



Catalysts for the production of styrene from ethylbenzene: Redox and deactivation study

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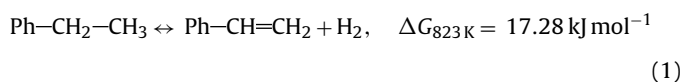
ABSTRACT

In this work, a pulse plant has been used to study the redox properties, activity and coke generation of four catalysts in ethylbenzene dehydrogenation to produce styrene. CO₂ was used as weak oxidant. A physicochemical and structural characterization was carried out in order to verify possible changes in the catalysts after the tests. The experiments consisted of a reduction test with H₂, oxidation with CO₂, reaction with ethylbenzene, regeneration with CO₂ and coke combustion and reoxidation with O₂. These experiments were carried out at three temperatures (450, 500 and 550 °C). With the catalyst that exhibited the best results, MnO₂–ZrO₂, additional experiments with different oxidation states were carried out in order to determine the influence on its activity and redox properties to assess the feasibility of using CO₂ as a regenerating agent during the ethylbenzene dehydrogenation reaction.

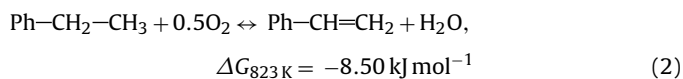
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1. Introduction

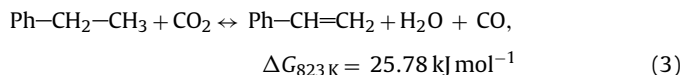
Styrene production by oxidative dehydrogenation in presence of CO₂ has been studied in a significant number of recent works. The reason for such interest is related with the difficulties associated with the currently employed process of styrene production by catalytic dehydrogenation of ethylbenzene: (a) the reaction is highly endothermic (1) and (b) a large volume of steam in the feed to avoid catalyst deactivation by coke is required. This interest is also a consequence of the large quantities of styrene produced worldwide, given that it is among the ten main base chemical products. Several production procedures have been proposed as alternatives to that currently employed in industry [1].



Oxidative dehydrogenation is considered as a promising alternative since the removal of hydrogen by the formation of water converts the global reaction to an exothermic and irreversible one (2).



Unfortunately, as is often found in oxidative dehydrogenation, the formation of carbon oxides appears as an undesired reaction, decreasing the selectivity to olefins. Oxidative dehydrogenation with CO₂ has appeared as an alternative to oxidative dehydrogenation with avoiding the problem of total combustion of the hydrocarbons (3).



Although CO₂ has historically been considered as an inert gas, many recent reports show that it can act as a weak oxidant in reactions such as methane coupling, oxidative dehydrogenation of C₂–C₄ alkanes, oxidative dehydrogenation of alkylbenzene, or aromatization of lower alkanes to benzene, as reviewed by Wang and Zhu [2]. In the oxidation of butane to maleic anhydride, the improvement in selectivity due to the presence of CO₂ has been explained by an increase in the oxidation degree of the catalyst [3]. Focusing on the oxidative dehydrogenation of ethylbenzene, a large variety of catalysts have been tested. Most of them include Fe, V or Cr oxides as active component ([4] and references therein), although supported Mn oxides [5], Sn oxides [6] and Ga oxides [7] have also been employed.

A question that has not been fully solved is the actuation mechanism of CO₂ in the oxidative dehydrogenation reaction. The high performance of catalyst containing vanadium oxides has been explained by a redox mechanism, specifically the Mars–van Krevelen mechanism [8,9]. de Araujo et al. [10] found a Fe⁺²–Fe⁺³ redox cycle in FeCrO_x catalysts, similar to the mechanism proposed by Atanda et al. [11] and Balasamy et al. [12,13]. Sugino et al. [14]

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suggested an oxidative dehydrogenation mechanism. Another factor contributing to the catalyst stability in the presence of CO₂ is the coke formation [15]. Krylov et al. [16] observed that heavy hydrocarbons are subject mainly to oxidative cracking upon interaction with CO₂ over manganese oxide catalysts.

Several catalysts found to be active and selective in literature, which were synthesised and characterized, have been tested using transient studies in a reactor with pulses of either H₂, ethylbenzene, CO₂ or O₂:

- (i) Vanadium oxides are frequently used for ethylbenzene dehydrogenation with CO₂. In the literature, several supports have been tested including active carbon [17], alumina [18–22] and mesoporous materials [23]. Moreover, antimony [18,20] has been proposed as additive.
- (ii) Zirconium oxides have been used in combination with other oxides, i.e. MnO₂ [5], SnO₂ [6] and TiO₂ [24] for ethylbenzene dehydrogenation at temperatures between 550 and 600 °C with high selectivities to styrene.
- (iii) Vanadium-doped titanium mixed oxides (V-TiO₂) were used by Li et al. [25]. These authors proposed a sol–gel method to synthesise the catalysts in order to achieve high vanadium dispersion and, after studying the effect of vanadium loading between 1 and 9 mol% on the catalytic performance, they obtained a maximum value with 6 mol% and high styrene selectivity.
- (iv) TiO₂–ZrO₂ mixed oxides, used as a support, give high specific surface area, good redox properties and high thermal and mechanical stability. Vanadium oxides provide the catalytic activity for the reaction and CeO₂ is well-known as oxygen storage/release material. Thus the combination of both vanadium and cerium was expected to achieve an improvement in the performance of the catalyst. Reddy et al. [4,26] studied the feasibility of the use of V₂O₅–CeO₂/TiO₂–ZrO₂ catalyst for the reaction.

The objective of these experiments was to assess the capability of the catalyst to be reduced by H₂ and then to be oxidized with CO₂ (i.e. to evaluate the redox capability of the catalyst) and also the effect of CO₂ on a catalyst after being employed in ethylbenzene dehydrogenation. The experimental results and the effect of the operating conditions are described and discussed, and the consequences of these results considered in relation to the role of CO₂ in the reaction will be proposed. In addition, these experiments will provide preliminary information to assess the feasibility of using a two-zone fluidized bed reactor [27] as a contacting device to counteract the catalyst deactivation by including a second zone where the catalyst is regenerated with CO₂.

2. Experimental

2.1. Catalyst selection and preparation

After reviewing the literature, the four different catalysts described below were selected from those with the better reported performances. They were synthesised following the authors' recommended procedures.

- (i) In accordance with the procedure described by Chen et al. [21], V₂O₅/Al₂O₃ (1.5 mmol V/g catalyst) was prepared using an incipient wetness impregnation of γ-Al₂O₃ with NH₄VO₃ dissolved in an aqueous solution of oxalic acid during 24 h. Later, the catalyst was dried at 120 °C for 4 h and calcined in air at 550 °C during a further 4 h more.

- (ii) Burri et al. [5] proposed a MnO₂–ZrO₂ binary oxide catalytic system for the effective utilization of CO₂ as an oxidant in the ethylbenzene dehydrogenation to styrene monomer. This catalyst exhibited a conversion of 73% with a selectivity of 98% at 650 °C. The recommended method to prepare MnO₂–ZrO₂ oxides with 10 mol% MnO₂ (0.84 mmol Mn/g catalyst) was coprecipitation. Zirconyl nitrate and manganese nitrate were selected as precursors (stirred at room temperature for 0.5 h) and aqueous ammonia solution was used as a hydrolyzing agent (added until the pH of the solution reached 9). After stirring for 1 h, the solution was aged for 12 h at 100 °C in an oven. The precipitate obtained was filtered under vacuum conditions and washed with distilled water. The solid was dried at 120 °C for 12 h and calcined at 550 °C for 6 h in a muffle furnace.
- (iii) According to Li et al. [25], the synthesis method of V-TiO₂ (1.25 mmol V/g catalyst) consists of several steps. First of all, titanium isopropoxide (Ti(OiPr)₄) was dissolved in ethanol to form Ti sol after which acetylacetone was added as chelating agent. Ammonium metavanadate (NH₄VO₃) was dissolved in 0.25 M oxalic acid and this solution slowly poured into the Ti sol and continuously stirred until the sol turns into a gel. After 7 days aging, the resulting dried gel was calcined in a muffle furnace at 550 °C during 4 h.
- (iv) Reddy et al. [4,26] synthesised V₂O₅–CeO₂/TiO₂–ZrO₂ with several TiO₂:ZrO₂ ratios. The optimum composition was TiO₂–ZrO₂ (1:1 molar ratio), CeO₂–ZrO₂ (7.5 wt.% + 7.5 wt.%) and 0.84 mmol V/g catalyst. TiO₂–ZrO₂ support was prepared using a coprecipitation method from TiCl₄ and ZrOCl₂ aqueous solutions by hydrolysis with ammonium hydroxide. Precursors were added under stirring until the pH reaches a value between 7 and 8. Later, the solution was aged hydrothermally during 12 h at 100 °C and then the precipitate was filtered under pressure and washed with deionized water. The obtained cake was dried at 120 °C and finally calcined at 550 °C for 6 h in a muffle furnace. The solid obtained was used as a support and an amount of CeO₂ (7.5 wt.%) and V₂O₅ (7.5 wt.%) was calculated to be deposited over the support by means of standard wet impregnation. The precursors used were ammonium metavanadate (NH₄VO₃) and ceria ammonium nitrate (CeH₈N₈O₁₈) which were dissolved in deionized water. The support was added under stirring. The excess water was removed by heating at 120 °C for 12 h. Finally, the solid obtained was calcined during 6 h at 550 °C in a muffle furnace.

2.2. Catalyst characterization

The samples were characterized after completing all the steps of the transient study at every temperature.

Specific BET surface areas of fresh samples and samples after reaction were obtained by static N₂ adsorption measurements using TriStar 3000 (V6.08 A) equipment on previously degassed samples. The degasification was carried out in two stages: the first at a heating rate of 10 °C min⁻¹ until 90 °C, maintaining this temperature during 1 h, and the second at a heating rate of 10 °C min⁻¹ until 200 °C, maintaining the temperature for 8 h.

XRD patterns were obtained using a Rigaku/Max System diffractometer Cu (Model D/max 2500) equipped with a graphite monochromator. The step size was 0.03° with 2θ scanning from 5° to 80°.

In order to know the redox capacity of the catalysts, the activity and distribution of the products in reaction, and the coke formation and regeneration, a pulse plant was designed and built (Fig. 1). This plant consists of four mass flow controllers (Alicat Scientific) to introduce the necessary gases into the system. Two helium controllers (one for the carrier and the other for diluting the other gases or sweeping the ethylbenzene at a partial pressure according to the

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