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Life cycle assessment of Ni-alumina and V-alumina catalysts for catalytic oxidative dehydrogenation of ethane

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In this work, the Life Cycle Assessment (LCA) analysis "from the gate to the gate" is used to compare environmental effects of the Ni- or V-alumina catalyst preparation and their use in heterogeneous catalytic oxidative dehydrogenation of ethane (C2-ODH) as the way of ethane production in laboratory conditions. The system boundary was defined as "laboratory production of catalysts and ethylene", the functional unit set up as "one-year production of ethene under specific laboratory conditions". The TRACI methodology and ILCD database, as well as laboratory data, were used in the study. The inputs of the product system were found to be higher for the V-alumina, then for Ni-alumina for resources, deposited goods, radioactive waste, and stockpiles. Results of the Life cycle impact analysis (LCIA) revealed worse environmental impacts for the V-alumina in all evaluated end-points. The V-alumina was more demanding in the view of total emission from the product system to the environmental compartments, as groups of emission to air or categories as Global Warming Potential (GWP), Acidification, Ozone Depletion and Human Health Cancer (HHC) parameters. The LCA analysis of the laboratory catalytic dehydrogenation of ethane has indicated that the Ni-alumina is a better choice in terms of environmental impacts.

Keywords: LCA, Oxidative Dehydrogenation of Ethane, Ni-alumina, V-alumina

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Introduction

An increasingly significant damage and a poor state of the Environment is observed to be a result of industrial activities of human society. There are many approaches aimed at limiting or, at least, mitigating such negative effects including various protective measures. One of the directions used to reduce pollution is the Green chemistry concept. The scope of this approach is based on a postulate introduced by Anastas and Warner: "Green chemistry is the utilisation of a set of principles that reduces or eliminates the use or generation of hazardous substances in the design, manufacture and application of chemical products" [1]. The Green chemistry is the platform involving some instruments for a control of pollution, such as Environmental Management, Environmental Risk Assessment, and Life Cycle Assessment (LCA).

The LCA method defined by international standards ISO 14040 [2] and 14044 [3] is used for description of impacts of technologies and products on the Environment. The LCA studies the environmental aspects and potential impacts of a life of product or whole product systems from a raw material acquisition through the production, use and disposal [4]. The method is also called "from the cradle to the grave". The environmental impacts of products or product systems are assessed based on effects of material and energy flows in categories as resource use, human health, ozone depletion, climate change, etc. [4]. The LCA analysis is, for example, used to analyse the process of the utilization and production of biofuels [5], hybrid, plug-in hybrid, and battery electric vehicles [6], photovoltaic cell [7] etc.

Ethene is a very valuable building block in the petrochemical industry and its production in the Western Europe is expected to grow continually. It has a wide scale of applications in the manufacture of many commercially important chemicals, especially plastics, synthetic lubricants, plasticizers, surfactants for detergents, antifreeze solutions, solvents etc. A percentage of 50–60 % of the total ethene production is consumed to produce polyethylene. Other substances significant in the polymer industry are also derived from ethen; among others, ethylbenzene (styrene) and chloroethene (vinyl chloride) [8–10]. Ethene is currently produced by pyrolysis and as a by-product of catalytic cracking of fractions obtained from distillation of natural gas and oil (catalytic dehydrogenation, steam or fluid-catalytic cracking). The overwhelming majority of ethene comes from the steam cracking of ethane and propane (from natural gas or crude oil) and naphtha or gas from crude oil. These manufacturing processes require large amounts of energy because they are endothermic and having thermodynamic limitations. In the steam cracking process, other products such as CO, H_2, CH_4, C_2H_2 are formed. Separation of by-products from the production of ethene brings additional manufacturing problems and costs [11]. The other technology for production of ethene is the oxidative dehydrogenation of ethane, which is an attractive process for producer and seems to be a very perspective alternative to the steam cracking. The C2-ODH is thermo-dynamically advantageous process because it is an exothermic reaction at a low temperature, when the reaction is not limited by coke formation. In the C2-ODH technology, ethene is produced in one step with less energy consumption. The disadvantage of the C2-ODH method is a small yield of the desired product and a need to clean the product [12–14]. The yield of the C2-ODH reaction can be increased by the use of catalysts, usually up to 20 %. Some superior catalytic systems based on oxides of rare earth elements reach up to 40 %. The Ni-alumina and V-alumina based catalysts are used with a yield up to 30 % [15]. These attractive industrial catalysts can find other use in hydrogenation [16,17], reforming [18], hydrocracking [19] etc.

This work is focused on using the LCA as an auxiliary tool for selecting an environmentally friendly heterogenous catalytic production of ethene. The respective catalytic reaction is assessed with respect to the Ni-alumina or V-alumina catalysts; both offering a high efficiency in the ethene production. Separate problems of Ni- and V-alumina catalysts preparation (impregnation, thermal treatment) and catalytic reaction are also included and discussed. The study is purposed for more ecologic way of how to prepare ethene.

Materials and methods

Materials for preparation of catalysts and C2-ODH reaction

The Ni-alumina catalyst was prepared by impregnation of alumina (9 g, Euro Support, Litvínov, Czech Republic) with an aqueous solution (8.3 g in 70 mL) of nickel nitrate hexahydrate 99 % (Lach-Ner, Neratovice, Czech Republic) [20].

The V-alumina catalyst was prepared by impregnation of alumina (9 g, Euro Support) with an ethanolic solution (5.61 g in 60 mL) of vanadyl acetylacetonate 99.98 % (trace metal basis, Sigma-Aldrich, Steinheim, Germany). The resulting slurry was evaporated to dryness under continuous stirring on an electromagnetic stirrer and left at room temperature overnight. The catalyst was filtered and washed out with redistilled H_2O. Then, the catalyst was granulated to a grain size of 0.25–0.5 mm. In the final step, the catalyst was calcinated in a quartz reactor in an air flow at 500 or 600 °C for 5 hours. Inputs of chemicals and energies for the preparing of catalysts are summarised in Table 1.

The C2-ODH preparation was performed under laboratory conditions with both catalysts according to the same scheme: $C_2H_6 + O_2 \rightarrow C_2H_4 + CO_x + H_2O$. The catalysts were activated before reaction for 1 h at 450 °C in a stream of oxygen. The C2-ODH reaction was carried out in a quartz through-flow microreactor at 500 °C (Ni-alumina catalyst) and 600 °C (V-alumina catalyst) and atmospheric pressure [21]. The total flow of the reaction mixture was in both cases 100 cm^3 min^{-1}.

Table 1 Inputs for preparation of catalysts

	V-alumina	Ni-alumina
Alumina weight [g]	9	9
$Ni(NO_3)_2{\cdot}6H_2O$ weight [g]	–	8.3
$Ni(NO_3)_2{\cdot}6H_2O$ amount [mol]	–	0.028
$VO(C_5H_7O_2)_2$ weight [g]	5.6	–
$VO(C_5H_7O_2)_2$ amount [mol]	0.02	–
H_2O volume [mL]	–	70
C_2H_5OH volume [mL]	60	–
Energy [kWh]	0.4	1.3

The power consumption was measured by Unitec 48415 (Unitec, Hanau, Germany). Inputs and reaction conditions for C2-ODH are summarised in Table 2; the outputs being summarised in Table 3.

Table 2 Inputs and reaction conditions for C2-ODH

	V-alumina	Ni-alumina
Catalyst weight [mg]	31	143.2
Temperature [°C]	600	500
C_2H_6 concentration, input [%, v/v]	7.5	8.0
O_2 concentration on input [%, v/v]	2.5	3.0
The total flow of reaction mixture [$cm^3\ min^{-1}$]	100	100

Table 3 Outputs for C2-ODH

	V-alumina	Ni-alumina
C_2H_6 concentration, output [%, v/v]	6.75	7.2
C_2H_4 concentration, output [%, v/v]	0.5	0.69
O_2 concentration on output [%, v/v]	1.6	2.31
CH_4 concentration on output [%, v/v]	0	0.003
CO concentration on output [%, v/v]	0.44	0.014
CO_2 concentration on output [%, v/v]	0.08	0.2
Catalyst weight [mg]	31	143.2

The LCA study

It includes four phases: (1) the goal and scope definition phase, (2) the inventory analysis phase, (3) the impact assessment phase, and (4) the interpretation phase [4]. In the goal and scope phase, the system boundary was defined as "the laboratory preparation of catalysts and ethene". The study did not cover the whole process of the ethane production; as already stated, it is "from the gate to the gate" study. The system boundary is shown in Figure 1. The goal was to compare the impacts of preparation of ethene with Ni-or V-alumina catalysts sufficient for 1 year production of ethene, therefore the functional unit was set up as "one-year production of ethene under specific laboratory conditions". The reference flow of Ni- alumina was defined as 143.2 mg and the reference flow of V-alumina was defined as 31 mg. A lifetime of both catalysts was estimated to be 5 years. The inventory analysis phase was based on the data measured at laboratory for preparation of specific catalysts and for catalytic reactions. Some date inputs were calculated because they could not be measured. In our product system, recycling or other products except ethene had not been included in the flow scheme, so the allocation was not in use. The diagram of a product system was created. For unit processes, ecovectors from inventory table of our process were compiled. The emissions to air coming from the catalysts preparation of C2-ODH were calculated on the basis of the technological data.

The decision on which product is more environmentally friendly was based on evaluation of the emissions and specific quantification of damages to the environment. This impact assessment phase was carried out with the LCA software GaBi (Thinkstep, Berlin, Germany) with ILCD database using the TRACI methodology. It converts the ecovector to impact categories for describing the influence of the assessed product to specific environmental problems. The TRACI methodology uses end-point indicators as Global Warming Air, Acidification Air, Eutrophication, Ozone Depletion Air, etc. Significant issues found were commented and evaluated.

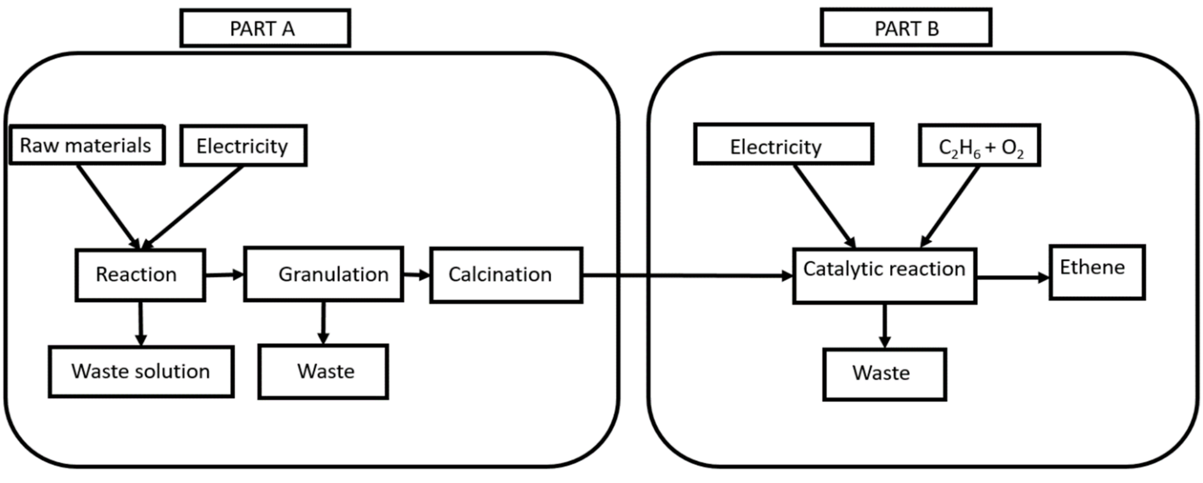

Fig. 1 Diagram of the product system of ethane

Results and discussion

The "from the gate to the gate" study involved the preparation of the catalysts and the production of ethene via the C2-ODH reaction. The model was processed by the GaBi software for the V-alumina and the Ni-alumina catalysts. Inputs and outputs were calculated for 1 year of the laboratory ethene production. The impacts of the ethene production were evaluated and compared together with the effects of the individual parts of the monitored processes for two ethene production systems. In Figure 1, the diagram of the product system of ethene is displayed: in the first step (part A), the catalyst has been prepared by impregnation the alumina with a solution of the appropriate salt. The second step (part B) is the catalytic production of ethene.

For preparation of the catalysts, the temperature (i.e. the amount of energy used) and raw materials are the parameters of a high importance with different impacts to the environment for both catalyst systems. Preparation of the V-alumina was more energy efficient compared to the Ni-alumina one. For the Ni-alumina preparation, water solution was used in contrast of the V-alumina catalyst prepared in ethanol solution. Although the Ni-alumina exhibited a higher consumption of alumina, more significant environmental impacts of the V-alumina catalyser were noticed as revealed in Table 4. All inputs, i.e. resources, deposited goods, stockpile goods, as well as radioactive waste, were found higher for V-alumina.

Table 4 The inputs of the product system of ethylene for 1 year

Inputs [mass kg^{-1}]	V-alumina	Ni-alumina
Resources	$1.42 \cdot 10^6$	$1.11 \cdot 10^6$
Deposited goods	$1.25 \cdot 10^4$	$9.75 \cdot 10^3$
Radioactive waste	2.51	1.96
Stockpile goods	$1.25 \cdot 10^4$	$9.75 \cdot 10^3$

In the study, the next impact categories were observed: Global Warming Air (kg CO_2 equivalent), Acidification Air (kg H^+ moles equivalent), Eutrophication (kg H^+ moles equivalent), Ozone Depletion Air (kg CFC 11 equivalent), Ecotoxicity (PAF m^3 day kg^{-1}), Human Health Cancer Effects and Non Cancer Effects (cases) and Smog Air (kg O_3 equivalent). In Table 5, the results of LCIA of ethene production within 1 year for both catalysts are summarized. Similarly as for resources, all impact categories followed for V-alumina were higher than for Ni-alumina.

Instead of a lot of single specific impact categories, the common environmental impact to the monitored environmental compartments can be evaluated also using summarising categories that are, maybe, more clear for interpretation. Besides Deposited Goods, Table 6 reveals the sum of the total emissions released to air, fresh and sea water, together with those in agriculture and industrial soil with the same result as mentioned above. The more important effect comes from the V-alumina laboratory production. Similarly, the evaluation can also be done using specific categories of air emissions: Heavy Metals, Inorganic Emission, Organic Emissions (group VOC), Other Emission, Particles, Pesticides and Radioactive Emissions to Air with the same results, i.e. the more significant impact of the V-alumina.

One year of continual ethene laboratory (as the functional unit) preparation was evaluated in the terms of LCA. In this model, the lifetime of catalyst being five years was included. For this product system, bigger environmental impacts for V-alumina were detected (Tables 5–7), mainly because of a higher need of energy for the ethene preparation (Table 4).

Table 5 The Life Cycle Impact Analysis for 1year ethene production

Impact category	unit	V-alumina	Ni-alumina
Global Warming Air	kg CO_2 equiv.	1570	1220
Acidification Air	kg H^+ moles equiv.	536	419
Eutrophication	kg N equiv.	0.258	0.202
Ozone Depletion Air	kg CFC 11 equiv.	$8.62\cdot10^{-9}$	$6.70\cdot10^{-9}$
Ecotoxicity Air	PAF m^3 day kg^{-1}	30.1	23.5
Ecotoxicity Soil	PAF m^3 day kg^{-1}	3.48	2.72
Ecotoxicity Water	PAF m^3 day kg^{-1}	23	17.9
Human Health Cancer Air	cases	$3.34\cdot10^{-7}$	$2.60\cdot10^{-7}$
Human Health Cancer Soil	cases	$1.66\cdot10^{-8}$	$1.30\cdot10^{-8}$
Human Health Cancer Water	cases	$5.13\cdot10^{-8}$	$4.01\cdot10^{-8}$
Human Health Criteria Air	kg PM10 equiv.	2.19	1.71
Human Health non Cancer Air	cases	849	664
Human Health non Cancer Soil	cases	$8.62\cdot10^{-6}$	$6.74\cdot10^{-6}$
Human Health non Cancer Water	cases	$2.50\cdot10^{-6}$	$1.95\cdot10^{-6}$
Smog Air	kg O_3 equiv.	90.4	70.7

Table 6 Total emissions from the product system to the environmental compartments

Outputs [mass kg^{-1}]	V-alumina	Ni-alumina
Desposited goods	$1.25{\cdot}10^4$	$9.75{\cdot}10^3$
Emission to air	$1.89{\cdot}10^4$	$1.47{\cdot}10^4$
Emission to fresh water	$1.39{\cdot}10^6$	$1.0{\cdot}10^6$
Emission to sea water	213	165
Emission to agriculture soil	$2.64{\cdot}10^{-4}$	$2.07{\cdot}10^{-4}$
Emission to industrial soil	$2.60{\cdot}10^{-3}$	$2.03{\cdot}10^{-3}$

Table 7 Groups of emissions to air

Outputs [mass kg^{-1}]	V-alumina	Ni-alumina
Heavy metals to air	$2.87{\cdot}10^{-3}$	$2.24{\cdot}10^{-3}$
Inorganic emission to air	$1.20{\cdot}10^4$	$9.39{\cdot}10^3$
Organic emission to air (group VOC)	2.34	1.77
Other emission to air	$6.83{\cdot}10^3$	$5.34{\cdot}10^3$
Particles to air	0.59	0.46
Pesticides to air	$5.68{\cdot}10^{-6}$	$4.43{\cdot}10^{-6}$
Radioactive emissions to air	$3.42{\cdot}10^{-11}$	$2.67{\cdot}10^{-11}$

In the study, the influence of catalysts preparation was assessed as Global Warming Potential, Acidification, Ozone Depletion, Human Health Cancer for Air, Soil and Water (Table 8). The GWP, a midpoint indicator of the contributions of the individual greenhouse gases converted to CO_2 equivalents, was found higher for the ethene production with V-alumina than the process for Ni-alumina. The catalyst preparation has an insignificant effect on GWP in both cases. The same results were shown in the Acidification and Ozone Depletion. Next, other monitored Human Health Cancer impact categories divided into impacts to air, soil and water expressed as a number of new cases of cancer were also observed. Only in the case of HHC Air, the production of ethene with Ni-alumina had higher environmental impacts than with V-alumina. the impact of HHC Soil and HHC Water was for Ni-alumina less than that with V-alumina (see Table 8).

Table 8 Comparison of Environmental inputs of preparing of catalyst and catalytic reaction for product system with V-alumina and Ni-alumina

	V-alumina		Ni-alumina	
	Catalytic reaction	Catalytic preparation	Catalytic reaction	Catalytic preparation
GWP [kg CO_2 equiv.]	$1.57 \cdot 10^{3}$	0.040	$1.22 \cdot 10^{3}$	$2.55 \cdot 10^{-2}$
Acidification [kg H^+ moles equiv.]	536	0.010	419	$8.74 \cdot 10^{-3}$
Ozone Depletion [kg CFC 11 equiv.]	$8.62 \cdot 10^{-9}$	$2.10 \cdot 10^{-13}$	$6.70 \cdot 10^{-9}$	$1.40 \cdot 10^{-12}$
HHC Air [cases]	$3.34 \cdot 10^{-9}$	$8.34 \cdot 10^{-12}$	$2.60 \cdot 10^{-7}$	$5.45 \cdot 10^{-12}$
HHC Soil [cases]	$1.66 \cdot 10^{-8}$	$4.14 \cdot 10^{-13}$	$1.30 \cdot 10^{-8}$	$2.71 \cdot 10^{-13}$
HHC Water [cases]	$5.13 \cdot 10^{-8}$	$1.28 \cdot 10^{-12}$	$4.01 \cdot 10^{-8}$	$8.36 \cdot 10^{-13}$

GWP – Global Warming Potential, HHC – Human Health Cancer

Conclusions

In this work, the environmental impacts of ethene production have been studied using the LCA analysis with the TRACI methodology. The object of interest, ethene, was produced under specific laboratory conditions by the C2-ODH method with two alumina-based (Ni- and V-) catalysts. The influence of the both catalysts has been investigated not for the whole process from "the cradle to the grave", but for the parts in which the respective procedure differed, i.e. from "the gate to the gate". The system boundary was defined as "the laboratory preparation of catalysts and ethene". The functional unit was set up as "one-year production of ethene under specific laboratory conditions".

Practically, all possible evaluations performed in the LCA analysis are in favour of the Ni-alumina catalyst used in the C2-ODH ethene production compared to the process with V-alumina. The use of the Ni-alumina represents the savings in emission and deposited goods. This conclusion has been demonstrated by many values of the impact categories (GWP, Acidification, Ozone Depletion, HHC, etc.). The most important effects came from energies for catalytic reaction because C2-ODH using of the Ni-catalyst is carried out at the temperature less than 100 °C in comparison with the V-catalyst.

Availability of electricity from sources with a lower environmental impact would significantly reduce the environmental load. The influence of raw materials for preparing the catalysts is insignificant because of its long lifetime. On the other hand, the Ni-alumina was more effective in the ethylene production.

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