INFLUENCE OF HYDRIDE PHASE ON HYDROGENATION ACTIVITY OF THE COBALT INERMETALLIC ALLOY

DANULO FATIEIEV, IGOR BYCHKO

L. V. Pisarzhevskii Institute of Physical Chemistry of NAS of Ukraine

This study evaluates the catalytic performance of the Cobalt inermetallic alloy and its hydride phase in the Fischer–Tropsch synthesis. Structural changes upon hydrogen absorption were characterized using X-ray diffraction and electron microscopy. The formation of the hydride phase was shown to significantly enhance hydrogenation kinetics, leading to improved reaction rate and hydrocarbon yield. These results provide valuable insights for the development and optimization of Cobalt inermetallic alloy-based catalysts in Fischer–Tropsch applications.

Keywords: alloy, hydride, carbon monoxide, activity, conversion, intermetallic compounds, hydrocarbons

Cobalt-based alloys are highly effective catalysts for hydrogenation, particularly in converting carbon monoxide (CO) to hydrocarbons via Fischer–Tropsch synthesis. Their catalytic activity, thermal stability, and durability under harsh conditions make them valuable for industrial and energy applications. A key factor in their performance is the formation of hydride phases on the cobalt surface in the hydrogenation, which can alter crystal structure, electronic properties, and surface chemistry, thereby influencing reactant adsorption, reaction pathways, and overall efficiency. The cobalt inermetallic alloy is especially promising due to its rare-earth and transition metal composition, promoting metastable hydride structures with favorable hydrogen transport. Understanding these hydrides is crucial for optimizing catalytic performance and advancing Fischer–Tropsch synthesis, hydrogen storage, and energy conversion technologies.

In the Fischer–Tropsch process, the formation of metal hydrides, such as the hydride of cobalt inermetallic alloy, enhances catalyst performance by increasing hydrogen availability at the reaction interface and improving its mobility through the lattice. This promotes efficient hydrogen transfer to CO-derived intermediates, accelerating hydrocarbon chain growth and enabling better control over product selectivity.

The synthesis of the initial compound was carried out by arc melting with subsequent sintering and annealing at 500 ºC. Cobalt inermetallic alloy absorbed hydrogen at room temperature and a pressure of 10 bar while maintaining the structure of the original matrix. The amount of hydrogen adsorbed was 1.92 mass. %, hydride lattice parameters a = 7.5884(3)Å, dV/V = 22.7%. The hydrogenation reaction of carbon monoxide and carbon dioxide was carried out in flow mode at

a pressure of 1.5 atm, $CO(CO_2)/H_2$ ratio was always kept constant at 1/4, WHSV = 2400 h^{-1} at 200–400 °C. The samples were pre-activated with hydrogen at a temperature of 400 °C for 1 hour [1].

The hydride demonstrated high activity in carbon oxide hydrogenation. Catalytic tests were performed in a fixed-bed flow reactor at temperatures between 250 and 300 °C, pressures of 5–10 atm, and H_2/CO ratios of 3 and 4. At 300 °C and a pressure of 10 atm, the maximum yield of liquid hydrocarbons was achieved. CO conversion over the hydride is an order of magnitude higher compared to the intermetallic compound, whereas the difference in CO_2 hydrogenation activity was less pronounced. The catalytic properties of the alloy were also examined after activation in a hydrogen flow at 250 °C and 10 atm, since under these conditions, hydride formation was reported in [1]. The hydrogenation results after hydrogen activation were similar to those observed for the hydride, indicating that hydride formation had occurred.

The intermetallic compound demonstrated catalytic performance comparable to that of an industrial cobalt-based catalyst evaluated under analogous conditions [2]. Catalyst stability tests conducted over a 24-hour time-on-stream (TOS) period at 300 °C, 10 atm, and an H_2/CO ratio of 4 revealed that activity stabilized within 3–4 hours of operation. In CO_2 hydrogenation, methane was identified as the primary product, accompanied by minor quantities of C_2–C_4 hydrocarbons. An increase in the H_2/CO ratio above 4 led to a predominant rise in methane formation.

The obtained results confirm the effectiveness of the catalysts for targeted conversion with high product quality. Both catalysts demonstrated activity in CO and CO_2 hydrogenation, with the hydride of cobalt inermetallic alloy exhibiting enhanced activity and selectivity compared to the alloy. This improvement is attributed to its superior hydrogen activation capability and increased surface chemical reactivity, which facilitate more efficient adsorption and dissociation of hydrogen molecules. A promising aspect of using metal hydrides is the significantly reduced formation of carbides and the extended lifetime of the catalyst.

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