

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

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### Introduction

Catalytic dehydrogenation of ethylbenzene [1] is the most representative process to obtain styrene, which is an important monomer to synthesize several polymers. However, the high endothermicity of the reaction ( $\Delta H_{298}^{\circ} = 28.1$  kcal/mol) and the coke formation are the problems encountered in ethylbenzene dehydrogenation. As alternative, the oxidative dehydrogenation was proposed in order to realize an exothermic reaction and shift completely the equilibrium towards the product formation and to carry out the reaction at lower temperature. Among the oxidant proposed, it has been demonstrated that in the dehydrogenation of ethylbenzene  $\text{CO}_2$  plays as a soft oxidant resulting in the enhanced activity and selectivity [2].

### Experimental

After a literature review, four catalysts were synthesized following the authors' recipes:  $\text{V}_2\text{O}_5/\text{Al}_2\text{O}_3$  [3],  $\text{MnO}_2\text{-ZrO}_2$  [4], Vanadium-doped titanium mixed oxide ( $\text{V-TiO}_2$ ) [5] and  $\text{V}_2\text{O}_5\text{-CeO}_2/\text{TiO}_2\text{-ZrO}_2$  [6]. In order to know the redox capacity, the activity and coke formation, a transient study was made by feeding series of pulses of  $\text{H}_2$ ,  $\text{CO}_2$ , ethylbenzene and  $\text{O}_2$  at three temperatures (450, 500 and 550°C). Products were analyzed by mass spectroscopy. The consumption of all reactants was quantified by comparison with pulses with the same percentage but without reaction. In all cases  $\text{CO}_2$  consumption after 15 pulses was not observed.

### Results/Discussion

In Figure 1, the conversion of ethylbenzene for the catalysts studied at 550°C is shown. It can be observed that  $\text{V}_2\text{O}_5/\text{Al}_2\text{O}_3$  and  $\text{V-TiO}_2$  exhibited high activity in the first pulses but, after 15 pulses, a sharp deactivation took place. It is consistent with the behaviour observed by other authors [3,5] and attributed to coke formation. The addition of  $\text{CeO}_2$  to  $\text{V}_2\text{O}_5/\text{TiO}_2\text{-ZrO}_2$  prevented catalyst deactivation, as it was evidenced in literature [6] but the conversion was lower. However,  $\text{MnO}_2\text{-ZrO}_2$  exhibited both high conversion and low deactivation.

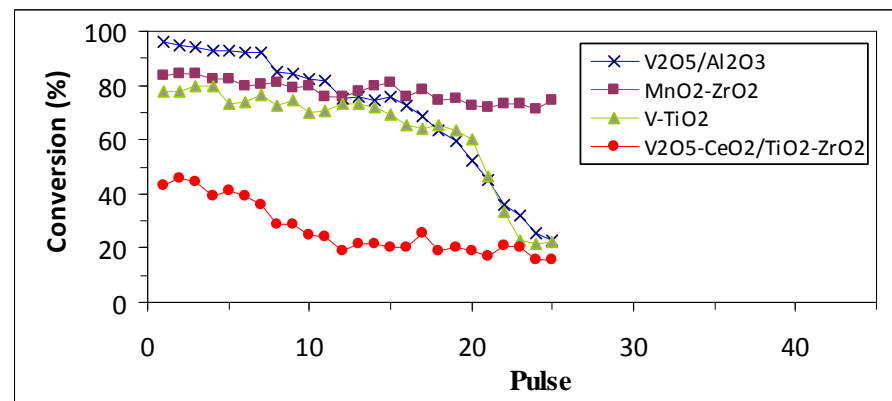


Figure 1. Conversion for every pulse for the catalysts studied at 550°C.

In Table 1, overall coke formed, coke gasified with  $\text{CO}_2$  and percentages of coke gasified at 550°C are presented. It can be seen that  $\text{MnO}_2\text{-ZrO}_2$  is the catalyst with a lower coke formation and, in addition, coke formed on it is removed in a higher proportion by  $\text{CO}_2$  that acts like a soft oxidant by improving both activity and stability.

Table 1. Coke formed and gasified (mg/ g catalyst) at 550°C

|                                  | Catalyst                            |                             |                  |   |
|----------------------------------|-------------------------------------|-----------------------------|------------------|---|
|                                  | $\text{VO}_x/\text{Al}_2\text{O}_3$ | $\text{MnO}_2\text{-ZrO}_2$ | $\text{V-TiO}_2$ | $\text{V}_2\text{O}_5\text{-CeO}_2/\text{TiO}_2\text{-ZrO}_2$ |
| Overall coke formed              | 15.96                               | 2.22                        | 10.10            | 5.40  |
| Coke gasified with $\text{CO}_2$ | 0.48                                | 0.20                        | 0.70             | 0.34  |
| Percentage coke gasified (%)     | 3.0                                 | 9.0                         | 6.9              | 6.3   |

### References.

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