THE INFLUENCE OF OVER-STOICHIOMETRY IN $LA_2NI_{0.9}V_{0.1}O_{4.15+\delta}$ ON SELECTIVE OXIDATIVE DEHYDROGENATION OF PROPANE

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Introduction

The ever increasing demand of propylene can be satisfied *via* dehydrogenation of propane, with limited conversion per pass because of thermodynamic constraints. An alternative way is oxidative dehydrogenation (ODH) of propane with the disadvantage of low selectivity caused by consecutive oxidation.

Another option is to use solid oxides as oxidant. Obviously, the oxide will be reduced when exposed to the hydrocarbons. After exposure to hydrocarbon, the oxide needs to be regenerated via oxidation. This is similar to the classical Mars – Van Krevelen mechanism, except that the oxidation and reduction steps are separated. This separation can be made in *time*, by using either moving bed technology or by switching between exposure to alkane and oxygen, respectively. Alternatively, oxidation and reduction can be separated in *space* by using a dense membrane reactor, performing oxidative conversion of the hydrocarbon at one side of the membrane, combined with diffusion of O^{2-} ions and electrons through the membrane and replenishing oxygen by exposing the other side of the membrane to molecular oxygen.

The goal of this study is to establish quantitatively how the oxygen content of $La_2Ni_{0.9}V_{0.1}O_{4.15+\delta}$, *i.e.* the value of δ, determines the reactivity with propane and the resulting selectivity pattern. This material was selected because of the relatively high oxygen permeability at relatively low temperature [1,2], which would be important for selective oxidation in a membrane reactor.

Experimental

The catalyst was prepared via sol-gel method using EDTA as chelating agent. The appropriate amount of V_2O_5 (Merck) was dissolved in diluted HNO_3 (Merck) at 80°C under stirring for 1h. A stoichiometric amount of $La(NO_3)_3*6H_2O$ (Merck), $Ni(NO_3)_2*6H_2O$ (Merck), EDTA and NH_4OH solutions were added and the obtained solution was heated for 2 hours under stirring. After drying at 230 °C, foam-type material was formed and pyrolysis took place after spontaneous ignition. The resulting solid mixed metal oxide was milled and calcined in air at 1050°C. The resulting material was ball milled, sieved and particles of 0.1 - 0.3 mm (2.0 m^2/g) were used for all experiments. The material was characterized with XRD, TPR and TGA.

The reactivity of the oxide with propane was tested with pulse experiments in home built equipment, using pulses of 600 µl containing 10% propane. The product mixture was analysed with MS.

Results/Discussion

The oxidation state of the oxide (δ) was modified via either the pretreatment, reduction with pulses with hydrogen, reduction with pulses propane or partial re-oxidation treatment with pulses of oxygen. The key result is presented in figure 1.

The reactivity of $La_2Ni_{0.9}V_{0.1}O_{4.15+\delta}$ with propane at 550 °C strongly depends on δ. When $\delta > 0.03$ the main product is CO_2, whereas selective conversion to propylene, ethylene and methane is achieved when $0.00 < \delta < 0.03$. Furthermore, oxidation-reduction cycles in propane and oxygen at 550 °C are reversible and the material is stable. Therefore, based on its chemical properties $La_2Ni_{0.9}V_{0.1}O_{4.15+\delta}$ is a promising option for selective oxidative dehydrogenation of propane with a dense membrane reactor, provided that the degree of over-stoichiometry is limited to 0.03 at the surface exposed to propane.
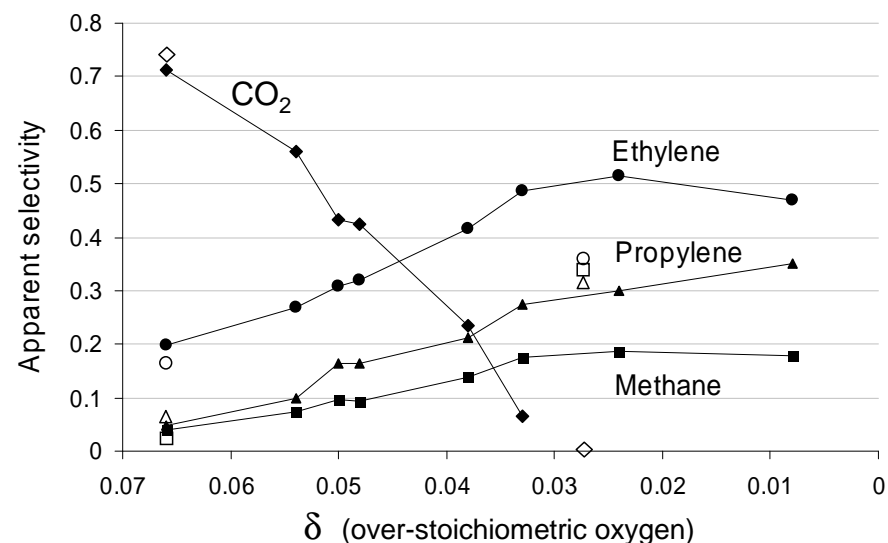

Fig. 1: Apparent selectivities of methane (■, □), ethylene (●, ○), propylene (▲, △) and CO_2 (◆, ◇) during the pulse test at 550 °C on fresh $La_2Ni_{0.9}V_{0.1}O_{4.15+\delta}$ (full symbols), and on re-oxidized $La_2Ni_{0.9}V_{0.1}O_{4.15+\delta}$ (open symbols). The two sets of open symbols represent apparent selectivity of totally ($\delta = 0.066$) and partially ($\delta = 0.028$) re-oxidized catalyst.

References

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