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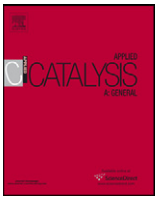

Effect of V in $La_2Ni_xV_{1-x}O_{4+\delta}$ on selective oxidative dehydrogenation of propane

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ABSTRACT

In this study, non-stoichiometric redox compounds such as $La_2NiO_{4+\delta}$, $La_2Ni_{0.95}V_{0.05}O_{4.07+\delta}$ and $La_2Ni_{0.9}V_{0.1}O_{4.15+\delta}$ have been tested as oxidants in selective oxidation of propane, in order to judge the suitability of these materials for a dense membrane reactor for selective propane oxidation. Reducibility of the samples has been investigated using temperature programmed reduction in H_2/Ar flow. The catalysts' activity and selectivity at 550 °C have been investigated employing sequential pulses of diluted propane over the oxides.

Pulsing with propane induces step-by-step reduction of the oxide; consequently, the activity of remaining oxygen decreases with the number of pulses, affecting the products distribution. It is observed that at 550 °C on oxidized catalysts CO_2 and H_2O are the main products and the selectivity towards propylene is very low. At a certain reduction level, obtained after pulse 8 in our experiments, the production of CO_2 stopped without changing the amount of C_3H_6 produced. At this stage, also CH_4 and C_2H_4 are being formed. V-doped catalysts have shown a constant level of C_3H_6 production within a broad window of oxidation degree, while the performance of $La_2NiO_{4+\delta}$, catalyst deteriorated drastically after just a few pulses. CO, CH_4 and coke deposits are formed with $La_2NiO_{4+\delta}$, caused by the formation of metallic Ni. Vanadium is able to prevent this phenomenon, thus drastically broadening the window of selective oxidation of propane.

1. Introduction

Selective oxidation of propane to light olefins is an important research subject since the demand of such olefins is growing. In the last few decades many catalytic systems have been investigated for this reaction including alkali salts [1], metal molybdates [2] and metal vanadates [3]. Promising performance of V/MgO was reported, showing 60% selectivity to olefins at 15% propane conversion employing co-feed of gaseous C_3H_8 and O_2 [4,5]. The major challenge in selective catalytic oxidation of alkanes is the fact that the desired products are more reactive than the alkane reactant, causing domination of total combustion especially at high conversion level.

One effective way to minimize deep oxidation is to avoid the direct contact between products and reactants such as molecular gaseous oxygen. This approach can be used in a moving bed reactor [6] or in a catalytic dense membrane reactor (CDMR) [7]. In the last case, the membrane, as physical separator between products and oxygen, defines two separate compartments, where reaction and regeneration occurs respectively. In case of oxidative dehydrogenation of propane, the reactive side of the membrane is depleted in oxygen. Regeneration of the membrane surface at reaction side occurs *via* ionic permeation (O^{2-} and/or O^-) through the membrane body, originated from oxidation of the membrane with molecular oxygen at the regeneration side. At the same time, to counterbalance the permeation of oxygen ions through the membrane body, migration of electrons in opposite direction occurs. Comparable ionic and electronic permeability rates are required to avoid charge accumulation, slowing down the diffusion of oxygen ions. If the reactivity of the surface oxygen and oxygen permeability are matched, continuous operation of the membrane reactor with high selectivity to olefins can be achieved. This would require tuning of the material composition, temperature as well as concentrations of propane and oxygen.

Suitable materials for this purpose are redox mixed metal oxides with a well organized structure, able to provide oxygen ions for oxidation reactions (Mars – Van Krevelen mechanism). Therefore materials such as perovskite and related compounds have been extensively studied for oxidative dehydrogenation of alkanes in CDMR mode. The ideal perovskite structure, indicated as ABO_3, consists on a cubic arrangement of corner-sharing BO_6 octahedra, where B is a transition metal cation. The A-site ions, located in inter-

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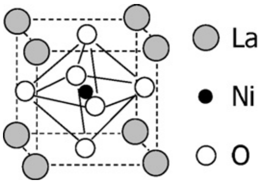

Fig. 1. Schematic representation of perovskite structure.

stitial position between the BO_6 octahedra, are usually occupied by an alkali, alkali earth or rare earth ion [8], as shown in Fig. 1 for $LaNiO_3$.

These materials allow easy redox transformations due to the presence of redox metals (V, Ni, Mo, Bi, Fe). Synthesis conditions, like calcination temperature, partial pressure of oxygen, heating and cooling rate, affect the structure as well as the amount of oxygen in the samples, and consequently the amount of vacant sites.

In the case of $LaNiO_3$, it was shown that under oxidative atmosphere the perovskite structure is stable up to 850 °C [9,10]. Exceeding that temperature, the material reversibly decomposes to NiO and La_2NiO_4, which shows a modified perovskite structure called K_2NiF_4-type structure. In the case of K_2NiF_4 structure, the material possesses a double layer structure: Ni, octahedrally coordinated, is present in the perovskite layer; and La, tetragonally coordinated, is present in a rock-salt layer, as shown in Fig. 2.

Such changes in crystallographic structure obviously influence the thermodynamic activity of oxygen ions in the oxide. In fact, the re-arrangement of the material in the double layer structure enables the formation of "interstitial oxygen" in the inter-layer position. This can bring about oxygen over-stoichiometry. As a result, K_2NiF_4 structure materials have one extra crystallographic type of oxygen ions which might have different thermodynamic activities as compared to strongly bonded lattice oxygen ions. The material is conventionally represented as $La_2NiO_{4+\delta}$, where δ corresponds to the amount of over-stoichiometric interstitial oxygen; Ni^{2+} is partially oxidized to Ni^{3+} in order to compensate for the extra negative charge [11–13].

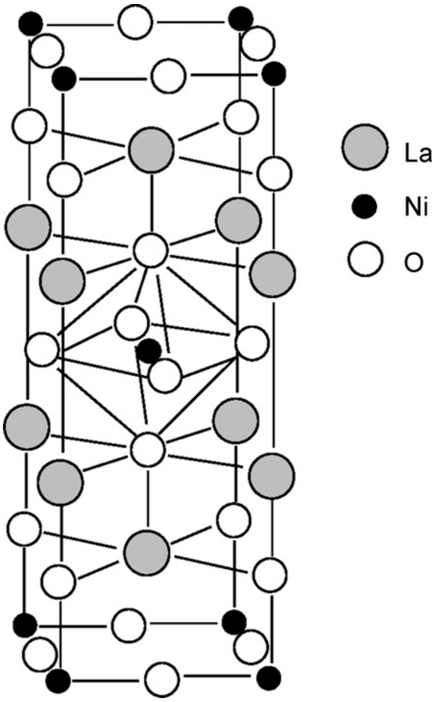

Fig. 2. Schematic representation of K_2NiF_4 structure for La_2NiO_4.

In addition, the chemical and physical properties of K_2NiF_4-type materials can be modified by adding dopants [14]. Structural distortion and variation of activity of oxygen species depend on ionic radius and valency of the dopant [15]. It was reported [16] that structural stability of Eu_2NiO_4 can be increased by adding Sr as dopant. Substitution of Ni^{2+} with V^{5+} in La_2NiO_4 brings extra positive charge to the material, which must be compensated with additional oxygen ions in interstitial positions or in oxygen vacant sites. To the best of our knowledge, the influence of addition of V on the reactivity of O^{2-} ions with propane was not addressed in the literature.

Reactivity of oxygen species can be elucidated from propane pulse experiments. Strictly speaking these are not catalytic experiments; nevertheless, we are using the term catalysts for brevity reasons. During the propane pulses the catalyst provides oxygen ion species to the reaction, increasing the reduction level of the materials with the number of pulses. Oxygen is not present in the gas phase, in contrast to classical co-feed catalytic test with propane and oxygen, and regeneration of the surface sites does not occur during the propane pulses, except for O^{2-} delivery from the bulk of the oxide. The consequent depletion of oxygen active species implies changes in the reactivity of the remaining oxygen species in the catalyst. In this way the influence of the reactivity of the oxygen species on conversion and selectivity can be determined. In addition, reaction pathways which involve gas phase oxygen and adsorbed oxygen are avoided.

In this study the variation of propane conversion and selectivity to olefins as a function of the reduction degree of $La_2Ni_xV_{1-x}O_{4+\delta}$ catalysts is reported. The role of V in enhancing the selectivity towards propylene is discussed.

2. Experimental

2.1. Catalyst preparation

$La_2NiO_{4+\delta}$ (LN), $La_2Ni_{0.95}V_{0.05}O_{4.07+\delta}$ (LNV-05) and $La_2Ni_{0.9}V_{0.1}O_{4.15+\delta}$ (LNV-10) were prepared *via* sol–gel method using EDTA as chelating agent [17]. 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 $La(NO_3)_3{\bullet}6H_2O$ (Merck), $Ni(NO_3)_2{\bullet}6H_2O$ (Merck), EDTA and NH_4OH solutions were 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, 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 particles size of 0.1–0.3 mm was used for all experiments.

2.2. Characterization

The chemical composition of samples were determined by X-ray fluorescence (XRF) using Philips (Panalytical) PW 1480 equipment.

Nitrogen adsorption measurements were carried out at −196 °C with a Micromeritics Tristar system. Prior the adsorption measurements the samples were degassed at 300 °C and 10^{-3} Pa for 24 h. The specific surface areas were calculated according to the Brunauer–Emmet–Teller (BET) method.

The crystal structure of the materials was determined in air with powder X-ray diffraction (XRD) using a Philips PW2050 (X'Pert-APD) diffractometer with Cu K_α radiation ($\lambda = 0.15406$ nm). Data were collected varying 2θ between 5° and 75° with a step size of 0.005° and a step time of 1 s.