



The role of RWGS in the dehydrogenation of ethylbenzene to styrene in CO₂

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ABSTRACT

The addition of CO₂ to the dehydrogenation of ethylbenzene (EB) to styrene over promoted and unpromoted vanadia, iron, and chromia catalysts on alumina improves the yield of styrene, in comparison with the use of N₂ as diluent. Depending on the catalyst, EB conversion increases 5–10%, while selectivity does not change significantly. The potassium promoted vanadium catalyst shows the highest CO₂ conversion for dehydrogenation with the largest increase in EB conversion. The activity of these catalysts in the reverse water–gas–shift (RWGS) reaction, in the presence and absence of the dehydrogenation, is very different. Vanadium catalysts exhibit the lowest CO₂ RWGS activity. The presence of coke on the catalyst suppresses the RWGS reaction over chromium and iron catalysts, but improves the activity of the vanadium catalyst. This is attributed to hydrogen spill-over from the coke to the metal catalyst. A two-step mechanism with a hydrogen spill-over is proposed for the EB dehydrogenation in CO₂. Step-response experiments show that the redox mechanism for the RWGS and the two-step pathway for dehydrogenation in CO₂ are the dominant routes. A slight RWGS activity of the bare alumina support is attributed to an associative mechanism.

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1. Introduction

The dehydrogenation of ethylbenzene to styrene with CO₂ is an alternative process option for the styrene production. It has several advantages over the normal production route via the steam-aided dehydrogenation. This new process has an improved conversion, higher selectivity, is safer, and is less energy consuming [1–6].

The steam-aided dehydrogenation process is responsible for about 85% of the worldwide production of styrene. This process uses a potassium promoted iron oxide catalyst and requires a high molar ratio of steam to ethylbenzene of 7–10. Steam is an essential part of the process. Several functions have been attributed to H₂O in the process [7,8]:

- provides the energy for the endothermic dehydrogenation reaction (125 kJ/mol at 600 °C);
- acts as a diluent, improving the equilibrium conversion of the reaction;
- brings the catalyst to the right active oxidation state;
- cleans the catalyst from coke deposits by coke gasification; and

- provides easy separation of diluent and product stream.

Carbon dioxide is believed to act in a similar way, with some additional advantages. Its heat capacity is higher, requiring less diluent from an energetic point of view. Under the dehydrogenation conditions, CO₂ is considered to be a mild oxidant like steam and is able to re-oxidize the catalyst. It is claimed that coke can be removed by the reverse Boudouard reaction. Carbon dioxide is a permanent gas, making the separation of the product stream easier. And most importantly, CO₂ can react with the formed H₂ via the reverse water–gas–shift (RWGS) reaction and, thereby, shifting the equilibrium conversion to higher values [1–6].

The RWGS reaction is a mildly endothermic reaction (36 kJ/mol at 600 °C) and makes the process more endothermic, but the increased conversion per pass easily makes up for those additional costs [2]. The RWGS reaction and its counterpart, the water–gas–shift (WGS) reaction, are well known and widely practiced. The WGS reaction is used in hydrogen production e.g. for the ammonia production, the methanol synthesis, and the Fischer-Tropsch synthesis. For the WGS reaction there is a high temperature and a low temperature process with different catalysts. The low temperature WGS process (210–240 °C) is most favorable for H₂ production, a copper based catalyst (Cu/ZnO/Al₂O₃) is used here [9]. A low temperature does not always match with the desired process conditions, and as copper is not stable at high temperatures another

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