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Selective Hydrogenation of Internal and Terminal C≡C Bonds on Rare Earth Catalysts Formed by Metal Vapor Deposition

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The rare earth catalysts obtained when Sm and Yb were vaporized into a frozen organic matrix exhibited selective hydrogenation of various acetylenic derivatives. Sm/THF and Yb/THF discriminated between internal and terminal triple bonds.

We have found that samarium and ytterbium catalysts prepared by vaporizing the metal atoms into a frozen organic matrix exhibit unusual activity and selectivity in the hydrogenation reactions; thus hydrogenation of alkenes and dialkenes,1) and partial hydrogenation of benzene to cyclohexene.2) The catalysts prepared by metal vapor deposition, possibly best regarded as pseudo-organometallic particles,3) do exhibit enhanced activity for the reactions. This letter presents our data regarding the catalytic features of such low valent, highly dispersed rare earth systems for the hydrogenation of alkynes.

The preparation of the rare earth catalysts is described in previous papers.1,2) The catalysts obtained when Sm and Yb were vaporized in a frozen tetrahydrofuran (THF) matrix referred to as Sm/THF and Yb/THF. Their BET surface areas were relatively large (Sm/THF=51 and Yb/THF=23 m^2/g).

Table 1. Results of hydrogenation reactions

Substrate	Catalyst	Activity a) at 80 °C $k/min^{-1}\ g^{-1}$	Product (%) c)
Acetylene	Sm/THF	no reaction	-
〃	Yb/THF	no reaction	-
Methylacetylene	Sm/THF	- b)	allene
1-Butyne	Sm/THF	- b)	1,2-butadiene, 2-butyne
2-Butyne	Sm/THF	$4.4x10^{-4}$	cis-2-butene(65), 1-butene(35), 1,2-butadiene
〃	Yb/THF	$1.6x10^{-5}$	cis-2-butene(70), 1-butene(30), 1,2-butadiene
2-Pentyne	Sm/THF	$8.1x10^{-4}$	cis-2-pentene(91), 1-pentene(9), 1,3-pentadiene
〃	Yb/THF	$9.4x10^{-5}$	cis-2-pentene(82), 1-pentene(18), 1,3-pentadiene
Ethene	Sm/THF	$2.1x10^{-2}$(at 21 °C)	ethane d)
〃	Yb/THF	$1.6x10^{-3}$(at 50 °C)	ethane d)
Propene	Sm/THF	$3.6x10^{-2}$(at 21 °C)	propane d)

a) The k values were determined using $v=kP_{H_2}$. b) Only isomerization occurred.
c) Parentheses represent selectivity for the hydrogenation. d) Ref. 1.

For both the samarium and ytterbium catalysts the hydrogenation of various acetylenic derivatives was carried out with a conventional gas circulation system at 80-150 °C. The results obtained are summarized in Table 1. These hydrogenation reactions exhibit some interesting features which may characterize the rare earth catalyst. The catalyst was highly selective, the C-C triple bonds being more difficult to reduce than the double bonds. A further useful property of rare earth catalysts is that they discriminate between internal and terminal triple bonds. Thus 2-butyne and 2-pentyne were effectively hydrogenated to cis-2-butene and cis-2-pentene, respectively, in high selectivity, whereas acetylene, methylacetylene and 1-butyne were not hydrogenated at all under the same conditions. No hydrogenation was detected even at 150 °C. However, the isomerization of these alkynes occurred. Methylacetylene was rapidly converted into allene with equilibrium composition. 1-Butyne was isomerized to 2-butyne and 1,2-butadiene although the conversion into 1,3-butadiene is most thermodynamically favorable. The catalytic activities of lanthanide metal vapor reaction products for homogeneous alkyne (3-hexyne and diphenylacetylene) hydrogenation have been studied,[4,5] in which neither activity nor selectivity are always consistent with those observed by us.

The hydrogenation of 2-butyne in the presence of Sm/THF is shown in Fig. 1. The hydrogenation rapidly occurred initially and then proceeded slowly. This is probably due to that the catalyst contained some hydrogen species as a result of the THF cleavage reaction which occurs during the metal vapor deposition.[6] Samarium was completely selective for alkene formation. cis-2-Butene and 1-butene were formed in 65 and 35% selectivity, respectively, and the yield of trans-2-butene was negligible. In 3-hexyne hydrogenation by lanthanide metal complexes a cis isomer in 3-hexene is also a predominant product (> 90%).[4] The hydrogenation obeyed first order kinetics with respect to hydrogen pressure (60-190 Torr). The Sm/THF catalyst rapidly yielded a slight 1,2-butadiene isomer, the amount of which remained unchanged ever afterward.

As shown in Table 1, ytterbium, as well as samarium, exhibited essentially same catalytic behavior, but samarium was more active than ytterbium. Faster samarium-catalyzed hydrogenation rates have been observed for alkenes, dialkenes,[1] and benzene.[2]

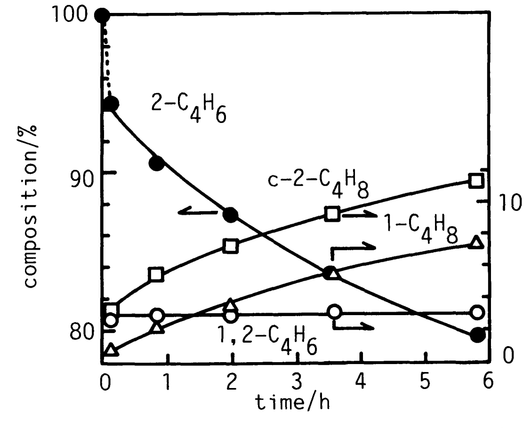

Fig.1. The reaction of 2-butyne(30 Torr) with H_2(90 Torr) at 80 °C over Sm/THF(0.12 g).

References
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