

VO_x/CaO-γAl₂O₃ FOR OXIDATIVE DEHYDROGENATION OF ETHANE TO ETHYLENE UNDER GAS PHASE OXYGEN FREE CONDITIONS

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Abstract

Novel VO_x/CaO-γAl₂O₃ catalysts are developed for ODH of ethane to ethylene under gas phase oxygen free atmosphere. Two catalysts are synthesized with different CaO/γAl₂O₃ ratios keeping vanadium loading at 10 percent. The catalysts show stable reduction and re-oxidation behavior in repeated TPR and TPO cycles, respectively. NH₃-TPD shows that catalyst acidity decreases with increasing the CaO content. The ODH of ethane experiments are conducted in a fluidized CREC Riser Simulator under gas phase oxygen free conditions. Between the two catalysts, VO_x/CaO-γAl₂O₃ (1:1) displays highest ethane conversion (65 %) and ethylene selectivity (85%) and the low CO₂ due to its excellent oxygen carrying capacity, balanced acidity and moderate active site-support interactions.

Keywords

Fluidized ODH, ethane, ethylene, VO_x, CaO, TPD kinetics, active site-support interaction.

Introduction

The conventional steam cracking and catalytic cracking processes for ethylene production are energy intensive and costly. Oxidative dehydrogenation (ODH) can overcome the drawbacks associated with conventional processes [Al-Ghamdi et al. 2013; Afees et al. 2016]. A metal based catalysts can play an important role achieving high ethylene selectivity by minimizing the undesired CO_x formation. The present research is focused on a novel fluidized bed ODH process under gas phase oxygen free conditions (instead used lattice oxygen of the catalysts) to minimize the CO_x formation and to increase the ethylene selectivity. Towards the end, VO_x/CaO-γAl₂O₃ has been investigated as suitable catalysts for gas phase oxygen free ODH of ethane to produce ethylene. CaO was introduced to control both the acidity and oxygen carrying capacity of the catalyst.

Methods

Two catalysts samples were prepared with CaO to γAl₂O₃ weight ratios of 1:4 and 1:1, respectively while

keeping same 10 wt% vanadium loading (VO_x/CaO-γAl₂O₃(1:4), VO_x/CaO-γAl₂O₃(1:1)). The catalysts were prepared by an impregnation method through soaking with excess ethanol as solvent.

TPR-TPO cycles were conducted to determine the catalyst thermal stability and oxygen carrying capacity over repeated redox cycles. NH₃-TPD was used to determine catalysts acidity and acid strengths. The performance of the catalysts for oxidative dehydrogenation of ethane the ethylene under gas phase oxygen free conditions was evaluated in a CREC Riser Simulator under fluidized bed conditions [Elbadawi et al. 2017, Al-Ghamdi et al. 2013].

Results and Discussions

Fig. 1 presents the TPR profiles of VO_x/CaO-γAl₂O₃ (1:1) and VO_x/CaO-γAl₂O₃ (1:4) catalysts. The TPR profiles show that the VO_x/CaO-γAl₂O₃ (1:1) sample has one wide reduction peak between 260-450 °C, while the

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$\text{VO}_x/\text{CaO}-\gamma\text{Al}_2\text{O}_3$ (1:4) sample shows no low temperature peak. On the other hand, both the samples exhibit a major reduction peak between 520-580 °C. While the initial reduction hump can be attributed to the reduction of bulk V_2O_5 -like surface species, the major peak confirmed the presence of monomeric and polymeric VO_x species.

It was observed that in the repeated TPR/TPO cycles, the hydrogen uptake for the samples were stable within 2.5 % error range. This observation indicates that the oxygen carrying capacity of the catalyst remain stable over the repeated redox (TPR/TPO) cycles. Between the two catalysts, $\text{VO}_x/\text{CaO}-\gamma\text{Al}_2\text{O}_3$ (1:1) showed higher oxygen carrying capacity (2.5 mmol/g) than that of $\text{VO}_x/\text{CaO}-\gamma\text{Al}_2\text{O}_3$ (1:4) catalyst (1.8 mmol/g). The total acidity of the catalyst samples, measured by NH_3 -TPD, decreased with increasing the CaO content (basic CaO).

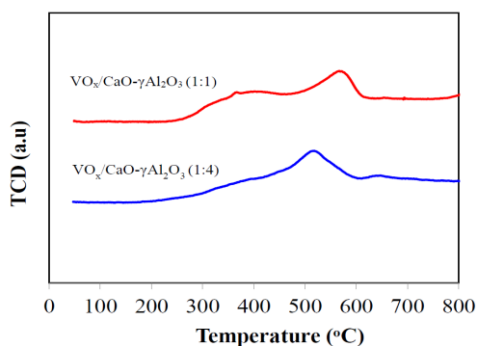


Fig. 1. TPR profiles of $\text{VO}_x/\text{CaO}-\gamma\text{Al}_2\text{O}_3$ catalysts

Fig. 2 (a, b) present ethane conversion and the desired products ethylene and undesired carbon dioxide selectivity at different reaction temperature and constant 10 sec reaction time. One can see that The $\text{VO}_x/\text{CaO}-\gamma\text{Al}_2\text{O}_3$ (1:4) catalyst sample gives very low ethane conversion at 500 °C, which is consistent to their reduction behavior as seen in TRP analysis. The $\text{VO}_x/\text{CaO}-\gamma\text{Al}_2\text{O}_3$ (1:4) catalyst sample mainly reduces between 520 and 580 °C. Therefore, only a small fraction of lattice oxygen available for reaction at 500 °C, leading to a low ethane conversion. On the other hand the $\text{VO}_x/\text{CaO}-\gamma\text{Al}_2\text{O}_3$ (1:1) sample show some reduction at low temperatures, which might have contributed to the higher ethane conversions at 500 °C with these two samples. With both the catalysts, ethane conversion increased with the increasing reaction temperature as the lattice oxygen of the catalyst activates at higher temperature (Fig. 1, TPR analysis). Interestingly, with increasing the reaction temperature, both catalysts showed increased ethylene selectivity and decreased carbon dioxide selectivity up to 600 °C (Fig. 2(b)). When the reaction temperature raised above 600 °C, ethylene selectivity started to drop and carbon dioxide selectivity started to increase. The variation in the degree of reduction of the catalyst with reaction temperatures was responsible for the rise in the selectivity of propylene. At higher temperatures, the degree of catalyst reduction increases (Fig. 1, TPR analysis) as a result of the lower binding energy of lattice oxygen. At such higher degrees of reduction of the catalysts, the selective pathway toward ODH is preferred over that for combustion. The good selectivity to ethylene can also be attributed to the

non-formation of larger molecules due to the interaction of the mixed support and the active site of each catalyst. However, the further increase of reaction temperature, helped for complete combustion of ethylene to carbon dioxide. Consequently, ethylene selectivity dropped at 630 °C which was compensated by carbon dioxide. Between the two catalysts, $\text{VO}_x/\text{CaO}-\gamma\text{Al}_2\text{O}_3$ (1:1) shows higher ethylene selectivity and lower carbon dioxide selectivity than those of $\text{VO}_x/\text{CaO}-\gamma\text{Al}_2\text{O}_3$ (1:4) catalyst. The superior ethylene selectivity of the $\text{VO}_x/\text{CaO}-\gamma\text{Al}_2\text{O}_3$ (1:1) is can be attributed to the balanced acidity and moderate level of metal support interaction of $\text{VO}_x/\text{CaO}-\gamma\text{Al}_2\text{O}_3$ (1:1) as depicted in the NH_3 -TPD results.

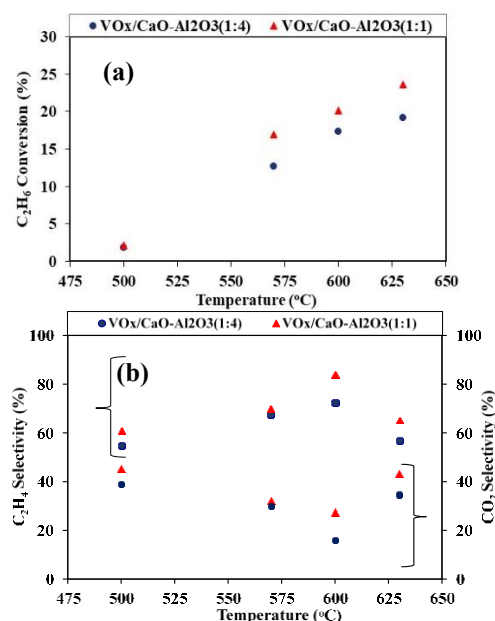


Fig. 2: a. Ethane Conversion b. Ethylene and CO_2 selectivity (Cat.: 0.65 g; C_2H_6 inj.: 1.0 ml, Time: 10s; experimental repeats: ± 3.1 % standard deviation)

Acknowledgments

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References

- Elbadawi, A.W.H., Khan, M.Y., Quddus, M.R., Razzak, S.A., Hossain, M.M. (2017), Kinetics of oxidative cracking of n-hexane to olefins over $\text{VO}_x/\text{Ce}-\text{Al}_2\text{O}_3$ under gas phase oxygen-free environment, *AIChE J.* 63, 130.
- Afees, A.A., Bakare, I.A., Binous, H., Al-Ghamdi, S., Razzak, S.A., Hossain, M.M. (2016), Oxidative dehydrogenation of propane to propylene over $\text{VO}_x/\text{CaO}-\gamma\text{Al}_2\text{O}_3$ using lattice oxygen, *Catal. Sci. Tech.*, 6, 5154.
- Al-Ghamdi S., Volpe M., Hossain M.M., de Lasa I. (2013), $\text{VO}_x/\text{c}-\text{Al}_2\text{O}_3$ Catalyst for Oxidative Dehydrogenation of Ethane to Ethylene Desorption Kinetics and Catalytic Activity, *Appl. Catal.*, 450, 120.