

**FCT** Fundação para a Ciência e a Tecnologia

MINISTÉRIO DA CIÊNCIA, TECNOLOGIA E ENSINO SUPERIOR

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**Referência do projecto**

Project reference

PTDC/EQU-EQU/65126/2006

**1. Identificação do projecto**

1. Project description

**Financiamento solicitado**

Requested funding

129.604,00 Euros

**Área científica principal**

Main Area

Engenharia Química - Engenharia Química

**Área científica Secundária**

Secondary area

Química e Bioquímica

**Título do projecto (em português) **

Project title (in portuguese)

Acoplamento de catalisadores com plasma não térmico para a decomposição a baixa temperatura de compostos orgânicos voláteis

**Título do projecto (em inglês)**

Project title (in english)

Coupling catalysts and nonthermal plasma for low temperature decomposition of organic volatile compounds

**Palavra-chave 1 **

Catálise

**Keyword 1**

Catalysis

**Palavra-chave 2**

Plasma não térmico

**Keyword 2**

Non thermal plasma

**Palavra-chave 3**

Compostos orgânicos voláteis

**Keyword 3**

Volatile organic compounds

**Palavra-chave 4**

Baixa temperatura

**Keyword 4**

Low temperature

**Objectivos sócio-económicos**

Socio-economic objectives

Promoção geral dos conhecimentos (investigação fundamental sem objectivo sócio-económico discriminado)

**Data de início do projecto**

Starting date

01-01-2007

**Duração do projecto em meses **

Duration in months

36

**2. Instituições participantes**

2. Participating institutions



**Instituição Proponente** 

**Principal Contractor**

**Instituto Tecnológico e Nuclear (ITN/MCTES)**

Estrada Nacional 10  
2686-953Sacavém

**Instituições Participantes** 

**Participating Institutions**

**Instituto Superior de Engenharia de Lisboa (ISEL/IPL)**

Rua Conselheiro Emídio Navarro - 1  
1950-062Lisboa

**Unidade de Investigação** 

**Principal Research Unit**

(vazio)  
(void)

**Instituição de Acolhimento** 

**Host Institution**

**Instituto Tecnológico e Nuclear (ITN/MCTES)**

Estrada Nacional 10  
2686-953Sacavém

3. Orçamento

3. Budget

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**Instituição Proponente**

**Principal Contractor**

**Instituto Tecnológico e Nuclear**

DESCRIÇÃO

DESCRIPTION

	2007	2008	2009	2010	2011	TOTAL
Recursos Humanos 	19800	19800	19800	0	0	59400
Human resources						
Missões 	1000	2000	2000	0	0	5000
Missions						
Consultores 	0	0	0	0	0	0
Consultants						
Aquisição de serviços e manutenção 	500	500	500	0	0	1500
Acquisition of services and maintenance						
Outras despesas correntes 	5000	5000	5000	0	0	15000
Other current expenses						
Despesas gerais 	8682	5461	5461	0	0	19604
Overheads						
Equipamento 	17100	0	0	0	0	17100
Equipment						
<b>TOTAL</b>	<b>52082</b>	<b>32761</b>	<b>32761</b>	<b>0</b>	<b>0</b>	<b>117604</b>

**Instituições Participantes**

**Participating Institutions**

**Instituto Superior de Engenharia de Lisboa**

DESCRIÇÃO

DESCRIPTION

	2007	2008	2009	2010	2011	TOTAL
Recursos Humanos	0	0	0	0	0	0
Human resources						
Missões	0	0	0	0	0	0
Missions						
Consultores	0	0	0	0	0	0
Consultants						
Aquisição de serviços e manutenção	0	0	0	0	0	0
Acquisition of services and maintenance						

Outras despesas correntes	10000	0	0	0	0	10000
Other current expenses						
Despesas gerais	2000	0	0	0	0	2000
Overheads						
Equipamento	0	0	0	0	0	0
Equipment						
<b>TOTAL</b>	<b>12000</b>	<b>0</b>	<b>0</b>	<b>0</b>	<b>0</b>	<b>12000</b>

**Orçamento Global**  
**Global budget**

DESCRIÇÃO	2007	2008	2009	2010	2011	TOTAL
DESCRIPTION						
Recursos Humanos	19800	19800	19800	0	0	59400
Human resources						
Missões	1000	2000	2000	0	0	5000
Missions						
Consultores	0	0	0	0	0	0
Consultants						
Aquisição de serviços e manutenção	500	500	500	0	0	1500
Acquisition of services and maintenance						
Outras despesas correntes	15000	5000	5000	0	0	25000
Other current expenses						
Despesas gerais	10682	5461	5461	0	0	21604
Overheads						
Equipamento	17100	0	0	0	0	17100
Equipment						
<b>TOTAL</b>	<b>64082</b>	<b>32761</b>	<b>32761</b>	<b>0</b>	<b>0</b>	<b>129604</b>

**Plano de financiamento**  
**Finance plan**

DESCRIÇÃO	2007	2008	2009	2010	2011	TOTAL
DESCRIPTION						
Financiamento solicitado à FCT	64082	32761	32761	0	0	129604
Requested funding						
Financiamento próprio	0	0	0	0	0	0
Own funding						
Outro financiamento público	0	0	0	0	0	0
Other public-sector funding						
Outro financiamento privado	0	0	0	0	0	0
Other private funding						
<b>Total do Projecto</b>	<b>64082</b>	<b>32761</b>	<b>32761</b>	<b>0</b>	<b>0</b>	<b>129604</b>
<b>Total of the project</b>						

**4. Justificação do orçamento**  
**4. Budget justification**

-

**4.1. Justificação dos recursos humanos**  
**4.1. Human resources justification**

Tipo	Nº de pessoas	Duração	Custo envolvido (€)
(BI) Bolsa de Investigação (Lic. ou Bacharel)	2	36	59400

**Justificação**

The project is a good opportunity for advanced training of graduate students. One of the students will be involved in the experimental areas involving the preparation and testing of catalysts, while the other will be involved on designing the NTP- catalyst reactors and on modeling the chemical reactions. The students will be strongly encouraged to pursue PhD studies in this field in 2008/9. A 36 months grant is the adequate effort to achieve the project goals. Other costs covers 36 months of 2BI Social Insurance (Seguro Social Voluntário).

**Custo total: 59400**

**4.2. Justificação de missões**  
**4.2. Mission justification**

Tipo	Local	Nº de deslocações	Custo envolvido (€)
Participação em congressos	n/a (various)	7	5000

**Justificação**

The money requested is needed to attend International and Nacional Conferences to present the obtained results

(2007-1 mission; 2008-2 missions; 2009-3 or 4 missions).

**Custo total:** 5000

**4.3. Justificação de consultores 7**

**4.3. Consultants justification**

(vazio)

(void)

**4.4. Justificação de aquisição de serviços e manutenção 7**

**4.4. Acquisition of services and maintenance justification**

Tipo	Custo envolvido (€)
Manutention of available equipment and services acquisition	1500

Justificação

Some money is needed for the acquisition of analytic services, e.g. EDS/TEM, for the characterization of the catalyst phase and maintenance of laboratories, e.g. ITN Laboratory of Catalysis.

The equipment available for the decomposition studies of chlorinated VOCs will be subject to high corrosive reagents and by-products, e.g. HCl. Therefore, their periodic (6 months) maintenance is very important.

**Custo total:** 1500

**4.5. Justificação de outras despesas correntes 7**

**4.5. Current expenses justification**

Tipo de despesa	Custo envolvido (€)
Reagents, catalysts, glassware, mechanical pieces	25000

Justificação

This budgeted amount will be used to purchase metals or inorganic precursors for the catalysts synthesis. Other reagents, such as consumables (screws, small mechanical parts, oil, o-rings, filaments, etc) will be purchased.

Some reference catalysts such as Ag/TiO<sub>2</sub> (if available, otherwise they will be synthesized in the Lab.) will be acquired.

The amount is also for the construction of the NTP prototype that, as an example, involves electronic components for the 10 kV power supply (e.g. solid state switches (IGBTs and MOSFETs), and passive components (transformers, capacitors, ...), to build a solid state based, regulated bipolar high voltage pulsed power supply, with innovator design (+/-) 1 kV - 10 kV, with frequency from 0.5 kHz to 5 kHz). About 10000 euros is the minimum required to build the NTP power supply (task implemented at ISEL).

**Custo total:** 25000

**4.6. Justificação do Equipamento 7**

**4.6. Equipment justification**

**4.6.1. Equipamento já disponível para a execução do projecto**

**4.6.1 Available equipment**

Tipo de equipamento	Fabricante	Modelo	Ano
GC with TCD detector, dedicated to TPR/TPO	Shimadzu	9A	1988
Glove-box (O <sub>2</sub> and H <sub>2</sub> O content < 5ppm)	(self assembled)	n/a	1994
2 Set-ups for catalytic studies (gas-solid phase)	ITN (self assembled)	Prototypes (Plug and flow type)	2001
Set-up for Temperature Programmed Reduction (H <sub>2</sub> -TPR)	ITN (self assembled)	Prototype-ITN/FCT	2001
Set-up for Temperature Programmed Oxidation (CO <sub>2</sub> , O <sub>2</sub> -TPO)	ITN (self assembled)	Prototype-ITN/FCT	2001
GC with tandem (TCD+FID), dedicated to catalytic oxidation studies	Shimadzu	9A	1988
GC with TCD, dedicated to studies with CO <sub>2</sub> and CH <sub>4</sub>	Agilent	4890D	2002
GC-Column (gases)	Supelco/Aldrich	100/120 Carbosieve S II	1990
GC-Column (gases, including H <sub>2</sub> )	Restek	100/200 ShinCarbon ST	2006
GC-Columns (hydrocarbons)	Supelco/Aldrich	80/100 Chromosob P AW, 23% SP-1700	1990
GC-Columns (solvents and phenols)	Supelco/Aldrich	80/100 Carbopack C/0.1% SP-1000	1990
GC-Columns (pollutants, EPA method 624)	Supelco/Aldrich	60/80 Carbopack B/1% SP-1000	2006
Furnaces for 20-1200 °C	Thermolab, Thermolyne	n/a, 21100	2001
Mass flow controllers and command modules	Aalborg, Omega, Bronkhorst	AFC, FMA and EI-Flow series (respectively)	2001
Circulator	Julabo	F25 (heating and cooling)	2001

2 Circulators	Julabo, Selecta	MV4, Ultraterm (heating)	2002
Digital oscilloscope	Tetronix	2430	2000
Quadrupole Mass Spectrometer	Larimax	DataQuad	1996
High voltage digitalmeter (0-10 kV)	Kikusui Electronica	149-10A	1996
Turbo molecular pump	Edwards	EXT70	2001
Workbench Electronics	Several	Several	1990
Voltage and current data acquisition for analyzing of signals (oscilloscopes, voltmeters, high voltage probes, ...	Several	Several	1990
Arc melting oven	ITN/Home made	n/a	1990
Induction oven (cold crucibles and crystal growth - Czochralski, Bridgman and Floating zone methods	Stanelco	STA-30	1990
TG-DSC	TA instruments	951	1990
DSC (IDEA - ITN/Thermolab)	ITN-Thermolab	Prototype (20-1200 °C)	2006
XRD (powder)	PANalytical	X'Pert	2004
XRD (crystal)	Enraf Nonius	Diffractis 586	1986
IR spectrophotometer	Bruker	Tensor 27	2004
Elemental analyzer	CE Instruments	EA1110 CHNS-O	1999
Mass spectrometer (FT-ICR)	Finningan	FT/MS 2001-DT FTICR	1995
NMR	Varian Oxford	300/54	1997

**4.6.2. Discriminação do equipamento a adquirir**

**4.6.2. List of new equipment requested**

Tipo de equipamento	Fabricante	Modelo	Custo envolvido (€)
1 Cooling circulator (-30/+100°C)	JULABO	F25 ou equivalente	4000
Justificação Needed for the catalytic studies (non gaseous reagents). We need a precise control of non gaseous reagents vapor pressure to control their introduction in the gas stream.			
2 Mass flow controller Aalborg	Aalborg	FC-2600	2500
Justificação For precise control and measure of gases flow, including gas uptake in a the catalytic reactor.			
Mass flow command module	Aalborg	AFC 2600-PRO 4-channel	2000
Justificação Command unit for the mass flow controllers			
1 Electric valve actuator for 6-port valves	VICI/VALCO Instruments Co.	VICI/VALCO	1000
Justificação For the GC analytic sampling unit.			
1 Thermostatized enclosure for 6-port valves	VICI/VALCO Instr. Co.	VICI/VALCO	1000
Justificação For the GC sampling unit.			
2 Personal Computer	Several	Several	1600
Justificação One PC will be dedicated to control of laboratory equipment. The other will be used for data acquisition and analysis.			
2 Data acquisition and control board	ITN/Home made	n/a	1400
Justificação For PC control the NTP-catalyst reactors.			
Mechanical stirrer	Heidolph	RZR 1	1500
Justificação To control the temperature on thermostatic baths.			
Mechanical pump	Edwards	E2M0.7	2100
Justificação To replace obsolete Quadrupole Mass Spectrometer mechanical pump.			

**Custo total: 17100**

5. Equipa de investigação  
5. Research team

-

**5.1 Lista de membros (4)****5.1. Members list (4)**

Nome Name	Função Role	Grau académico Academic degree	%tempo %time
Joaquim Miguel Badalo Branco	Inv. Responsável	DOUTORAMENTO	35
António Cândido Lampreia Pereira Gonç...	Investigador	DOUTORAMENTO	10
Nuno Rombert Pinhão	Investigador	DOUTORAMENTO	35
Luis Manuel dos Santos Redondo	Investigador	DOUTORAMENTO	10

(O curriculum vitae de cada membro da equipa está disponível clicando no nome correspondente)

(Curriculum vitae for each research team member is available by clicking on the corresponding name)

**5.2. Lista de membros a contratar durante a execução do projecto (2)****5.2. Members list to hire during project's execution (2)**

Membro da equipa Team member	Função Role	Duração Duration	%tempo %time
(BI) Bolseiro de Investigação (Lic. ou Bacharel) 1	Bolseiro	36	100
(BI) Bolseiro de Investigação (Lic. ou Bacharel) 2	Bolseiro	36	100

6. Projectos financiados  
6. Funded projects

-

(Sem projectos financiados)

(No funded projects)

7. Indicadores previstos  
7. Expected indicators

-

**Indicadores de realização previstos para o projecto  
Expected output indicators**

DESCRIÇÃO DESCRIPTION	2007	2008	2009	2010	2011	Total
<b>A - Publicações</b> <b>Publications</b>						
Livros Books	0	0	0	0	0	0
Artigos em revistas internacionais Papers in international journals	0	2	2	0	0	4
Artigos em revistas nacionais Papers in national journals	0	1	1	0	0	2
<b>B - Comunicações</b> <b>Communications</b>						
Comunicações em encontros científicos internacionais Communications in international meetings	0	2	2	0	0	4
Comunicações em encontros científicos nacionais Communications in national meetings	1	2	2	0	0	5
<b>C - Relatórios</b> <b>Reports</b>	1	1	1	0	0	3
<b>D - Organização de seminários e conferências</b> <b>Organization of seminars and conferences</b>	0	0	0	0	0	0
<b>E - Formação avançada</b> <b>Advanced training</b>						
Teses de Doutoramento PhD theses	0	0	0	0	0	0
Teses de Mestrado Master theses	0	0	0	0	0	0
Outras Others	0	0	0	0	0	0
<b>F - Modelos</b> <b>Models</b>	0	0	0	0	0	0
<b>G - Aplicações computacionais</b> <b>Software</b>	0	0	0	0	0	0
<b>H - Instalações piloto</b>						

<b>Pilot plants</b>	0	0	0	0	0	<b>0</b>
<b>I - Protótipos laboratoriais</b>	0	1	1	0	0	<b>2</b>
<b>Prototypes</b>						
<b>J - Patentes</b>	0	0	1	0	0	<b>1</b>
<b>Patents</b>						
<b>L - Outros</b>						
<b>Other</b>	0	0	0	0	0	<b>0</b>
	0	0	0	0	0	<b>0</b>
	0	0	0	0	0	<b>0</b>

**Ações de divulgação da actividade científica****Scientific activity spreading actions**

Apart from publication and conference communications is not expected other scientific activity spreading action.

Dados temporariamente indisponíveis

**8. Anexo técnico**

8. Technical addendum

**8.1. Resumo****8.1. Abstract****Resumo (em português)****Abstract (in portuguese)**

O estabelecimento de limites legais para a emissão de gases tóxicos tem conduzido a um crescente interesse no desenvolvimento de métodos energeticamente eficientes para a decomposição de poluentes.

A gama típica de concentrações com interesse em problemas de poluição atmosférica situa-se entre a dezena e a centena de ppmv. Para esta gama de concentrações têm sido usados, de forma independente, quer catalisadores activados pela temperatura quer métodos baseados na criação de plasmas. Em particular, a utilização de plasmas não térmicos (NTPs) tem-se provado eficiente, compacta, exigindo pouca manutenção e um baixo custo.

Contudo ambas estas tecnologias apresentam algumas desvantagens: (i) não tem sido possível remover completamente alguns compostos orgânicos voláteis (VOCs) exclusivamente com recurso a catalisadores e estes requerem temperaturas relativamente elevadas (400-600 °C); (ii) NTPs produzidos à pressão atmosférica apresentam, uma baixa selectividade para oxidação total. Além disso a complexidade das reacções químicas que ocorrem no plasma pode conduzir à formação de (outros) produtos nocivos ou à formação de um aerossol.

Uma das opções para ultrapassar estes problemas e que tem vindo a despertar atenção, é a combinação de um plasma com um catalisador para promover a decomposição oxidativa de VOCs promovendo sinergias entre o plasma e o catalisador e permitindo uma redução significativa da temperatura de trabalho do catalisador.

O objectivo principal deste projecto é estudar a eficiência de novos catalisadores para a decomposição de diferentes classes de VOCs (álcoois, compostos aromáticos e clorados), em reactores associando um NTP e um catalisador (NTP – catalisador).

O projecto envolve quer o estudo experimental de reactores NTP – catalisador para avaliar a eficiência de decomposição em função do tipo de reactor, condições da descarga e catalisador usado, quer o estudo de novos catalisadores.

Estudar-se-ão dois tipos de reactores NTP – catalisador: um reactor catalítico assistido por plasma (PEC), onde o catalisador é colocado a jusante do plasma e um novo tipo de reactor – reactor catalítico activado por plasma (PDC) onde o catalisador é colocado directamente no reactor. O primeiro (PEC) permite ter condições optimizadas quer para o NTP quer para o catalisador, as quais são em geral muito diferentes entre si. Neste caso o papel do NTP é a conversão parcial dos reagentes e a formação de ozono o qual se demonstrou, aumentar a decomposição dos VOCs sobre o catalisador. Nos reactores PDC o catalisador é activado pelo NTP na região de baixa temperatura onde normalmente a catálise térmica não ocorre. Esta activação ocorre quer pela acção de radicais livres quer por fotões UV. Nestes reactores têm lugar todas as reacções em fase gasosa ou em superfície, bem como as suas interacções, têm lugar simultaneamente. A compreensão do funcionamento dos reactores PDC é ainda muito limitada e esperamos contribuir para a sua compreensão.

Estes reactores serão estudados quer com Ag/TiO<sub>2</sub>, que tem sido referido como produzindo bons resultados para a decomposição de alcanos saturados, alcenos, compostos aromáticos e compostos halogenados como o tricloroetileno, quer com novos catalisadores. Por entre estes últimos, mostrou-se recentemente que catalisadores com base em óxido de cobre são úteis na oxidação total de CO, hidrocarbonetos, álcoois e compostos clorados. O óxido de cobre também catalisa a decomposição de NO<sub>x</sub> e SO<sub>2</sub>. Por isso, catalisadores incorporando cobre são considerados candidatos potenciais à substituição dos catalisadores baseados em metais nobres para o controle de emissões. Mais, estudos recentes mostram que a presença de lantânio aumenta a actividade e estabilidade temporal dos catalisadores com base em óxido de cobre.

Assim neste projecto, estudaremos o comportamento de óxidos heretometálicos catalisadores do tipo cobre-lantanídeos Ln-Cu-O (Ln=La, Ce, Sm, Eu, Gd) e correlacionaremos os resultados obtidos com os do comportamento de Ag/TiO<sub>2</sub> nas mesmas condições. Os óxidos heterometálicos serão obtidos por uma nova estratégia desenvolvido no nosso grupo em que se usa compostos intermetálicos do tipo LnCu<sub>2</sub> (Ln=La, Ce, Sm, Eu, Gd) como precursores catalíticos. Os estudos catalíticos serão realizados num reactor do tipo "plug and flow", continuamente, à pressão atmosférica usando cromatografia gasosa (GC), análise em tadem (com detectores de condutividade térmica - TCD)



e ionização de chama - FID) para a detecção em simultâneo de gases e compostos orgânicos.

### **Resumo (em inglês)**

#### **Abstract (in english)**

Regulations on the allowable emissions of toxic gases have resulted in increasing interest in the development of energy efficient methods for remediation.

The typical concentration range of concern in air-pollution problems is of the order of several tenths to several hundredths ppmv. For this range of concentration, both temperature activated catalysts and plasma based methods have been used independently. In particular, methods using a nonthermal plasma (NTP) have proved to be compact, efficient, requiring low maintenance and with low cost.

However both technologies have shown some disadvantages: (i) it is not possible to remove completely some volatile organic compounds (VOCs) exclusively by catalysts, and it requires a relatively high temperature (400-600 °C); (ii) NTPs generated at atmospheric pressure have low selectivity towards total oxidation. Moreover, the complex chemistry taking place in the discharge plasma can result in (other) toxic byproducts or in the formation of aerosols.

One of the options that have been gaining attention to overcome these problems is to combine plasma with a catalyst to promote oxidative decomposition of VOCs via the activation of the catalyst by the species formed in the plasma, allowing a significant reduction of the catalyst working temperature.

The main objective of this project is to compare the efficiency of new catalysts for the decomposition of different classes of VOCs (alcohols, aromatic and chlorinated compounds) in NTP – catalyst reactors. The project involves (i) the synthesis and characterization of new catalysts; (ii) the experimental study of NTP – catalyst reactors to evaluate the decomposition efficiency as a function of type of reactor, discharge conditions and catalyst used. Two types of NTP – catalyst reactors will be studied: (i) a plasma-enhanced catalytic reactor (PEC), where the catalyst is placed downstream to the plasma and, (ii) a novel plasma-driven catalytic reactor (PDC) where the catalyst is placed directly in the reactor. The former (PEC) combines the optimum conditions of the NTP and the catalyst, which are usually quite different from each other. In this case the role of the NTP is to partially convert the reactants and to produce ozone which has been shown to enhance the decomposition of VOCs over the catalyst bed. On the other hand, in PDC reactors the catalyst is activated by the NTP in the low-temperature region where thermal catalysis does not normally occur. This activation is attributed to free-radicals and UV photon. In these reactors all gas-phase and surface reactions, as well as their interaction, take place simultaneously. However, the present level of understanding of PDC reactors is still quite limited. This project aims to contribute to a better understanding of this subject.

In these reactors, Ag/TiO<sub>2</sub>, which has been reported to lead to very good results in the decomposition of saturated alkanes, alkenes, aromatics and halogenated molecules like trichloroethylene, will be compared with new catalysts. Among the latter, catalysts based on copper oxide are useful for the total oxidation of CO, hydrocarbons, chlorinated hydrocarbons and alcohols. NO<sub>x</sub> and SO<sub>2</sub> reductions are also catalyzed by copper oxide. Thus, supported copper catalysts have been considered as potential candidates to substitute noble metal-based emission control catalysts. Moreover, recent reports show that the presence of lanthanum stabilizes the copper oxide oxidation activity and enhances their stability.

Therefore in this work, we intend to study the behaviour of new lanthanide based heterometallic oxide catalysts Ln-Cu-O (Ln=La, Ce, Sm, Eu, Gd) and the data compared with that obtained from commercially available Ag/TiO<sub>2</sub>. To prepare the heterometallic oxides, we will employ a new route developed in our group using intermetallic compounds of the type LnCu<sub>2</sub> (Ln=La, Ce, Sm, Eu, Gd) as catalytic precursors. The catalytic studies will be carried out on a plug and flow type reactor, continuously, at atmospheric pressure using Gas Chromatography (GC) with tandem flame ionization (FID) and thermal conductivity (TCD) detectors for simultaneous analyses of gases and organic compounds.

### **8.2. Objectivos**

#### **8.2. Objectives**

##### **Descrição dos Objectivos do Projecto**

###### **Project Objectives (description)**

The main goals of this project are: (1) to study the decomposition of different classes of VOCs (alcohols, aromatics and chlorinated compounds) in systems coupling a nonthermal plasma and a catalyst; (2) to study the efficiency of new catalysts (namely lanthanide copper oxides) in association with a NTP; (3) to study and compare the efficiency of two types of NTP reactors: a plasma-enhanced catalytic reactor (PEC), and a plasma-driven catalytic reactor (PDC); and (4) to train two young researcher in this field.

Specific objectives are the following:

- To synthesize and characterize copper-lanthanide oxide catalysts (Ln-Cu-O (Ln=La, Ce, Sm, Eu, Gd));
- To study the catalytic oxidation of representative VOCs such as ethanol, benzene, carbon tetrachloride and methane (single and mixtures);
- To construct and optimize two NTP reactors for diluted VOC decomposition;
- To perform NTP - catalyst decomposition studies using Ag/TiO<sub>2</sub> as reference and correlating their performance with that of copper-lanthanide oxide catalysts.

##### **Descrição dos Objectivos do Investigador Responsável**

###### **Principal Investigator Objectives (description)**

PI is a member of the ITN Inorganic and Organometallic Group and his main area of research is catalysis. The PI long term objective is to enhance the value of lanthanide (Ln) and actinide (An) inorganic, organometallic or



intermetallic compounds as catalysts or catalytic precursors for environmental challenging reactions, e.g., OCM with carbon dioxide (POCTI/QUI/35394/2000). One of PI short-medium term objective is to expand the catalytic applications of actinide and lanthanide based heterometallic oxides to the decomposition of a wide range of VOCs, a field where uranium oxide based catalysts have proved to be exceptionally active and long term stable. In the last 3 years, the PI has also been involved in two projects (IAEA POR/8/010 (2003-2006) and IAEA 302-F2-POR-12017 (2002-2005, renewed until Nov. 2006)) concerning the application of ionizing radiation (gamma) technologies to slaughterhouse wastewater treatment. Therefore, other PI short-medium term objective is to expand the use of radiation technologies to agro-industries waste water (slurry's) treatment.

### **8.3. Estado da Arte**

#### **8.3. State of the Art**

##### **Descrição do Estado da Arte**

##### **State of the Art (description)**

Two different fields converge in this project: catalysis and nonthermal plasmas. In both fields we find important work related to pollution control. Only in the 1990s did systems combining an NTP and a catalyst begin to be investigated.

When compared with thermal oxidation ( $T > 1000$  °C), catalytic oxidation offers high efficiency at lower temperatures (400-600 °C), has lower fuel demand, lower capital cost, and has no associated pollution by undesirable by-products such as nitrogen oxides, dibenzofurans or dioxins [1-3]. In the case of the oxidation of chlorinated hydrocarbons a major drawback is the deactivation of the catalysts by decomposition products such as  $Cl_2$  and HCl [4, 5].

The literature reports two main types of catalysts: noble metals (e.g. Pt, Pd, Rh), supported on  $Al_2O_3$ ,  $SiO_2$  or zeolites, and metal oxides, either single (e.g. oxides of Cr, Mn, Cu, Co) or mixed (e.g. Perovskites) [6-8]. Chromium is reported to be the most active transition metal for VOC combustion but his high toxicity is a main disadvantage. Noble metals, especially platinum and palladium, have also been widely applied in the catalytic combustion of chlorinated VOCs [9]. The intrinsic disadvantage of noble metals is their strong deactivation due to the interaction with Cl and formation of polychlorinated by-products.

Metal oxides are, in general, less active but more resistant to poisoning. However, significant losses of catalytic material as volatile oxychlorides can exist [10]. An exception seems to be uranium oxide based catalysts that have recently been demonstrated to be exceptionally active for the decomposition of a wide range of VOCs, including short chain alkanes, chlorohydrocarbons and mixtures of VOCs [2, 11 and 12]. Another crucial observation is that they show long-term stable activity. In recent publications, the dispersion of  $U_3O_8$  in mesoporous materials of MCM-41 and MCM-48 type that result in the increase of exposed surface area and hence the catalytic activity of uranium oxide for methanol decomposition/oxidation reactions has also been reported [13, 14].

Among oxides,  $ABO_3$  (A represents a lanthanide, e.g. La, Ce, Pr, Nd, and/or alkaline earth metal, e.g. Ca, Sr or Ba, and B a d metal, e.g. Co, Mn, Cr, Cu, V) perovskite-type catalysts have been found to be very efficient for the total oxidation of hydrocarbons, oxygenated and chlorinated VOCs [6, 15-17]. They also have the advantage of being cheaper than noble metal supported catalysts.

Recently, photocatalysts, namely  $Ag/TiO_2$ , have been reported to lead to very good results on the decomposition of saturated alkanes (hexane, heptane, octane and isobutene), alkenes (ethylene and 1-butene), aromatics (benzene and toluene) and halogenated molecules like trichloroethylene [18]. On the other hand, the importance of compounds based on copper oxide seems a well established fact in catalysis. Copper catalysts proved to be useful for the total oxidation of CO, hydrocarbons, chlorinated hydrocarbons and alcohols [19].  $NO_x$  and  $SO_2$  reductions are also catalyzed by copper oxide [19]. Thus, supported copper catalysts have been considered as potential candidates to substitute noble metal-based emission control catalysts. Moreover, recent reports show that the presence of lanthanum stabilizes the copper oxide oxidation activity and enhances their stability [20]. Moreover, only a few detailed studies on the catalytic combustion of mixtures can be found.

Therefore, it is evident that the development of high active and selective oxide catalysts for the decomposition of VOCs is a major goal and that copper and lanthanide based oxide catalysts can play a major role.

In nonthermal plasma (NTP), the kinetic energy of the particles (electrons, ions, atoms and molecules) is not in thermal equilibrium and differs substantially between the electrons (between 1 – 20 eV) and the other particles. Collisions of these energetic electrons in the gas produce a wide range of primary processes taking place in a typical time-scale of 10<sup>-8</sup> s. They also produce highly reactive free-radicals which can selectively decompose toxic compounds. The decomposition can be achieved at low gas temperature and at atmospheric pressure, conditions that are of utmost importance for flue gas or off gas treatment. At diluted pollutant concentrations, NTPs require substantially less energy than incineration or thermal-plasma treatment.

The studies of NTPs for air-pollution control started in the 70's using corona discharge but their efficiency was not high [21]. The application of NTP in this field gained importance after a lab-scale  $SO_2$  removal test using a pulsed corona discharge in 1984 [21] and considerable progress has been made since then.

There are a variety of types of NTP reactors – corona discharges, dielectric-barrier discharges (DBD), surface discharges, ferroelectric pellet packed-bed reactor, microwave, gliding arc, etc. Their classification also depends on type of power supply [21].

In this work, the NTP – catalyst reactors will be based on a DBD. These reactors have at least one dielectric material between the electrodes and have reached maturity due to their application to ozone generation. Presently they can operate at high power levels and treat large atmospheric-pressure gas flows with negligible pressure drop. The use of DBD for the control of gaseous pollutants and the destruction of poisonous components has been addressed by

several researchers [22, 23]. Much work has been devoted to the decomposition of VOCs [22, 24]. Recently the combination of NTP and a catalyst as a way of increasing energy efficiency and optimizing the byproduct distribution has gained attention [25-31]. Two types of NTP – catalyst reactors have been successively used: (i) a plasma-enhanced catalytic reactor (PEC), where the catalyst is placed downstream to the plasma and, (ii) a novel plasma-driven catalytic reactor (PDC) where the catalyst is placed directly in the reactor. The former (PEC) combines the optimum conditions of the NTP and the catalyst, which are usually quite different from each other. In this case the role of the NTP is to partially convert the reactants and to produce ozone which has been shown to enhance the decomposition of VOCs over the catalyst bed. On the other hand, in PDC reactors the catalyst is activated by the NTP in the low-temperature region where thermal catalysis does not normally occur. This activation is attributed to free-radicals and by UV photon. In these reactors all gas-phase and surface reactions, as well as their interaction, take place simultaneously. Nevertheless, the understanding of PDC reactors is still quite limited.

The use of PEC reactors in the removal of NO<sub>x</sub> and SO<sub>2</sub> from stationary [32] or mobile sources [33] has been studied. Complete removal of NO<sub>x</sub> was obtained at 150 °C. In these reactors ozone produced in the plasma enhances the decomposition of VOCs [26]. PDC reactors using Ag/TiO<sub>2</sub> as catalyst have shown very promising results for aromatic compounds with a high reaction selectivity, energy efficiency, and carbon balance and without aerosol formation [34, 35].

One of the lines of research at ITN concerns the use of Ln and An intermetallic compounds as catalysts or catalytic precursors [36-40]. A systematic study has shown: (i) binary Cu-Ln and Cu- or Ni-An intermetallic compounds are interesting precursors achieving supported Cu catalysts via an oxidation-reduction cycle. These catalysts are active on the oxidative decomposition of methane with CO<sub>2</sub> [40]; (ii) a method for the synthesis of a new type of heterometallic oxide catalysts [37-39].

Also at ITN research on NTP has been conducted for several years mainly on gaseous radiation detectors and low pressure discharge modeling [41-43]. Experimental work on DBD discharges for the decomposition of VOCs started with the study of ethanol (1000 ppm, decomposition efficiency > 93%) and the characterization of the discharge [44].

Therefore, we propose in this project to foster the use of copper-lanthanide based oxide catalysts for the oxidation of volatile organic compounds (VOCs) that clearly have unexplored potentialities and to improve the efficiency and development of low cost NTP as complementary technology for the decomposition of VOCs.

#### References

(See attachments)

### **8.4. Resultados e Repercussões**

#### **8.4. Results and Repercussions**

##### **Divulgação de Resultados (descrição)**

##### **Diffusion of Results (description)**

The results will be published in appropriate international journals dedicated to chemistry, physics, environment and catalysis. The design of a new laboratorial reactor may lead to a special publication or report. These are not foreseen until the second year of the project. It is expected that after this time the BI will apply for a PhD grant. Concerning patents, at least one will be aimed at. Results will also be reported to national and international meetings and conferences. An annual report will be sent to the funding institution.

The expected output indicators are summarized on the proposal form.

##### **Repercussões (descrição)**

##### **Repercussions (description)**

Owing to its laboratory experimental and exploratory nature, no ethic, social and environment impacts are expected at this level. However the results can have high impact on environment, in particular in gas-pollution problems.

### **8.5. Regionalização**

#### **8.5. Regionalization**


Região	Percentagem
Region	Percent
Norte	20
Centro	20
Lisboa e Vale do Tejo	30
Alentejo	10
Algarve	10
Região Autónoma dos Açores	5
Região Autónoma da Madeira	5

#### Descrição

##### Description

Being a general promotion of knowledge, the results that will be obtained will have an impact in all the Portuguese territory. It is difficult to quantify which amount to attribute to each region. Tentative numbers are given taking in to account the universities and faculties existing in each region.

**8.6. Tarefas****8.6. Tasks****Lista de tarefas (9)****Task list (9)**

Designação da tarefa 	Data de início	Data de fim	Pessoas * mês 
Task denomination	Start date	End date	Person * months
<a href="#">Synthesis and characterization of interm...</a>	01-01-2007	30-06-2007	6,3
<a href="#">Synthesis and characterization of the co...</a>	01-04-2007	31-03-2008	12,3
<a href="#">Influence of the catalyst preparation me...</a>	01-07-2007	31-12-2007	6,3
<a href="#">Construction of NTP-catalyst reactors</a>	01-07-2007	31-12-2008	14,8
<a href="#">Stability of catalysts</a>	01-01-2008	30-06-2008	6,3
<a href="#">Catalytic oxidation studies</a>	01-01-2008	31-12-2008	15,3
<a href="#">NTP decomposition of dilute VOCs</a>	01-04-2008	31-12-2008	6,3
<a href="#">Decomposition of diluted VOCs compositio...</a>	01-10-2008	30-09-2009	18,4
<a href="#">Decomposition of dilute VOCs composition...</a>	01-01-2009	31-12-2009	18,4

*(Os detalhes de cada tarefa estão disponíveis clicando na designação correspondente)*

*(Details for each task are available by clicking on the corresponding denomination)*

**8.7. Referências Bibliográficas****8.7. Bibliographic references****Ano Publicação****Year Publication**

- 1995 "High-Temperature Oxidation of LnCu<sub>2</sub> Intermetallics and their Catalytic Behavior in 4-Methyl-2-pentanol Decomposition", D. Ballivet-Tkatchenko, J. Branco, A. Pires de Matos, J.Phys.Chem., 99 (1995) 5481.
- 2001 "Selective Isoprene Hydrogenation over LnNi (Ln=Pr, Gd, Tm) Intermetallic Compounds", J. Branco, T. Almeida Gasche, A.P. Gonçalves, A. Pires de Matos, J. Alloys and Comp., 323/324 (2001) 610.
- 2001 N R Pinhao, "PLASMAKIN: A chemical kinetics package for plasma physics modeling", Computer Physics Communications 135 (2001), no.1, 105.
- N R Pinhao, Z Donko, D Loffhagen, M Pinheiro, and E A Richley, "Comparison of kinetic calculation techniques for the analysis of electron swarm transport at low to moderate E/N values", Plasma Sources Sci. Technol. 13 (2004), 719.
- 2004 "Actinide Heterobimetallic oxides (Th, U). Reduction Studies", C. J. Dias, J. Branco, A. P. Gonçalves, T. Almeida Gasche, A. Pires de Matos, Thermochim. Acta, 420 (2004) 169.

**8.8. Artigos Anteriores****8.8. Previous Articles**

Ano	Artigo (endereço na Internet - URL)
Year	Paper (Link in the Internet - URL)
1995	<a href="http://dx.doi.org/10.1021/j100015a034">http://dx.doi.org/10.1021/j100015a034</a>
2001	<a href="http://dx.doi.org/10.1016/S0925-8388(01)01190-2">http://dx.doi.org/10.1016/S0925-8388(01)01190-2</a>
2001	<a href="http://dx.doi.org/10.1016/S0010-4655(00)00226-5">http://dx.doi.org/10.1016/S0010-4655(00)00226-5</a>
2004	<a href="http://dx.doi.org/10.1088/0963-0252/13/4/023">http://dx.doi.org/10.1088/0963-0252/13/4/023</a>
2004	<a href="http://dx.doi.org/10.1016/j.tca.2003.11.060">http://dx.doi.org/10.1016/j.tca.2003.11.060</a>

**9. Ficheiros Anexos****9. Attachments**

Nome	Tamanho
Name	Size
<a href="#">Schedule.doc</a>	42Kb
<a href="#">State of the art references.doc</a>	30Kb

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