Applied Catalysis A: General 423–424 (2012) 59–68

Contents lists available at SciVerse ScienceDirect

Applied Catalysis A: General

journal homepage: www.elsevier.com/locate/apcata

The role of RWGS in the dehydrogenation of ethylbenzene to styrene in CO_2

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ARTICLE INFO

Article history:
Received 6 January 2012
Accepted 15 February 2012
Available online 23 February 2012

Keywords:
Heterogeneous catalysis
Reverse water–gas-shift reaction
Ethylbenzene
Styrene
Dehydrogenation
CO_2
Hydrogen spill-over
Coke
Vanadia
Iron
Chromia
Redox mechanism
Associative mechanism

ABSTRACT

The addition of CO_2 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 N_2 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 CO_2 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 CO_2 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 CO_2. Step-response experiments show that the redox mechanism for the RWGS and the two-step pathway for dehydrogenation in CO_2 are the dominant routes. A slight RWGS activity of the bare alumina support is attributed to an associative mechanism.

1. Introduction

The dehydrogenation of ethylbenzene to styrene with CO_2 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 H_2O 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, CO_2 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, CO_2 can react with the formed H_2 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 H_2 production, a copper based catalyst ($Cu/ZnO/Al_2O_3$) 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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doi:10.1016/j.apcata.2012.02.019

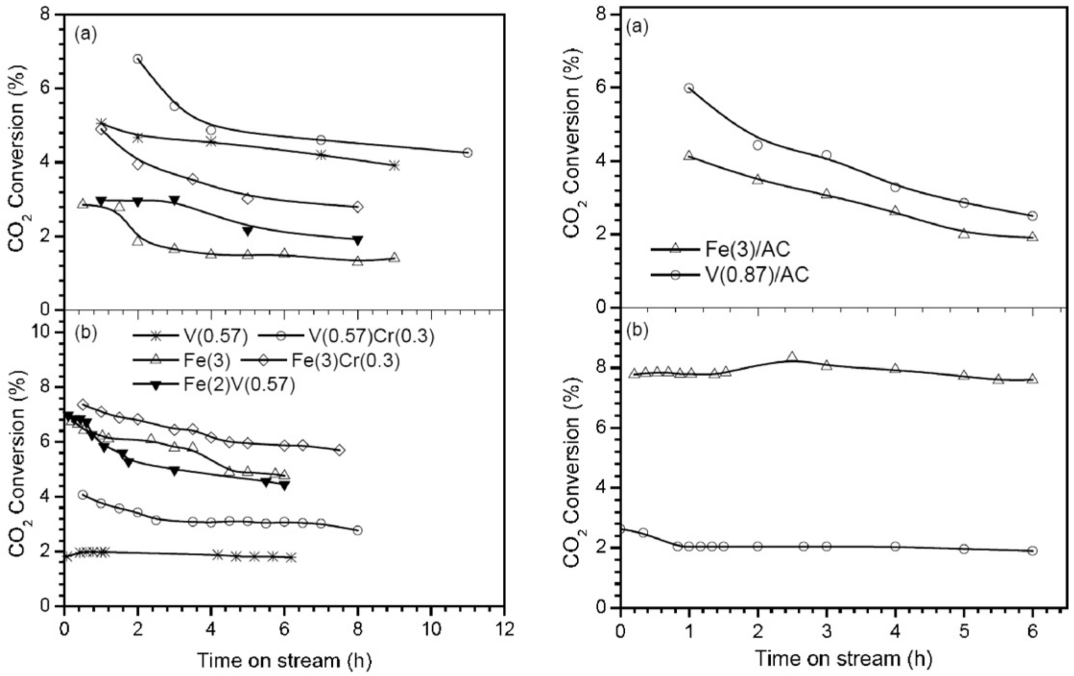

Fig. 1. Comparison of CO_2 conversions in the (*a*) coupled EB dehydrogenation and (*b*) single RWGS for catalysts supported on Al_2O_3 (*left*) and activated carbon (AC) (*right*). RWGS conditions: 550 °C, 0.1 MPa, $CO_2/H_2 = 11$, $W/F = 2.04$ g-cat h/mol. EB dehydrogenation conditions: 550 °C, 0.1 MPa, $CO_2/EB = 11$, $W/F = 4.07$ g-cat h/mol.
The figure is taken from Sun et al. [17].

catalyst is required [10]. The high temperature (300–500 °C) WGS process uses an iron oxide based catalyst (Fe_2O_3/Cr_2O_3), but the conversions are lower because of the equilibrium limitations [9].

The mechanism of (R)WGS can be either an associative or redox type [9]. In the associative mechanism, the reactants adsorb, form an intermediate, break into the products, and desorb [11,12]. The redox mechanism consists of adsorption, reduction of the catalyst by H_2 or CO, and oxidation of the catalyst by CO_2 or H_2O, and desorption [12–16]. In the associative mechanism, CO can only be formed in the presence of hydrogen. With the redox mechanism, the CO production or H_2O production should be observed without the presence of the other reactant.

The dehydrogenation process in CO_2 can be considered as two consecutive reactions: a dehydrogenation (1) followed by the RWGS (2); or as a direct dehydrogenation by CO_2 (3) [2,6,17]. These two variations are comparable to the associative and redox mechanism in (R)WGS. Carbon dioxide will oxidize the catalyst, or form a reactive intermediate. Ethylbenzene, or hydrogen for that matter, will reduce the catalyst, or it reacts with the intermediate species on the catalyst. Both pathways are discussed in literature and both seem to be possible. The two-step pathway, where both hydrogen and CO are produced is most favorable from a thermodynamic point of view and will give the highest theoretical styrene yield.

$$C_8H_{10} \rightleftarrows C_8H_8 + H_2 \tag{1}$$

$$H_2 + CO_2 \rightleftarrows H_2O + CO \tag{2}$$

$$C_8H_{10} + CO_2 \rightleftarrows C_8H_8 + H_2O + CO \tag{3}$$

The role of the RWGS reaction has already been subject of previous research [2,6,17]. However, the RWGS experiments were often done under different reaction conditions, making good comparison with the dehydrogenation results cumbersome. Sun et al. [17]. compared the CO_2 conversions of the different catalysts in the presence and absence of dehydrogenation (Fig. 1). Catalysts, containing iron or chromium, were quite active for the RWGS alone, but the vanadium containing catalysts performed much better in combination with the dehydrogenation reaction. Vanadium catalysts in the dehydrogenation yield higher CO_2 conversions than the iron or chromium catalysts. This was explained by a difference in mechanism for vanadium and other catalysts. Vanadium would follow more the one-step pathway with the involvement of atomic hydrogen; whereas the other catalysts would follow more the two-step pathway with molecular hydrogen (Fig. 2). Conditions in those experiments were not exactly the same for dehydrogenation and RWGS: the contact time was doubled for dehydrogenation experiments, and EB was never completely converted making the amount of hydrogen produced deficient compared to the RWGS reaction conditions. An absolute comparison of the CO_2 conversions is, therefore, extremely difficult [17].

The goal of this study is to investigate the role of the RWGS reaction in the dehydrogenation in CO_2. This systematic study applies the most used catalysts in the dehydrogenation: iron, vanadium, and chromium, supported on alumina; un-promoted and promoted with potassium or magnesium. RWGS experiments are done in the presence and absence of the dehydrogenation under comparable conditions for good comparison. Based on our recent insights into dehydrogenation catalysis [18], also coked catalysts and support are included. Based on the results, the reaction pathway of the dehydrogenation in CO_2 and the mechanism of RWGS is discussed.

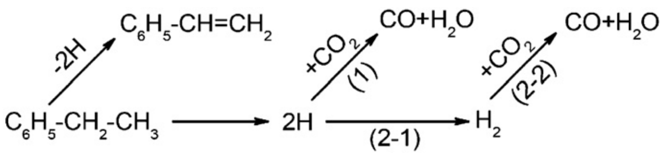

Fig. 2. Role of CO_2 in the coupled EB dehydrogenation in the presence of CO_2. The routes of the one-step (1) and two-step pathways (2-1 / 2-2) are indicated.
The figure is taken from Sun et al. [17].