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Composite Mechanism of the Catalytic Hydrogenation of Unsaturated Hydrocarbons on Hydrided Magnesium Intermetallides

V. V. Molchanov, V. V. Goidin, and R. A. Buyanov

Boreskov Institute of Catalysis, Siberian Branch, Russian Academy of Sciences, Novosibirsk, 630090 Russia
e-mail: molchanov@catalysis.nsk.su

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Abstract—Two temperature ranges are distinguished in the catalytic hydrogenation of unsaturated hydrocarbons on magnesium intermetallide hydrides. In the lower temperature range, the reaction proceeds by a composite mechanism, as is indicated by the fact that the rate of the catalytic hydrogenation of ethylene, *n*-butenes, and butadiene is equal to the rate of the reduction of these hydrocarbons with hydride hydrogen. It is assumed that, at higher temperatures, the reaction proceeds by a heterogeneous–homogeneous mechanism.

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It has been demonstrated that the oxidation of hydrogen, CO, and hydrocarbons proceeds by a composite mechanism [1]: oxygen of the catalyst is added to the reactant being oxidized, and the active site is then regenerated by gas-phase oxygen. At high temperatures, the oxidation proceeds by a homogeneous–heterogeneous mechanism that includes the formation of radicals on the catalyst surface, the desorption of these radicals from the catalyst surface, and their conversion in the gas phase [1]. Earlier, we assumed that a composite mechanism must also be observed for hydrogenation reactions [2]. Here, we report an experimental verification of this assumption. Hydrogenation mechanisms have not been adequately elucidated in the literature. The purpose of this study is to narrow this gap in knowledge. The studies on the hydrogenation mechanism that are known to us have dealt with metal catalysts. Some descriptions of the reaction mechanism are limited to reaction schemes ignoring the catalyst, as in some publications on the hydrogenation of butadiene over supported platinum catalysts [3, 4]. In other works, the schemes describing the reaction mechanism are based on kinetic data (as in the case of benzene hydrogenation on a nickel catalyst [5]), which cannot be considered to be direct evidence that a composite mechanism takes place. Apparently, the only exception is the works in which the realization of a composite mechanism is proved by isotopic kinetic studies [6, 7]. We do not know any studies dealing with hydrided intermetallides as hydrogenation catalysts.

EXPERIMENTAL

The magnesium intermetallide hydrides Mg_2NiH_4, Mg_2FeH_6, and Mg_2CoH_5 were obtained by the mechanical activation of a mechanical mixture of metals followed by hydriding the activated mixture in an autoclave. The hydriding procedure is described in [3]. The hydride Mg_2NiH_4 and the hydride of the magnesium–copper intermetallide were prepared by the mechanochemical activation of a magnesium–nickel or a magnesium–copper mixture under an elevated hydrogen pressure of 2.5–10.0 MPa.

Mechanochemical activation was carried out in an AGO-12 planetary mill using a stainless steel drum of volume 150 cm^3 with steel balls 5 mm in diameter. The drum was charged with 200 g of balls and 5 g of a stoichiometric mixture of metals. The rotational speed of the drum was 17 rps, causing the balls to move with an angular acceleration of 100 *g*.

The hydrogenation of ethylene, *n*-butenes, and butadiene-1,3 was studied. The catalytic activity of hydrides was studied in a circulating flow reactor. The reactor was charged with 5 g of powdered catalyst with a particle size of several micrometers. This particle size rules out the effect of internal diffusion. The hydrocarbon and hydrogen flow rates were 2 and 10 l/h, respectively. The reaction products were identified by gas chromatography. The chromatographic phase was the triethylene glycol *n*-butyrate supported on diatomaceous earth, and the carrier gas was hydrogen. The products of ethylene hydrogenation were separated on activated alumina with helium as the carrier gas.

The reduction of unsaturated hydrocarbons with hydride hydrogen was carried out in a pulsed differential reactor with an inner diameter of 5 mm, using a 0.3- to 0.4-mm-thick catalyst bed (0.2 g) placed between two quartz layers. The reaction rate was derived from hydrocarbon conversion data. The carrier gas in these experiments was argon. The hydrocarbon pulse size was 0.1 cm^3.

The specific surface area of catalysts was determined by the thermal desorption of argon.

RESULTS AND DISCUSSION

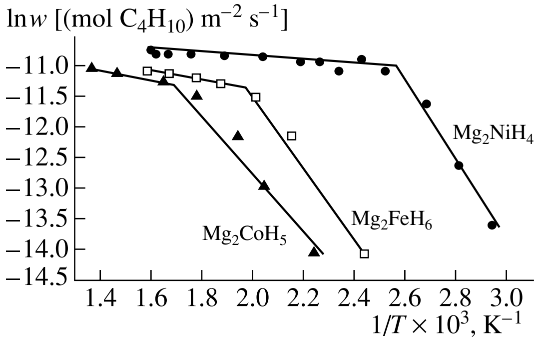
As is noted above, we hold that hydrogenation, like the well-studied oxidation reactions, proceeds by a composite mechanism [2] in which hydrogen is abstracted from the catalyst and is added to the unsaturated hydrocarbon and the stoichiometric composition of the catalyst is then restored through the absorption of gas-phase hydrogen. This composite mechanism of hydrogenation has been verified in part by indirect evidence presented in a few works [8, 9]. In our opinion, the impossibility of comparing the rate of catalytic hydrogenation to the rate of hydrogenation by hydride hydrogen, which was noted by Sobolev and Panov [8], is due to the low mobility of hydrogen in individual metal hydrides. Intermetallide hydrides are free of this drawback. Hydrides prepared via mechanochemical activation are single-phase materials, unlike pyrometallurgical hydrides, whose preparation includes oxidation and reduction treatment. Furthermore, the hydrides of alloys obtained by mechanochemical activation are characterized by a higher hydrogen mobility than the hydrides of pyrometallurgical alloys.

Our investigation of the olefin, acetylene, and butadiene hydrogenation activities of Mg–M (M = Fe, Co, Ni) intermetallide hydrides has revealed two distinct temperature ranges in the temperature dependence of the specific hydrogenation rate. Here, this dependence is plotted for *n*-butenes (figure). Similar dependences are observed for the other hydrocarbons examined.

At lower temperatures, the composite mechanism of catalytic hydrogenation takes place, as is indicated by the coincidence between the rate of catalytic hydrogenation and the rate of the reduction of double bonds by hydride hydrogen (Tables 1–3). This coincidence is convincing evidence that the hydrogenation reactions proceed by a composite mechanism.

The activation energy of hydrogenation in this temperature range is 35–150 kJ/mol, depending on the intermetallide and unsaturated hydrocarbon [10]. At higher temperatures, the activation energy takes much lower values of 4–6 kJ/mol. This dramatic change in activation energy is a clear indication of a crossover to radical and chain radical mechanisms [11]. Note that the low values of activation energy are not due to the effect of external diffusion, since the hydrogenation rate is independent of the circulation rate of the reaction mixture in the reactor. The occurrence of heterogeneous–homogeneous reactions is also suggested by the following findings:

(1) The temperature demarcating the above temperature ranges is equal to the temperature at which the magnesium intermetallide hydride begins to release hydrogen.



Arrhenius plot of the specific rate of *n*-butene hydrogenation in the presence of magnesium intermetallide hydrides.

(2) Methane is among the reaction products. This can be explained by the free-radical decomposition of the long-chain radical $C_4H_9^{\bullet}$ into shorter olefins and the more stable radical methyl, which then adds a hydrogen atom.

Table 1. Rates of the catalytic hydrogenation and reduction of *n*-butenes with metal hydrides

Hydride	T, K	w, (mol C_4H_8) m^{-2} s^{-1}	
		$C_4H_8 + H_2$	$C_4H_8 + Mg_2MH_x$
Mg_2NiH_4	373	2.02×10^{-5}	1.89×10^{-5}
Mg_2FeH_6	473	1.70×10^{-6}	1.96×10^{-6}
Mg_2CoH_5	473	6.63×10^{-6}	6.39×10^{-6}
$MgCuH_2$	473	9.8×10^{-6}	9.03×10^{-6}

Table 2. Rates of the catalytic hydrogenation and reduction of butadiene with metal hydrides

Hydride	T, K	w, (mol C_4H_6) m^{-2} s^{-1}	
		$C_4H_6 + H_2$	$C_4H_6 + Mg_2MH_x$
Mg_2NiH_4	373	1.67×10^{-5}	1.83×10^{-5}
Mg_2FeH_6	473	6.07×10^{-6}	5.96×10^{-6}
Mg_2CoH_5	473	2.23×10^{-6}	2.09×10^{-6}

Table 3. Rates of the catalytic hydrogenation and reduction of ethylene with metal hydrides

Hydride	T, K	w, (mol C_2H_4) m^{-2} s^{-1}	
		$C_2H_4 + H_2$	$C_2H_4 + Mg_2MH_x$
Mg_2NiH_4	373	1.8×10^{-6}	1.8×10^{-5}
Mg_2FeH_6	473	1.9×10^{-7}	2.2×10^{-6}
Mg_2CoH_5	473	4.2×10^{-7}	4.0×10^{-7}
$MgCuH_2$	473	6.7×10^{-7}	6.9×10^{-7}

(3) The hydrocarbon conversion shows an unusual dependence on the volume fraction of catalyst in the reactor: the conversion curve has a plateau or a maximum.

The hypothesis that the hydrogenation of unsaturated hydrocarbons can proceed by either mechanism, depending on the process temperature, appears to be in good agreement with experimental data. The occurrence of heterogeneous–homogeneous reactions would be proved more rigorously if radicals were detected in the reaction products.

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