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The effect of V in $La_2Ni_{1-x}V_xO_{4+1.5x+\delta}$ on selective oxidative dehydrogenation of propane: Stabilization of lattice oxygen

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ABSTRACT

In this study, the non-stoichiometric redox compounds $La_2NiO_{4+\delta}$ and $La_2Ni_{0.9}V_{0.1}O_{4.15+\delta}$ have been tested as an oxidant in selective oxidation of propane in pulse experiments at temperatures between 450 and 650 °C. The oxygen contents in the samples at different temperatures were calculated based on back-titration with O_2 pulses as well as on TGA. In the case of $La_2Ni_{0.9}V_{0.1}O_{4.15+\delta}$ over-stoichiometric oxygen was the only active species, responsible for the formation of CO_2, C_3H_6, C_2H_4 and CH_4 while pulsing propane at all investigated temperatures. Contrary, the reactive species in $La_2NiO_{4+\delta}$ changed from over-stoichiometric oxygen only at 450 °C, to both over-stoichiometric and lattice oxygen at 550 °C, to lattice oxygen only at 650 °C. The activation of lattice oxygen and the consequent formation of Ni metal were detrimental for selectivity to propylene as formation of CO_x, CH_4 and coke mainly occurred and no olefins were formed.

1. Introduction

The demand for small olefins is growing in the last years. Propylene demand, for example, is expected to rise to 80 million tonnes in 2010 worldwide [1–3]. Nowadays the main industrial routes to propylene production are endothermic reactions such as steam cracking [4], fluid catalytic cracking and catalytic dehydrogenation [5]. Promising production of alkenes is achieved by catalytic dehydrogenation but this reaction is equilibrium limited and it suffers from catalyst deactivation due to coke deposition [6]. Oxidative dehydrogenation (ODH) employing molecular oxygen or oxygen containing compounds, i.e. CO_2 and N_2O, as oxidant, can overcome these limitations [7,8]. On the other hand, the possible presence of highly reactive propyl and oxygen radicals in gas phase in addition to adsorbed oxygen species on the catalyst surface can further oxidize the products to CO_x. Deep oxidation can in principle also be suppressed using a catalytic dense membrane reactor (CDMR), acting as supplier of oxygen ions to drive oxidative dehydrogenation of propane. In CDMR, the membrane acts as physical separator between propane (reaction side) and molecular oxygen (regeneration side). As the reaction side is depleted in oxygen due to reaction with the alkane, membrane regeneration is required, occurring *via* ionic permeation of O^{2-} ions through the mixed conducting dense membrane, which are generated at regeneration side interface. By matching the conversion and oxygen permeation rates, oxygen recombination at the alkane side can be prevented and alkane oxidation may proceed *via* oxygen lattice ions exclusively.

Several perovskite-like materials have been investigated as CDMR [9–11] because they possess structural defects, i.e. vacancies, as observed for many redox compounds in the literature [12–14], which are beneficial for oxygen permeation. Among the perovskite-like structures, K_2NiF_4-type of materials like $La_2NiO_{4+\delta}$ are promising because these can host over-stoichiometric oxygen as an additional type of structural defects (indicated with δ in the catalyst nominal composition).

In this work as well as our previous work [15], we studied the suitability of un-doped and V-doped $La_2NiO_{4+\delta}$ for CDMR, applying pulse experiments on powdered samples, revealing activity and selectivity with propane of the oxygen species in the materials. As pulsing with propane induces step-by-step reduction of the oxide and consequent decrease of the activity of remaining oxygen, the possible variation of selectivity with pulses was additionally investigated. In our previous work [15], it was shown that over-stoichiometric and lattice oxygen, which were identified and quantified *via* TPR, possess different reactivitieswards propane at 550 °C. Doping $La_2NiO_{4+\delta}$ with vanadium stabilizes over-stoichiometric oxygen, similarly to what was reported in the literature for Fe and Co as dopants [16,17], broadening the window of the level of reduction in which the catalyst is selective towards propylene at 550 °C [18].

In this study, $La_2NiO_{4+\delta}$ (LN) and $La_2Ni_{0.9}V_{0.1}O_{4.15+\delta}$ (LNV-10) are investigated at temperatures between 450 and 650 °C to test the validity of the conclusions on the difference in reactivity between over-stoichiometric and lattice oxygen towards propane. Variation

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of temperature of operation is very relevant because temperature is the most important variable influencing the oxygen permeability in a CDMR. Obviously, changing temperature would also influence reactivity and selectivity of the relevant oxygen species. It will be confirmed that the presence of vanadium stabilizes the lattice oxygen, inhibiting the formation of Ni metal, which would be detrimental for selectivity towards propylene.

2. Experimental

2.1. Catalyst preparation

LN and LNV-10 were prepared *via* sol–gel method using EDTA as chelating agent [19]. The appropriate amount of V_2O_5 (Merck) was dissolved in diluted HNO_3 (Merck) at 80 °C under stirring for 1 h. A stoichiometric amount of $La(NO_3)_3{\cdot}6H_2O$ (Merck), $Ni(NO_3)_2{\cdot}6H_2O$ (Merck), EDTA and NH_4OH solutions was added and the obtained solution was heated for 2 h under stirring. After drying at 230 °C, foam-type material was formed and pyrolysis took place after spontaneous ignition. The resulting solid mixed metal oxides were milled and calcined in air by slowly increasing temperature (1 °C/min) up to 1050 °C. The resulting materials were finally ball milled in acetone for 5 h and dried at 80 °C. The materials were sieved and particle size of 0.1–0.3 mm was used for all experiments.

2.2. Characterization

Temperature programmed reduction in H_2 (H_2-TPR) of the samples was carried out with a home-built set-up, equipped with a TCD detector. First, 40 mg of sample mixed with 40 mg quartz particles were placed in a reactor with a 4-mm inner diameter and heated in a flow of 5% O_2 in He up to 500 °C (10 °C/min) and kept at 500 °C for 1 h. Then the sample was cooled down to room temperature in the same atmosphere. At room temperature the flow was changed to 5% H_2 in Ar and TPR was carried out with a heating rate of 5 °C/min up to 800 °C. The TCD was calibrated *via* reduction of NiO.

Temperature programmed reduction in C_3H_8 (C_3H_8-TPR) of the samples was carried out in the equipment described above, employing quadrupole mass spectrometer as analyzer (Pfeiffer AG Balzers, OmniStar, equipped with Channeltron and Faraday detectors) to follow the consumption of propane. Preparation of reactor and pre-treatment was identical to the H_2-TPR; at room temperature the flow was changed to 3% C_3H_8 in Ar and TPR was carried out with a heating rate of 10 °C/min up to 800 °C.

Stability of LN and LN-10 under redox treatment was studied with TPR. First the fresh samples were reduced following the procedure described above for H_2-TPR with the only difference that the reduction was performed up to 450 °C. Then, after flushing the reactor with pure He for 15 min at 450 °C, the flow was changed to 5% O_2 in He and the catalyst was re-oxidized for 1 h at 450 °C. The system was cooled down to room temperature under the same atmosphere and flushed with pure He for 15 min. Afterwards TPR was repeated in 5% H_2 in Ar.

Thermal gravimetric analyses (TGAs) of both samples were carried out using a Mettler-Toledo TGA-SDTA 851 unit. The sample (around 55 mg) was placed in a TGA cup and kept at 140 °C for 8 h to remove H_2O and any organic volatile compound adsorbed on the surface. Then the catalyst was heated up to 550 °C and, subsequently, up to 650 °C, with rate of 10 °C/min in Ar flow of 40 ml/min. The weight loss was considered after 30 min of isothermal treatment at 550 °C, mimicking the pre-treatment of pulse experiment. To check the sample stability, the compound was kept at 550 °C for 14 h and the weight loss was considered. Experimental results were corrected for the buoyancy effect using a cup filled with quartz particles with similar volume.

2.3. Titration test

Pulse experiments were carried out in a fix-bed reactor using a 400-mm long quartz tube with an internal diameter of 2 mm, at temperatures between 450 and 650 °C. About 40 mg of catalyst particles were sieved with particle size of 0.1–0.3 mm and packed between two quartz-wool plugs which were approximately 10 mm long. The remaining volume of the reactor was filled up with quartz particles, in order to reduce the void space and minimize gas phase reactions. Before each titration test, the catalysts were pre-treated in 10% of O_2 in He flow (20 ml/min, 30 min) at 720 °C in order to remove any trace of water or inorganic compounds physisorbed on surface and keep the catalyst oxygen level as high as possible. The samples were cooled down to reaction temperature under the same atmosphere, where after the gas flow was changed to He (3 ml/min). After flowing pure He for 30 min, pulses of 300 μl at atmospheric pressure containing 10% C_3H_8 in He were introduced, whereas pulses containing 10% O_2 in He were used to re-oxidize the catalyst, after exposure to C_3H_8 pulses. Re-oxidation resulted in complete regeneration in all experiments in this study; both conversion levels as well as product distributions were completely recovered.

Product distributions were monitored by sampling on-line to a quadrupole mass spectrometer (Pfeiffer AG Balzers, OmniStar) equipped with Channeltron and Faraday detectors (2–200 amu). Prior to each experiment, the fragment pattern of fresh propane and fresh oxygen was recorder and compared with the fragmentation pattern of the produced gas mixture to qualitatively identify the products distribution. Water, propane, oxygen and carbon dioxide were identified monitoring $m/z = 18$, 29 and 32, respectively, since no other products contribute to those m/z signals significantly. To determine presence of methane, ethane, ethylene, propylene and CO_2, two or three m/z signals were monitored for each compound. Because of the similarity in fragmentation patterns and the consequent contribution of several products to the same m/z signal (cross-contamination effect), matrix-type calculation was performed. In this way, formation of CO was also determined *via* $m/z = 28$, although many compounds as propane, ethylene and carbon dioxide contribute to $m/z = 28$. These additional contributions were taken into account and subtracted from $m/z = 28$, resulting in no significant detection of CO. However, formation of small amounts cannot be excluded. The detection of H_2 was unfortunately not reliable. This procedure allows quantitative determination of propane and oxygen conversion only, with an experimental error of about 5%.

As the formation of products could not be quantified, only semi-quantitative comparison of selectivity patterns, called "apparent selectivity", will be reported. The apparent selectivity is based on the integrated area of peaks of the corresponding m/z signals of each compound versus time on stream, divided by total integrated areas of all carbon containing products (e.g. for methane: $A(m/z_{CH_4})/A(m/z_{CH_4}) + A(m/z_{C_2H_6}) + A(m/z_{C_2H_4}) + A(m/z_{C_3H_6}) + A(m/z_{CO}) + A(m/z_{CO_2})$). In case of methane, ethane, ethylene and propylene, which were monitored using two or three m/z signals, only the most intense signal was included in the figures. Obviously, water was not included in the calculation, despite the fact that water was always formed. The conversion of propane at 650 °C was below the detection limit when pulsing propane to the reactor filled with quartz particle exclusively and therefore we can exclude gas phase initiation during the pulse tests.

The amount of oxygen removed from the fresh catalyst during propane pulsing was quantified *via* back-titration with O_2.