11
	200	20	49	15	81	4
	400	22	7.0	17	73	10
Yb/THF	200	25	1.8	19	52	28
Sm–THF	400	65	4.0	27	63	10
Sm–benzene	400	64	38	16	79	5
Sm–pentane	400	61	9.7	9	72	19

[a] Catalyst = 0.07 g, buta-1,3-diene = 44 Torr, hydrogen = 88 Torr.

[b] For 2 h.

[c] After 2 h.

though the catalytic hydrogenation of the benzene ring is one of the most difficult of all unsaturated compounds, the reaction was possible even at room temperature. Since a theoretical development based on the geometry has been proposed for benzene hydrogenation (*16*), this metal vaporization technique would cause the rare earth metals to be dispersed into frozen organic matrices in a suitable arrangement, resulting in unusual selectivity and activity changes in rare earth metals. Moreover, if the metal aggregates formed in this way behave like pseudoorganometallic particles as mentioned by Klabunde (*6*), they would possess coordinatively high abilities due to large ionic radius of 4*f*-elements and, hence, would be more reactive.

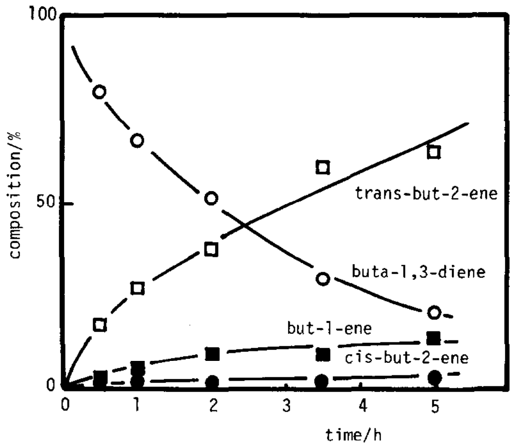

FIG. 2. Time courses of the hydrogenation of 1,3-butadiene by Sm/THF. Sm/THF was degassed at 200°C for 2 h before use. Sm/THF = 0.07 g, 1,3-C_4H_6 = 44 Torr, H_2 = 88 Torr.

1,3-Butadiene was hydrogenated at 20–65°C to butenes very selectively and the products were solely butene isomers, as shown in Fig. 2. 2-Butene was a major product (>80%) with a high *trans* : *cis* ratio (2 ~ 20). The type of butene composition obtained somewhat depended either upon the nature of organic solvents employed in metal vapor deposition or upon the degree to which the catalyst was sintered (Table 3). The butene composition remained unchanged throughout the reaction in the presence of the diene.

The mode of hydrogen addition to the diene was examined from the distributions and locations of deuterium in the products of samarium-catalyzed 1,3-butadiene deuterogenation. As shown in Table 4, the fraction of approximately 92% d_2-products at 7.6% of the conversion was realized. Mass spectrometry and NMR studies showed that 1 : 4-addition of hydrogen to the diene resulted in the formation of 2-butene, while 1-butene was via 1 : 2-addition process; no isomerization of butenes occurred before desorption. Hence, it appears that relative yields of *trans*- and *cis*-2-bu-

TABLE 4

Distribution of Deuterium in Butenes Formed in the Hydrogenation of Buta-1,3-diene over Sm/THF

Conversion (%)	d_0	d_1	d_2	d_3	$>d_4$
7.6	4.8	0	92.1	3.2	0
11.1	14.2	0.8	83.3	1.6	0
13.8	10.1	0	87.5	2.4	0

tene formed by this process depend on the conformation characteristics of adsorbed precursors. The (*trans/cis*) ratio of 2-butene formed was different from that in the isomerization, suggesting that rapid and successive hydrogen addition to 1,3-butadiene occurs before interconversion of half-hydrogenated adsorbed species into π-allylic intermediates. In this system, the distribution of deuterated butenes closely resembles that shown by certain nonmetal catalysts. Experimental findings are found which various workers have cited as evidence to show that the molecular identity of hydrogen is conserved during the hydrogenation of unsaturated hydrocarbons (*17*).

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