

DEVELOPMENT OF INORGANIC MEMBRANE REACTORS FOR OXIDATIVE DEHYDROGENATION OF PROPANE AND SELECTIVE OXIDATION OF PROPANE

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Contract JOE3-CT95-0022

PUBLISHABLE FINAL REPORT
(1 January 1996 - 31 December 1998)
NON CONFIDENTIAL

Research funded in part by
THE EUROPEAN COMMISSION
in the framework of the
Non Nuclear Energy Programme
JOULE III

Abstract

The present research programme involves development of inert and catalytic membrane reactors for oxidation of light alkanes mainly focused on propane oxidative dehydrogenation to propene and oxidation of propane to acrylic acid and based on catalytic formulations which consist in a magnesium vanadate oxide (V/VMgO) and vanadium phosphorus oxide VPO.

For the oxidative dehydrogenation of propane to propene, the composition of the surrounding atmosphere does not seem to determine the state of oxidation of the V/VMgO catalyst. However, under HC rich atmosphere (low oxygen concentration), the catalyst is less active but more selective towards propene. An advanced description of the working surface and of the ODHP mechanism has been provided, which ascertains a Mars-van Krevelen mechanism.

In view of their application in membrane reactors, a special method of preparation for a V-Mg-O catalyst was developed. Starting from a mixture of magnesium and vanadium alkoxides, synthesis of a series of V-Mg-O catalyst samples exhibiting relatively high surface areas was developed.

The sol-gel derived infiltrated VPO membranes showed an original gas permeance behavior due to their reversible redox (V^{4+}/V^{5+}) properties. The permeance drastically changes with the oxidative/reducing nature of the permeating gas. Such VPO membranes are potentially attractive to regulate O_2 transport in oxidative reactions. The powder catalysts xV/VMgO derived from metallo-organic precursors revealed original attractive properties (texture, structure and performance) in comparison with those of the "classical" VMgO catalysts derived from salts. These studies help in understanding the VMgO catalyst function in ODHP reaction.

A ceramic membrane reactor has been used as an efficient contactor in the oxidative dehydrogenation of propane (ODH). The composite silica membrane used as a reactant distributor provided an adequate permeation flux and performance. The best configuration involves the feeding of propane and inert gas to the tube side and oxygen to the shell side. The best improvement achieved in the Inert Membrane Reactor (IMR) relative to the Fixed Bed Reactor is around 10 percentage points in selectivity for a given propane conversion. The best propene yield achieved is c.a. 18%. Experiments designed to demonstrate the applicability of the IMR concept to the production of oxygenates from propane have shown that the predominant oxygenated products formed are mixtures of alcohols and aldehydes. Cofeeding of a proportion of the oxygen on the tube side gave an increase in the production of propanol and also more propene.

When properly engineered (suitable diffusion resistance in the support, distribution of catalytic material, feed arrangement), a catalytic membrane with segregated propane and oxygen feeds gives a clearly superior performance in the oxidative dehydrogenation of propane (ODHP), compared to a conventional reactor with a premixed feed. The Catalytic Membrane Reactor (CMR) performed efficiently in the oxidative dehydrogenation of propane. Propene yields above 15% have been obtained. The best results were obtained with mesoporous membranes in which V/Al_2O_3 or V/MgO were the active phases. It has been shown that

reactant segregation is useful to achieve a higher selectivity especially when it is carried out through a support layer of sufficient resistance.

Standard samples of VMgO phases were prepared, characterised and effectively 'fingerprinted' by different physicochemical techniques. A reversibility between the V⁵⁺ and V³⁺ oxidation states during redox cycles was observed by in-situ EXAFS which correlates well with the in-situ electrical conductivity measurements and also with in-situ XRD. By EM studies it was observed that the 14V/VMgO catalyst is a three component system comprising discrete magnesium orthovanadate Mg₃V₂O₈ particles, magnesium oxide and a disordered vanadium containing layer supported on the MgO. When the catalyst is exposed to typical ODHP conditions at 550°C, in-situ EXAFS indicates a change in oxidation state from +5 to +3. Under the same conditions in-situ XRD suggests that Mg₃V₂O₈ transforms to a cubic spinel structure. These changes are reversible on exposure to air at 500°C. HREM shows that the overlayer changes from a disordered to a weakly ordered structure after exposure to normal reaction conditions whilst pure propane induces the formation of a cubic spinel MgV₂O₄ phase in parallel epitaxy with the MgO support. During the course of this project, several new techniques for TEM specimen preparation and HREM image analysis have been developed.

A process flow diagram was established for a commercial plant for an Inert Membrane Reactor (IMR) in the ODH of propane. The basis for the process is a production of 100.000 MTPY of propylene. It is assumed that a 90% selectivity to propene is obtained and that the overall conversion per pass of propane is 65%. In order to optimize the oxidative dehydrogenation of propane as a commercial process, five different cases have been studied. A scheme of the two process flow diagrams used is proposed. The main differences between the cases studied are related to the length of the membrane tubes and to the composition of the shell side stream permeating through the membrane wall. A multitubular reactor configuration immersed in a fluidized sand bath has been adopted for the plant study. The insertion of reaction tubes (fixed bed catalyst inside) and refrigeration tubes (generating 600 psi steam) within a fluid bed shell is the final design.

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Objectives of the project

Two objectives were considered :

1) Development of an inert membrane reactor (IMR) system in which the oxygen/air is supplied by the membrane.

2) Development of a catalytic membrane reactor (CMR) system in which the fine pore structure of the membrane is filled with catalyst and oxygen is transported through the catalyst.

It was expected that when this research programme was concluded a technology package should exist that allows construction of a pilot or demonstration reactor. Construction and operation of such a unit would probably take another 3-4 years whereafter design of industrial units can take place. A similar time scale is expected for the adaptation of the membrane reactor for other oxidation reactions.

The membrane reactor could in principle allow a more efficient contacting :

1) In an inert membrane reactor (IMR) configuration, the membrane would be used to supply oxygen to a fixed bed of catalyst located on the inside of the tube. The membrane in this case would act solely as an oxygen distributor to the bed. The main advantages expected are :

A higher selectivity : as oxygen is to be supplied along the reactor, a lower oxygen partial pressure can be maintained over the catalyst. This should increase selectivity, since total oxidation reactions are favoured at high oxygen partial pressures.

A safer, more controllable reactor : Hot-spots can be avoided or minimized since the reaction is now more evenly distributed throughout the bed. Also, the reactor can be operated outside the explosion limits (and still obtain high conversions with concentrated propane feeds) by lowering the oxygen supply to a safe value.

2) In the catalytic membrane reactor (CMR) configuration, the VMgO or the VPO catalyst would be introduced inside the membrane. This would give a sharp, controllable residence time distribution and, therefore, could in principle be optimized to increase selectivity.

Of main interest for membrane reactors is the combination of two distinct functions reaction and separation into a single operation. The use of membranes in chemical reactors is motivated primarily by the equilibrium shift caused by selective permeation of reaction products, leading to higher conversion or allowing less severe conditions of temperature and pressure. Selective or preferential permeation may prevent further reaction of a product and this may improve the yield of a desired component in a multiple system. On the other hand, the ability to introduce a reactant in a controlled manner through a permeating membrane may allow the regulation of the reaction, leading to better yield and selectivity. The success of high temperature membrane reactors mainly will depend on whether or not highly selective, sufficiently permeable and stable membranes will be manufactured.

Technical description of the project - Results

We have summarized the main results obtained during this contract. They correspond to six tasks :

- Task 1 : Kinetic and mechanistic studies
- Task 2 : Catalyst and process development
- Task 3 : Membrane development
- Task 4a : Inert Membrane Reactor study
- Task 4b : Catalytic Membrane Reactor study
- Task 5 : Characterisation
- Task 6 : Engineering aspects

Task 1 - Kinetic and Mechanistic Studies

Task Manager: Claude Mirodatos (IRC-CNRS, Villeurbanne, France)

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University of Limerick : E. O'Keeffe, A. Sexton.

The aim of this task has been to develop advanced kinetic and mechanistic studies on vanadium magnesium oxide catalysts with a special emphasis on operating conditions (partial pressure and contact time close to the ones expected to prevail in the membrane reactor). The kinetic studies at the exit of the reactor have been performed in the same way as the general kinetic study for the whole reactor. Steady-state isotopic transient kinetic analysis involving carbon and oxygen tracing have been used to measure the mean residence time and the surface accumulation of reacting intermediates under reaction conditions.

The three reporting groups have provided interesting and complementary results from which some general features can be underlined :

- The composition of the surrounding atmosphere does not seem to determine the state of oxidation of the catalyst. However, under HC rich atmosphere (low oxygen concentration), the catalyst is less active but more selective towards propene.

- An advanced description of the working surface and of the ODHP mechanism is provided, which ascertains a Mars-van Krevelen mechanism.

- Three kinetic studies were completed, leading to rate equations which could be used satisfactorily for reactor design. Note however that despite a large effort on mechanistic investigation, the choice between the various kinetic models obtained during that contract remains open. A possible explanation could come from the inherent difficulty to define precisely which kind of catalytic site has to be considered. This would directly be related to the unstable character of the active top layer phase, depending on the operating conditions and the surrounding atmosphere.

Large technical difficulties were encountered for the kinetic and mechanistic study of the partial oxidation of propane to acrolein (no acrylic acid was found to be significantly produced under the prevailing conditions). However, power law rate equations were derived and preliminary mechanistic features were obtained from W/F and in situ DRIFT experiments. Though a complete assignment of IR peaks still needs to be obtained, a clear picture of the surface reactions was attained. From the kinetic study of propane oxidation, it was suggested that the reaction takes place between propane from the gas phase and strongly bound (probably lattice) oxygen on the surface. A series of transient experiments could further elucidate this reaction mechanism, still open to Eley-Rideal or Mars-Van Krevelen options.

Task 2 - Catalyst Development

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IRC, CNRS : J. Volta,

LMPM, CNRS : A. Julbe

The aim of this task has been to modify the physicochemistry of the catalysts considered in this study in order to adapt them to the conditions prevailing in the membrane reactor. This study consisted in the preparation of the VMgO and VPO precursors which were developed by HTAS with further studies by IRC, CNRS. The development of the corresponding catalysts deposited in the pore structure has been performed by LMPM, CNRS.

Two catalyst systems were chosen for the work in this project: magnesia supported magnesium vanadium oxides (V-Mg-O) for the oxidative dehydrogenation of propane, and vanadium phosphates (V-P-O) used in mild oxidation of propane. In view of their application in membrane reactors, the objectives for this

task were to develop applicable preparation and activation procedures producing optimized standard catalysts or catalyst precursors in sufficient amounts. The optimization was mainly done by modification of their physicochemical and mechanical properties.

Standard catalysts of magnesia supported magnesium orthovanadate (V-Mg-O) and vanadium phosphate(s) (V-P-O) were prepared in larger amounts (pilot scale). The catalysts were optimized for their use in membrane reactors in close relation to the work performed in Tasks 1 and 5. Initial characterization of the catalysts revealed that the desired products were obtained. The catalysts were distributed to all partners involved in the project. Thus, the main objectives of this task were reached.

In case of the V-Mg-O catalyst, the combined efforts in detailed characterization and mechanic studies resulted in the identification of the active phase working in oxidative dehydrogenation of propane. This phase consists of a disordered V^{5+} -containing overlayer supported on MgO which under reducing reaction conditions transforms into a weakly ordered cubic spinel type structure. The surface regions of bulk magnesium orthovanadate particles also undergo structural modification under those conditions, decomposing to MgO and MgV_2O_4 . Under oxidizing conditions, the changes are found to be reversible, indicating that the catalyst is working according to a Mars and van Krevelen mechanism.

As to the V-P-O catalyst used in selective oxidation of propane/propene, an appropriate activation procedure was developed for the catalyst precursor. Both a catalyst precursor from DuPont and another one prepared by HTAS according to a recipe by IRC were activated. The addition of water demonstrated to be crucial for the formation of acrylic acid.

Task 3 - Membrane development

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The aim of this task has been to establish a procedure for the development of membranes for inert and catalytic membrane reactors. This has been the main goal of LMPM, CNRS. It has involved a strong cooperation between IRC, CNRS (which contributed to the catalyst know-how) and the Universities of Zaragoza and Limerick (which contributed with their experience on membrane materials). The University of Liverpool was involved for the characterization by Electron Microscopy of both fresh and spent catalytic membranes.

In accordance with the objectives of this task, the involved groups focused on the preparation and characterisation of both inert and catalytically active membranes for respectively IMR and CMR applications. The investigated membrane materials were either mesoporous or microporous and were prepared by salt impregnations, by the sol-gel process or by hydrothermal synthesis.

MFI zeolite microporous membranes with calibrated pores have been prepared, whose permeance is stable with the transmembrane pressure. These ZSM-5 membranes are stable up to 650°C and after 40 heating-

cooling cycles at 500°C. Silica or stabilized alumina mesoporous membranes ($\downarrow_{\text{pores}} > 4$ or 10 nm) have been prepared, whose permeance increases with ΔP . Silica membranes were stable up to 650°C and after more than 200h experiments (heating-cooling cycles). Concerning the membrane "inertia" for ODHP : a small catalytic activity was observed for alumina, silica and MFI zeolite membranes. The propene selectivities were low but higher in case of silica and MFI membranes. Concerning the "O₂ distributor function" a non-selective O₂ transport was observed with these porous membranes at 500°C. The O₂ distributor function can be obtained by controlling ΔP through membranes with a sufficient thickness and with a viscous flow contribution (i.e. with pores > 5 nm). Concerning the "synthesis of the catalytic membranes" the deposition of VMgO and VPO catalysts into the porous network of a ceramic membrane" has been optimised through a strong collaboration.

VMgO membranes with good catalytic performance for ODHP were prepared from salts or from metallo-organic precursors. A better control of the composition but a lower catalyst loading was obtained with metallo-organic precursors.

VPO membranes with low S_{BET} were obtained from salts or metallo-organic precursors. The VPO membranes were not selective for acrylic acid production from C₃H₈. On an other hand, a reversible redox behaviour (V⁴⁺/V⁵⁺) was observed for composite VPO/ α -Al₂O₃ membranes whose permeance was influenced by the oxidative/reducing nature of the permeating gas.

V-MFI membranes (Si/V ~ 160) with reversible redox properties (V⁴⁺/V⁵⁺) have been prepared. Their relatively low performance in ODHP was attributed to the insertion of Al from the support (V-ZSM-5). These membrane are more efficient as contactors than as O₂ distributors.

V-Al₂O₃ membranes (with 3 to 6wt% of V) were prepared in or on supports whose transfer resistance has been modified for improving ODHP performance. The effect of the reactor configuration and parameters affect the catalytic performance of these materials.

Concerning the "reaction and separation functions of the catalytic membranes" :

The C₃H₈ yield in the prepared CMRs was similar to that achieved in IMRs. In the studied conditions, CMRs were not efficiently "capable of doing reaction and separation simultaneously". Anyway, for a given conversion the maximum propene selectivity has been obtained with segregated feeds, except for the V-MFI zeolite membrane.

Original results have been also obtained in this Task :

*The sol-gel derived infiltrated VPO membranes (also incorporating Al from the support) showed an original gas permeance behavior due to their reversible redox (V⁴⁺/V⁵⁺) properties. The permeance drastically changes (up to a factor 10 at 500°C) with the oxidative/reducing nature of the permeating gas. Such VPO membranes are potentially attractive to regulate O₂ transport in oxidative reactions.

*The powder catalysts xV/VMgO derived from metallo-organic precursors revealed original attractive properties (texture, structure and performance) which were specifically studied in Liverpool and Villeurbanne, in comparison with those of the "classical" VMgO catalysts derived from salts. These studies help in understanding the VMgO catalyst function in ODHP reaction.

Task 4a - Inert membrane reactor testing

Task Manager : Julian R.H. Ross (University of Limerick)

List of Task Workers and Affiliation :

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University of Limerick : A.Sexton , E. O’Keeffe and J.R.H. Ross

In this task, inert membrane reactors have been studied under realistic conditions (i.e. under conditions leading to performances in the range of those of conventional (non-membrane) reactors). Factors such as the stability of the membrane materials and of the catalysts have been studied in specific experiments. The stability of the reactor operation, temperature profiles, risk of hot-spot formation have received special care. This work was conducted mainly in the Universities of Zaragoza and Limerick.

A ceramic membrane reactor has been used as an efficient contactor in the oxidative dehydrogenation of propane (ODH). The composite silica membrane used as a reactant distributor provided an adequate permeation flux and performance. The operating conditions required to give an improvement in the selectivity to propene in the Inert Membrane Reactor have been identified. The best configuration involves the feeding of propane and inert gas to the tube side and oxygen to the shell side. The best improvement achieved in the IMR relative to the FBR is around 10 percentage points in selectivity for a given propane conversion. The best propene yield achieved is c.a. 18%. It has been confirmed that improvements of selectivity are related to a lower oxidation degree of the catalyst. Experiments designed to demonstrate the applicability of the IMR concept to the production of oxygenates from propane have shown that the predominant oxygenated products formed are mixtures of alcohols and aldehydes. No acrylic acid was detected. Cofeeding of a proportion of the oxygen on the tube side gave an increase in the production of propanol and also more propene.

Task 4b - Catalytic membrane reactor testing

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This task has concerned the same partners as the previous task : mainly the Universities of Zaragoza and Limerick. The objective of this task was to test the catalytic membranes developed under Task 3, with the reactions of oxidative dehydrogenation of propane to propene (Univ. of Zaragoza and LMPM, CNRS using V/MgO and V/Al₂O₃ membranes), and partial oxidation of propane to acrolein (Univ. of Limerick, using VPO membranes).

The Catalytic Membrane Reactor (CMR) performed efficiently in the oxidative dehydrogenation of propane. Propene yields above 15% have been obtained, and the selectivity at a given conversion using the membrane to segregate oxygen and propane was consistently higher compared to that obtained with conventional feed arrangements. The best results were obtained with mesoporous membranes in which V/Al₂O₃ or V/MgO were the active phases, while the performance of V-MFI membranes was less satisfactory.

The effect of several design variables in catalytic membrane reactors (feed configuration, different degrees of diffusion resistance in the support layer, concentration of catalytic material in the active layer) has been experimentally explored. It has been shown that reactant segregation is useful to achieve a higher selectivity especially when it is carried out through a support layer of sufficient resistance. Also, the results clearly show the importance of preventing the back permeation of hydrocarbons. Several methods can be used to reduce back permeation of the hydrocarbon reactant, of which increasing the convective flow towards the product side is perhaps easiest to implement. The experiments discussed above indicate other possible procedures. On the one hand, the activity of the catalytic layer can be increased by increasing the operating temperature and/or the catalyst loading. On the other, a higher diffusion resistance of the support layer can be obtained by modifying its pore structure. When as in this work, this is done by deposition of pore plugging material, it is necessary to ensure that the new deposits do not contribute appreciably to the reaction.

Task 5 - Structural Characterisation

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The aim of this task has been to describe the vanadium phosphorus oxide catalysts and the vanadium magnesium oxide catalysts in the membrane structure at an atomic level. We have particularly studied the solid state reactions which occur and which change the description of the materials. The influence on the catalysts of the conditions of the reaction occurring in the inert membrane and in the catalytic membrane reactor systems have been examined. The University of Liverpool acted as a central microstructural characterization facility for the other partners.

Before a meaningful analysis of the active VMgO catalyst could be carried out, it was deemed necessary to carry out a detailed structural characterisation of standard specimens of all the known bulk magnesium vanadate phases. These are described in Section 1 of this report. In addition, since the catalyst preparation route adopted involved the calcination of $Mg(OH)_2$, it was also essential to characterise the microstructural development of the MgO phase from brucite, as MgO would be a major constituent of any active catalyst formulation (Section 2).

Based on previous experience of the VMgO catalyst system acquired by Mirodatos (IRC), the 14V/VMgO catalyst was adopted as the 'basis' material by all groups in the programme. This VMgO material has been subjected to rigorous structural analysis using both in-situ and ex-situ characterisation techniques as described in Section 3. These studies have given us new insight into the physical state of the active catalyst. In order to adapt the VMgO catalyst into a form suitable for an active catalytic membrane, Montpellier have developed a novel preparation route for producing VMgO utilising alkoxide precursors. The results of our analyses of these new ex-alkoxide material are outlined in Section 4.

In parallel with the work on VMgO, we have been investigating the possible use of VPO catalysts in the production of acrylic acid from propane. This work involves the activation of $VOHPO_4 \cdot 0.5H_2O$ precursor

material in a propane/air atmosphere. In Section 5 we compare the DuPont (VPD) and HTAS (VPO) materials in the precursor and activated states.

Finally, during the course of this project several new techniques for TEM specimen preparation and HREM image analysis have been developed. These are briefly summarised in Section 6.

Task 6 - Engineering study

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In this task the reactors (inert membrane and catalytic membrane reactors) have been modeled by integrating the kinetic schemes related to the catalytic zone with the hydrodynamics of the reactors. The models have been compared with the experimental data obtained in task 4. On the basis of the reaction modelling, the operating conditions have been optimised. At least this task aimed at providing an estimation of the minimum level of performance required for the membrane reactor to replace existing technologies.

The reaction kinetics of the oxidative dehydrogenation of propane over a V-Mg-O catalyst has been investigated. A Langmuir-Hinshelwood model involving two types of adsorption sites, selectives and nonselectives, predicts the experimental results well. The kinetics of the propene oxidation to carbon oxides has been obtained from the experiments with propene as reactant. The evident inhibition effect of water on the catalyst performance has been included into a Langmuir adsorption constant which affects all reactions involved. Agreement between the kinetics obtained for a fixed bed reactor and the experimental data collected in an inert membrane reactor can be improved through a refinement of the kinetic parameters.

Feedstock pricing affects process profitability significantly. A thorough price volume forecast for pure propane and oxygen has been undertaken for the purpose of this study. An average price of 0.13 \$ / kg C₃H₈ and 0.026 \$ / kg O₂.has been assumed.

Due to the scale of the commercial plant, the propane and oxygen requirements demand a regular supply, which would be guaranteed in any case by means of storage tanks. Rather, the location of the plant has to cover these aspects in order to maintain the propene rate as fixed.

All the factors concerning the production rate and therefore the process profitability has to be considered during the commercial plant development.

In the commercial plant study we have assumed a capacity of 100.000 MTPY for a single line, which is a reasonable value compared to the conventional processes. According to the preliminary IMR simulations more than one IMR unit operating under the same conditions, will be necessary.

This production rate is suitable for being compared with the available technologies, specifically the Catofin process, in order to analyze the economy of the IMR unit. In order to optimize the oxidative dehydrogenation of propane as a commercial process, five different cases have been studied. The main differences between the cases studied are related to the length of the membrane tubes and to the composition of the shell side stream permeating through the membrane wall (air, pure oxygen and a mixture of oxygen and carbon dioxide).

In terms of the operation conditions for the I.M.R, several parameters have to be considered. Some of these conditions have been fixed taking into account the experiments carried out with inert membrane reactors for ODHP: absolute pressure, pressure drop across the fixed bed, reaction temperature, feed composition, gas velocity, gas flow through membrane/oxygen concentration in the shell side, recycle: particle size/shape, catalyst dilution with inerts,

Several situation that can result in a dangerous situation have been considered, as well as the safety measurements to be employed. The feasibility of some operational problems cannot be predicted with the available data, but the experimentation in pilot plant will serve to check some of them, related with the long term stability of materials.

Conclusions

Kinetic and mechanistic studies have demonstrated that for the oxidative dehydrogenation of propane to propene, the composition of the surrounding atmosphere does not seem to determine the state of oxidation of the V-Mg-O catalyst. However, under hydrocarbon rich atmosphere (low oxygen concentration), the catalyst is less active but more selective towards propene. An advanced description of the working surface and of the ODHP mechanism has been provided, which ascertains a Mars-van Krevelen mechanism.

An applicable preparation and activation procedures have been developed to produce optimized standard V-Mg-O catalysts or catalyst precursors in sufficient amounts. The optimization was mainly done by modification of their physicochemical and mechanical properties. A special method of preparation for a V-Mg-O catalyst was developed. Starting from a mixture of magnesium and vanadium alkoxides, synthesis of a series of V-Mg-O catalyst samples exhibiting relatively high surface areas was developed.

Original results were obtained in the development of the membranes. Sol-gel derived infiltrated VPO membranes (also incorporating Al from the support) showed an original gas permeance behavior due to their reversible redox (V^{4+}/V^{5+}) properties. The permeance drastically changes (up to a factor 10 at 500°C) with the oxidative/reducing nature of the permeating gas. Such VPO membranes are potentially attractive to regulate O_2 transport in oxidative reactions. The powder catalysts xV/VMgO derived from metallo-organic precursors revealed original attractive properties (texture, structure and performance) which were specifically studied in Liverpool and Villeurbanne, in comparison with those of the "classical" VMgO catalysts derived from salts. These studies help in understanding the VMgO catalyst function in ODHP reaction.

In the Inert Membrane Reactor study, a ceramic membrane reactor has been used as an efficient contactor in the oxidative dehydrogenation of propane (ODH). The composite silica membrane used as a reactant distributor provided an adequate permeation flux and performance. The best configuration involves the feeding of propane and inert gas to the tube side and oxygen to the shell side. The best improvement achieved in the IMR relative to the FBR is around 10 percentage points in selectivity for a given propane conversion. The best propene yield achieved is c.a. 18%. It has been confirmed that improvements of selectivity are related to a lower oxidation degree of the catalyst. Experiments designed to demonstrate the applicability of the IMR concept to the production of oxygenates from propane have shown that the predominant oxygenated products formed are mixtures of alcohols and aldehydes. No acrylic acid was

detected. Co-feeding of a proportion of the oxygen on the tube side gave an increase in the production of propanol and also more propene.

In the Catalytic Membrane Reactor study, the results show that, when properly engineered (suitable diffusion resistance in the support, distribution of catalytic material, feed arrangement), a catalytic membrane with segregated propane and oxygen feeds gives a clearly superior performance in the oxidative dehydrogenation of propane (ODHP), compared to a conventional reactor with a premixed feed. The Catalytic Membrane Reactor (CMR) performed efficiently in the oxidative dehydrogenation of propane. Propene yields above 15% have been obtained, and the selectivity at a given conversion using the membrane to segregate oxygen and propane was consistently higher compared to that obtained with conventional feed arrangements. The best results were obtained with mesoporous membranes in which V/Al₂O₃ or V/MgO were the active phases, while the performance of V-MFI membranes was less satisfactory. The effect of feed configuration, different degrees of diffusion resistance in the support layer, concentration of catalytic material in the active layer has been experimentally explored. It has been shown that reactant segregation is useful to achieve a higher selectivity especially when it is carried out through a support layer of sufficient resistance.

For the characterisation study, standard samples of (i) magnesium orthovanadate (Mg₃V₂O₈), (ii) magnesium pyrovanadate (Mg₂V₂O₇) and (iii) magnesium metavanadate (MgV₂O₆) were prepared. These were characterised and effectively 'fingerprinted' by different physicochemical techniques. Electronic changes were observed to occur in the 14V/VMgO catalyst during oxidation/reduction cycles. A reversibility between the V⁵⁺ and V³⁺ oxidation states during redox cycles was observed by in-situ EXAFS which correlates well with the in-situ electrical conductivity measurements carried out under Task 1 and also with in-situ XRD. By EM studies it was observed that the 14V/VMgO catalyst is a three component system comprising discrete magnesium orthovanadate particles, magnesium oxide and a disordered vanadium containing layer supported on the MgO. When the catalyst is exposed to typical ODHP conditions at 550°C, in-situ EXAFS indicates a change in oxidation state from +5 to +3. Under the same conditions in-situ XRD suggests that Mg₃V₂O₈ transforms to a cubic spinel structure. These changes are reversible on exposure to air at 500°C. HREM shows that the overlayer changes from a disordered to a weakly ordered structure after exposure to normal reaction conditions whilst pure propane induces the formation of a cubic spinel MgV₂O₄ phase in parallel epitaxy with the MgO support.

During the course of this project, several new techniques for TEM specimen preparation and HREM image analysis have been developed.

A process flow diagram was established for a commercial plant for an Inert Membrane Reactor (IMR) in the ODH of propane. As the base case for comparing with IMR oxidative dehydrogenation, the Catofin process has been chosen (Ullmann's). The basis for the process is a production of 100,000 MTPY of propylene. It is assumed that a 90% selectivity to propene is obtained and that the overall conversion per pass of propane is 65%. In order to optimize the oxidative dehydrogenation of propane as a commercial process, five different cases have been studied. An scheme of the two process flow diagrams used is proposed. The main differences between the cases studied are related to the length of the membrane tubes and to the composition of the shell side stream permeating through the membrane wall.

A multitubular reactor configuration immersed in a fluidized sand bath has been adopted for the plant study. The insertion of reaction tubes (fixed bed catalyst inside) and refrigeration tubes (generating 600 psi steam)

within a fluid bed shell is the final design. According to a propene rate of 100.000 MTPY, two or three reactor units will be necessary .

Exploitation plans and anticipated benefits

The bulk part of this project has been of a fundamental character. A new reactor design based on simultaneous use of heat exchange medium and distribution of reactants to a catalytic reaction zone is considered between the two industrial partners. In terms of inventions/Major improvements developed during the execution of the project, the following results have been obtained :

N _i	Title of exploitable result	Category	Partner(result owners) involved	Exploitation intention
1	Method for more cost effective preparation of a material of vanadium on magnesium oxide. Method for preparing high surface area magnesium oxide via hydrothermal tretment	C	Haldor Topsoe A/S	No
2	Method for making high surface area mixed vanadium-magnesium oxides using a new preparation technique based on alkoxides	C	LMPM-CNRS	No
3	A new reactor concept that uses the membrane support as distributor, making it possible to keep an oxidant at a low concentration in a reaction zone	C	University Zaragoza IRC-CNRS University Limerick	No
4	New reactor design based on simultaneous use of heat exchange medium and distribution of reactants to a catalytic reaction zone	A	DuPont Iberica, S.A Haldor Topsoe A/S	joint RTD or product developmen t

Photographs, diagram or figure to illustrate potential applications of the project.

No information is available for reason of confidentiality.

