CHEMISTRY LETTERS, pp. 203 - 204, 1984.

REACTIONS AND CATALYTIC PROPERTIES OF RARE EARTH METALS WITH UNSATURATED COMPOUNDS: SAMARIUM AND YTTERBIUM CATALYSTS FORMED IN LOW-TEMPERATURE MATRICES

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Active samarium and ytterbium catalysts were prepared by dispersing rare earth atoms in frozen organic matrices at -196 °C. They exhibited specific properties for the hydrogenation of ethylene, and buta-1,3-diene in which trans-but-2-ene was selectively formed by 1,4-addition. Enhanced isomerization activity of methylacetylene to allene was also observed.

Much attention has been paid to all the characteristics of rare earth metals and their related compounds. However, very little has been reported on the catalytic properties of these materials. We have found that the rare earth particles formed by clustering metal atoms in frozen organic matrices at -196 °C were catalytically active. Thus this matrix method should be of general applicability of the preparation of catalysts of rare earth metals difficult to reduce, and it is likely that enhanced activity can be obtained for a variety of reactions.

The preparation vessel for the catalyst, containing an organic vapour inlet system, is fitted with a heating part consisting of a spiral-shaped tungsten filament. Tetrahydrofuran (THF) and benzene were used as the substances into which the rare earth atoms were vaporized. In a typical preparation of Sm-THF the reaction zone was evacuated to a pressure of ca. 10^{-6} Torr and was then cooled using liquid nitrogen. The tungsten heater was gradually energized to vaporize samarium atoms (>99.9%) and the inlet needle valve was slowly opened to introduce THF vapour (freshly distilled over a sodium wire) into the system at the same time. High temperature samarium species were brought into contact with THF molecules and simultaneously condensed on the inner cold surfaces of the reactor, resulting in the formation of a dark green Sm-THF matrix. The vessel was allowed to warm to room temperature and the excess THF was pumped off leaving dry active Sm-THF powder.

Some scanning electron micrographs of the rare earth catalysts prepared in this way showed that they were made up from small particles which were individually 15-20 nm in size, which were loosely combined without any preferred orientation, to give a porous structure. The surface area of Sm-THF, as measured by the BET method, was 5.6 m^2/g.

Rare earth-catalyzed reactions have been studied in a circulation reactor. The hydrogenation of carbon-carbon double bonds readily occurred by the samarium catalyst and to a lesser extent by the ytterbium catalyst, but a triple bond could not be reduced. No hydrogenation of acetylene and methylacetylene was detectable up to 100 °C, whereas methylacetylene was rapidly converted into allene at 0 °C. Kokes observes methylacetylene-allene isomerization via a 1,3-hydrogen shift, catalyzed effectively by ZnO$^{1)}$ and, in addition, some bases are similarly available.$^{2)}$ In the hydrogenation of methylacetylene on the catalysts of supported Ni, Pd and Pt, however, nothing has been reported about the isomerization.$^{3)}$ An example using Fe and Co catalysts at 165-200 °C is given.$^{4)}$

Table 1. Hydrogenation of C_2H_4

Catalyst	Evacuation$^{a)}$ temp/°C	Reaction temp/°C	Activity$^{b)}$ k/min^{-1}g^{-1}
Sm-THF	18	82	2.9×10^{-2}
Sm-THF	200	80	2.8×10^{-1}
Sm-Ar-THF$^{c)}$	23	40	2.7×10^{-2}
Sm-Ar-THF$^{c)}$	200	40	6.1×10^{-1}
Sm-benzene	400	18	1.6×10^{-2}

a) 2 h.
b) Catalyst=75 mg, C_2H_4=47 Torr and H_2=88 Torr.
c) The catalysts formed when the rare earth atoms were vaporized in the presence of 10^{-2} Torr of argon onto frozen THF matrices are referred to as Sm(Yb)-Ar-THF.

The hydrogenation activity markedly varied with the evacuation temperatures of the catalysts before each run although it was a function of the nature of the material into which the rare earth atoms were vaporized. When the first-order rate constant k is used as index of the activity, for the hydrogenation of ethylene it increased by over an order of magnitude with change in temperature form 18 to 200 °C (Table 1). Considering the observation that the organic molecules solvated on the rare earth aggregates were cleaved upon pyrolysis with an increase in temperature, this variation in activity may be responsible in part for the extent of exposure of the active sites on the samarium catalysts.

Table 2. Distribution of n-C_4H_8 (%)

	1-C_4	t-C_4	c-C_4
Sm-Ar-THF	15	81	4
Yb-Ar-THF$^{a)}$	19	52	28

a) See c) in Table 1.

Buta-1,3-diene was hydrogenated at 20-64 °C to butenes very selectively and the products were solely n-butene isomers (Table 2). The reaction of diene with D_2 took place over Sm-Ar-THF to give high yields of d_2-products. The fraction of d_2-products was over 92% at 7.6% of the conversion, indicating that the distribution of deuteriated butenes closely resembles that shown by certain non-metal catalysts.$^{5)}$ NMR and mass spectrometry confirmed the formation of trans-but-2-ene-d_2 by 1,4-addition of deuterium.

This note is a preliminary account of work which will be described more fully later.

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(Received November 4, 1983)