*Eleni Heracleous, Angeliki A. Lemonidou*
*Department of Chemical Engineering*
*Aristotle University of Thessaloniki and Chemical Process Engineering Research Institute (CERTH/CPERI)*
*Thessaloniki, Greece*
*lemonido@auth.gr*

# SELECTIVE OXIDATION OF $C_2$- $C_3$ ALKANES TO ALKENES

## USE OF NANOSTRUCTURED OXIDIC CATALYSTS

**Light $C_2$-$C_3$ olefins, ethene and propene, are the keystones of petrochemical industry.** Light olefins are currently produced by steam cracking of various petroleum fractions, but the reactions involved are highly endothermic, and thus the process energy demands are extremely high. So the development of an alternative less expensive method for the production of light olefins

The most attractive alternative to steam cracking, the process mainly used to produce light olefins, is the catalytic dehydrogenation of light alkanes in the presence of an oxidizing agent. The energy requirements are minimal due to the low operation temperature and mild exothermicity of the reaction, while alkanes constitute a low-cost and readily available feedstock, conforming to the general need for sustainable development. Furthermore, the presence of oxygen surmounts the main problems associated with the pure dehydrogenation of alkanes, such as thermodynamic limitations, coking and endothermicity. However, the development of both active and selective catalytic materials for the oxidative dehydrogenation (ODH) of light alkanes proves to be a very hard task, since the formation of carbon oxides is the thermodynamically favored route and the resulting product, alkene, is generally more reactive than the alkane. Viable development of the ODH process requires a catalyst able to activate and selectively convert the alkane to the corresponding alkene at relatively low temperature and also preserve the alkene from secondary oxidation.

The oxidative dehydrogenation of light alkanes has been studied over a wide range of catalytic materials. Most of the catalysts investigated so far are based on supported early-transition metal oxides (V, Mo, Cr), which operate at low temperature (<550 °C) and exhibit high initial olefin selectivity. However, high activity can only be achieved at the expense of alkene production, as these catalysts are as a rule more reactive toward olefins. The reaction proceeds via a Mars and van Krevelen (MVK) mechanism, which involves reduction of the catalyst by the alkane with participation of the lattice oxygen, followed by re-oxidation with oxygen. In the case of ethane ODH, high ethylene yields have been reported over chlorine-promoted non-reducible oxides (e.g. LiCl/MgO), where the reaction proceeds at high temperature (>600 °C) via a homogeneous-heterogeneous reaction scheme. Nonetheless, serious problems, such as low catalyst stability and the release of chlorine, are associated with the use of these catalysts.

Our group at the Laboratory of Petrochemical Technology of the Aristotle University of Thessaloniki has an extensive experience in the field of oxidative dehydrogenation and has performed several studies on transition metal oxides catalysts for the ODH of $C_2$-$C_4$ alkanes. In this communication, we summarize our most recent results in the oxidative dehydrogenation of (a) ethane over highly active and selective Ni-based catalytic systems and (b) propane over supported V-based catalysts. The catalytic performance of the investigated systems is coupled to their structural and physicochemical properties, derived from detailed characterization using a wide range of techniques, leading to fundamental insight in the mechanistic pathway of the catalytic reaction and the nature of the active and selective sites.

## Oxidative dehydrogenation of ethane over Ni-based catalysts

The good performance of nickel-containing materials in ODH was first reported by Schuurman [1]. $Al_2O_3$-supported nickel catalysts were tested in ethane ODH and exhibited very promising results [2]. The promotion of nickel with several metals has a great effect on the ability of the catalysts to both activate the ethane feed and selectively convert it to ethene. However, reports in literature dealing with the nature of the active sites in such materials in correlation with their performance in oxidative dehydrogenation are scarce. In our studies [3], the effect of nickel loading (8-24 wt% Ni) and the impact of promoters (Mo, V, Nb, Ta, Co) on the catalytic performance of a series of $NiO/Al_2O_3$ catalysts were investigated in light of detailed characterization of the physico-chemical properties of the catalysts by $N_2$ adsorption, XRD, XPS, TGA-$H_2$, and UV-DRS. These complementary methods provided valuable insight into the nature of the surface species on the supported catalysts.

Catalytic performance data of the $NiO/Al_2O_3$ catalysts demonstrate that nickel, a low-cost metal, is effective in the activation and selective conversion of ethane to ethylene at temperatures below 450 °C, offering ethylene yields much higher than conventional transition metal catalysts. Moreover, the production principally of $CO_2$ and not CO as the major by-product makes these catalysts very attractive from an engineering point of view, since the separation costs downstream the reactor would be greatly reduced in a potential industrial application of such a process.

Characterization with XRD and XPS [3] shows that nickel interacts strongly with alumina, forming a non-stoichiometric surface nickel aluminate phase. At loading higher than 15 wt% Ni, the alumina surface becomes saturated by a two-dimensional $NiAl_2O_4$-like film, and capping islands of NiO particles with increasing size begin to form atop the nickel/alumina interface. The presence of larger three-dimensional NiO particles on the catalyst surface does not seem to affect the catalytic performance, as ethane conversion increases with increasing Ni loading, with ethylene selectivity maintained at high levels (~90%). This indicates that both nickel aluminate-like species and NiO

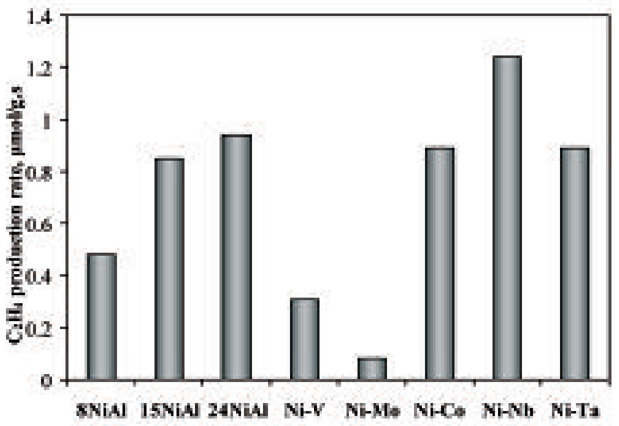

Fig. 1 - Ethene production rate at 400 °C over $NiO/Al_2O_3$ catalysts (W/F=0.54 g·s/$cm^3$, $C_2H_6/O_2$=1/1) in the same image

particles are active and selective. Unsupported NiO was also tested in the reaction and exhibited a similar activity per mole of nickel with the 24NiAl catalyst. However, the selectivity for ethylene was very low, with 90% $CO_2$ production even at low conversion levels. Even though NiO particles on alumina maintain their crystallographic identity (detected by XRD), the XPS results indicate electronic differences and chemical modification of these NiO particles, evidenced by perturbed Ni 2p peak positions for NiO crystallites on 24NiAl compared with that of bulk NiO. These modifications render NiO particles on alumina capable of selectively activating ethane to ethylene and not to $CO_2$.

The introduction of promoters (Mo, V, Co, Nb, Ta) in the Ni/Al system induces significant changes in both ethane activity and selectivity for ethene. The most important feature from a structural perspective is the significant nickel surface enrichment, measured by XPS, following addition of the second metal. With the exception of Mo, the promoters seem to be accommodated between the alumina support and nickel phase. This reduces the strong metal-support interaction, inhibiting the incorporation of nickel into the alumina lattice, and results in a larger number of exposed Ni reaction sites. The most positive effect in the performance of nickel catalysts in ethane ODH was realized by niobium, as shown in Fig. 1 [3].

The addition of Nb mainly influenced the activation step of the reaction, increasing the ethane conversion by over 50%, while maintaining a high selectivity for ethene (10% selectivity drop compared to 24NiAl). The XPS results show that niobium causes a considerable nickel surface enrichment, and the Ni $2p_{3/2}$ binding energy suggests that Nb weakens the strong interaction between nickel and alumina, with nickel existing in almost pure NiO-like form on the surface of the catalyst. Thus, the enhanced activity of the Ni-Nb catalyst in ethane ODH may be related to a highly dispersed pure NiO phase and/or a more facile electron transfer process facilitated by Nb.

Further study of the Nb-promoted catalyst revealed that the unsupported Ni-Nb-O phase actually yields a much-improved catalytic material. We therefore prepared and tested a series of Ni-Nb-O mixed oxides (Nb/Ni=0.11-0.66), which proved to be highly active and selective catalytic materials for the production of ethene via ethane ODH, exhibiting an overall ethylene yield of 46% at 400 °C [4]. In comparison with the equivalent $Al_2O_3$-supported catalyst, the binary Ni-Nb-O mixed oxides exhibit an impressive improvement (160%) in ethene yield. Characterization of the bulk and surface properties of the oxides showed that the key component for this excellent catalytic behavior is the Ni-Nb solid solution formed upon doping NiO with Nb. Even small amounts of niobium effectively convert NiO from a total oxidation catalyst to a very efficient ODH material. Calculation of the NiO lattice constant from the respective XRD patterns showed that up to a Nb/Ni atomic ratio of 0.176, $Nb^{5+}$ ions efficiently substitute $Ni^{2+}$ ions and/or fill the cationic vacancies in the NiO lattice, with higher Nb content leading to saturation of the bulk lattices sites and format-ion of the mixed $NiNb_2O_6$ phase and pure $Nb_2O_5$. These conclusions were further supported by in-depth structural characterization of pure NiO and the Ni-Nb-O mixed oxide catalysts, with high-resolution transmission electron microscopy (HRTEM) coupled with energy dispersive X-ray analysis (EDS) [5]. It was found that low-temperature treatment of pure NiO leads to the formation of a non-stoichiometric oxidic phase with characteristic structural defects due to cationic deficiency. On the Nb-doped oxides (see Fig. 2 [5]), two distinct structural phases, formed via the reaction of the Nb cations with the cationic vacancies, were identified: a NiO phase having Nb cations incorporated in the host lattice, which retains its initial cubic structure (Ni-Nb solid solution), and a highly distorted Nb-rich phase, precursor for the formation of the mixed $NiNb_2O_6$ crystal compound. The reduction of the structural defects in NiO via their interaction with the niobium ions can be correlated to the extremely high selectivity of the Ni-Nb-O catalysts to ethylene, since these vacancies lead to the formation of strong oxidizing electrophilic oxygen species ($O^-$), responsible for the total oxidation of ethane to $CO_2$.

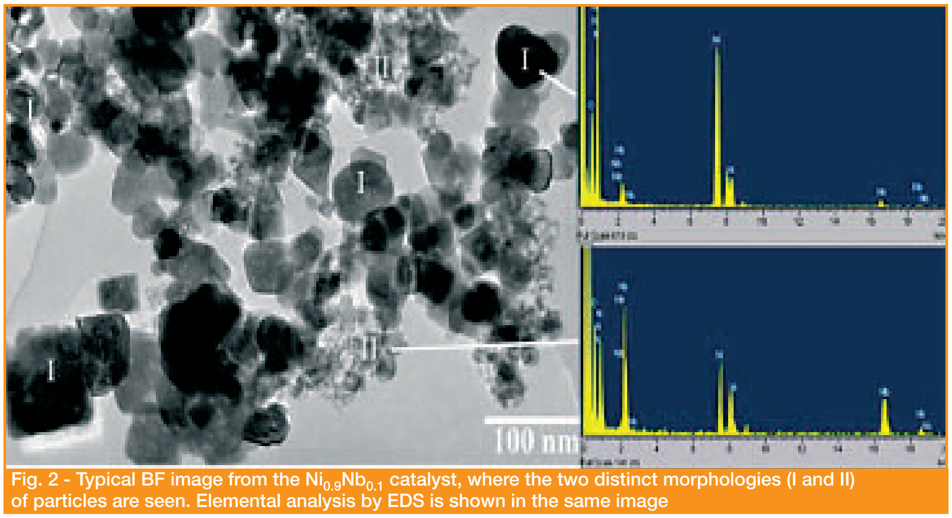

Fig. 2 - Typical BF image from the $Ni_{0.9}Nb_{0.1}$ catalyst, where the two distinct morphologies (I and II) of particles are seen. Elemental analysis by EDS is shown in the same image

To further elucidate the functionality of niobium, $^{18}O_2$-isotopic studies were performed on pure NiO and the $Ni_{0.85}Nb_{0.15}$ catalyst [6]. Niobium doping was found to significantly decrease the activation energy and exchange rate of labeled oxygen, indicating the elimination of non-stoichiometric electrophilic active oxygen species on NiO, responsible for the total oxidation of ethane to $CO_2$, in accordance with the previous results. Although the ethane ODH reaction was found to proceed on both oxides via a MVK mechanism, the route for replenishing surface oxygen differs between the two oxides, leading to different oxygen species on the surface and consequently to the different product distribution observed in the ethane ODH reaction. On NiO, replenishment occurs by rapid dissociation of gaseous oxygen on the cation vacancies with slower incorporation and diffusion, hence leading to large concentrations of electrophilic oxygen species on the surface. Niobium fills the cationic vacancies and reduces the active sites available for dissociation, thus making diffusion the fast step of the process. Therefore, strongly bonded, less labile nucleophilic oxygen species, selective for converting ethane to ethylene, are abundant on the catalyst surface.

## Oxidative dehydrogenation of propane over supported V-based catalysts

The most investigated and promising systems for the oxidative conversion of propane to propene are based on vanadia. The interaction of $VO_x$ species with the supporting material affects the dispersion of these species on the surface and is crucial for the catalytic performance. In general, basic metal oxide supports, such as MgO, strongly interact with $VO_x$, resulting in the formation of a mixed metal oxide, while supports like alumina, zirconia, and titania allow good dispersion of surface $VO_x$ species. Efforts aiming at the structural characterization of supported vanadium oxide on $TiO_2$ and $ZrO_2$ reveal that under dehydrated conditions and at low vanadia loadings vanadium exists as isolated monovanadates, whereas with increasing surface vanadia loading two- and three-dimensional polyvanadate layers are formed, which ultimately crystallize into bulk $V_2O_5$. Despite the great concern in literature, a structure-reactivity/selectivity relationship for the ODH of propane over supported vanadium oxide catalysts still remains under debate. Most of the characterization studies have been focused on the identification of molecular structures of supported vanadia catalysts either under ambient conditions or after pretreatment in $O_2$, $H_2O$, or hydrocarbon flow streams. Our investigations [7] focused on the effect of the specific oxide support ($ZrO_2$, $TiO_2$) and the $VO_x$ surface densities on the molecular structure and catalytic properties of surface vanadia species under propane ODH conditions at temperatures 300-550 °C. In situ Raman spectra obtained under oxygen, propane, and reaction conditions allowed us to obtain useful structural information, contributing to a better understanding of the behavior of these materials.

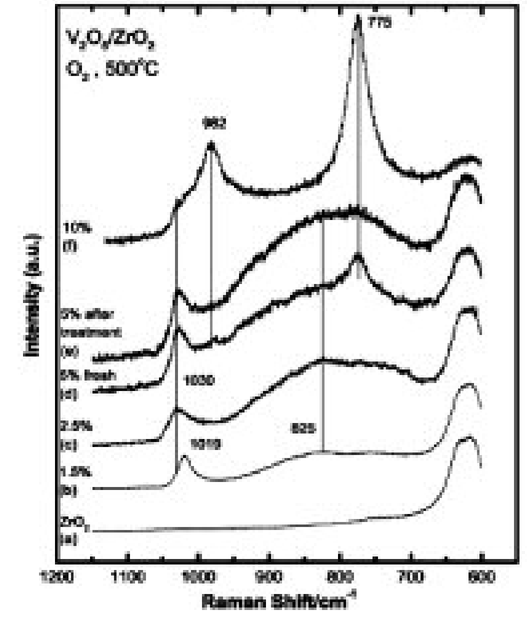

Fig. 3 - In situ Raman spectra of $ZrO_2$-supported $V_2O_5$ catalysts: a) $ZrO_2$; b) 1.5 wt% $V_2O_5/ZrO_2$; c) 2.5 wt% $V_2O_5/ZrO_2$; d) 5 wt% $V_2O_5/ZrO_2$ (fresh); e) 5 wt% $V_2O_5/ZrO_2$ (used); f) 10 wt% $V_2O_5/ZrO_2$

The vanadia catalysts with densities from 1.3 to 22 $VO_x/nm^2$ supported on titania and zirconia exhibit interesting catalytic properties in propane oxidative dehydrogenation. In situ Raman spectra, illustrated in Fig. 3 [7] for $V_2O_5/ZrO_2$, show that the fully oxidized surface at 500 °C consists of two types of $VO_x$ species: monovanadates and polyvanadates depending on the density of $VO_x$. Polyvanadates (along with monovanadates) are formed on $ZrO_2$ even at low $VO_x$ densities (1.3 $VO_x/nm^2$), while on the $TiO_2$ surface monovanadates prevail at low $VO_x$ densities. Furthermore, the polyvanadates formed on $TiO_2$ seem to consist of small chains of V-O-V. For $VO_x$ densities over monolayer (>8 $VO_x/nm^2$) crystalline $V_2O_5$ and $ZrV_2O_7$ are formed on $TiO_2$ and $ZrO_2$, respectively. Under propane flow (reducing conditions), a red-shift of V=O band accompanied by reduced intensities of both monovanadate and polyvanadate bands is observed in the Raman spectra, ascribed to the reduction of $V^{5+}$ centers to lower oxidation and/or to perturbations of V-O bonds caused by neighboring propane molecules. Significantly higher degrees of reduction of $VO_x$ species were observed with the $TiO_2$- than with the $ZrO_2$-supported catalysts. The reactivity studies revealed that under the same reaction conditions oxidative dehydrogena-

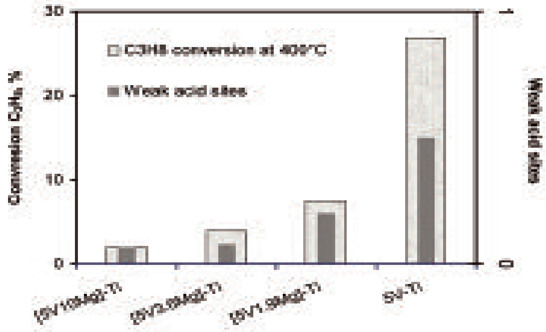

Fig. 4 - Correlation between acidity and ODH activity

tion rates expressed per V atom are functions of the specific support and the $VO_x$ density. $VO_x$ species supported on $TiO_2$ are more active than those supported on $ZrO_2$, showing that the role of V-O-support bonds in the C-H bond activation, the kinetically relevant step, is determinant. The ability of V to activate the C-H bond appears to weaken with increasing vanadia loading for both cases of support materials studied ($ZrO_2$ and $TiO_2$). Formation of polyvanadate domains in catalysts with high vanadia loadings, where the number of V-O-M bonds per V is lowered due to incorporation of vanadium in V-O-V bridges, is accompanied with moderate reduction of their activities.

In an attempt to further improve the good performance of the $V_2O_5/TiO_2$ catalyst, promotion with Mg was investigated. The effect of magnesia loading and preparation procedure of vanadia-on-titania catalysts on the physico-chemical characteristics and the performance in propane oxidative dehydrogenation was studied [8]. A series of magnesia promoted vanadia catalyst (5 wt% $V_2O_5$) with varying amounts of MgO (1.9-10 wt%) were synthesized by synchronous and sequential deposition on titania support and characterized using several techniques (BET, XRD, $H_2$-TPR and $NH_3$-TPD). Both MgO loading and preparation procedure were found to affect the catalyst surface properties and the behavior in the ODH of propane. Magnesia addition resulted in drastic increase in propene selectivity, while the effect on activity was negative. The activity was inversely related with the magnesia loading. Deposition of $V_2O_5$ on previously prepared $MgO/TiO_2$ induced a beneficial effect in the activity of the sample. Acidity was identified as an important factor, with weak acid sites favoring activity in propane. Fig. 4 [8] shows clear correlation between weak acidity, determined by $NH_3$-TPD, and propane conversion.

The catalyst containing 5 wt% $V_2O_5$ and 1.9 wt% MgO prepared by sequential deposition of $V_2O_5$ on already doped with MgO titania exhibited the most interesting results. The reaction mechanism on this material was further explored via transient experiments in a TAP reactor. In particular, the role of lattice oxygen and gas phase oxygen in the oxidative dehydrogenation reaction was investigated. Reaction proceeds via a Mars-van Krevelen redox mechanism, with the exclusive participation of $VO_x$ surface species to the formation of both desired and undesired products, whereas the role of oxygen of the gas phase is only limited to re-oxidation of the reduced catalyst.

## Conclusions

Oxidative dehydrogenation of light alkanes represents an attractive alternative process for the production of $C_2$-$C_3$ olefins, given that an active and selective catalyst can be developed. Recent investigations in AUTH have shown the great potential of nickel-based oxide catalysts for the ODH of ethane to ethene. The developed Ni-Nb-O mixed oxides appear superior to most catalytic systems reported in literature, combining both high activity at low temperature and high ethene selectivity at high conversion levels, with additionally very stable catalytic performance. Their performance competes with ethane steam cracking in terms of ethylene yield per pass (46% vs 48%) at 400 °C lower temperature. Necessity for the further development and implementation of the ethane ODH process is the coupling of the catalyst and ODH reactor design, an aspect that has mostly been neglected, but can offer significant improvement and dynamic for the industrial use of ODH. In the case of propane ODH, an optimized $V_2O_5$-$MgO/TiO_2$ catalyst prepared by sequential deposition of $V_2O_5$ on MgO-doped titania was developed, exhibiting a satisfactory catalytic performance. In general, there is room for improvement in propane ODH and further research efforts are required for the design of a catalytic system with performance good enough to be considered for industrial application.

## References

[1] Y. Schuurman *et al., Appl. Catal. A,* 1997, **163,** 227.
[2] X. Zhang *et al., J. Mol. Catal. A*, 2002, **180,** 293.
[3] E. Heracleous *et al., J. Catal.*, 2005, **231,** 159.
[4] E. Heracleous, A.A. Lemonidou, *J. Catal.*, 2006, **237,** 162.
[5] E. Heracleous *et al., Appl. Catal. A*, 2007, **325,** 220.
[6] E. Heracleous, A.A. Lemonidou, *J. Catal.*, 2006, **237,** 175.
[7] A. Christodoulakis *et al., J. Catal.*, 2004, **222,** 293.
[8] M. Machli, A.A. Lemonidou, *Catal. Letters*, 2005, **99,** 221.