

TABLE OF CONTENT

CHAPTER 1. INTRODUCTION	1
1.1 TRANSITION TO SUSTAINABLE ENERGY AND CHEMICALS PRODUCTION	3
1.1.1 Evolution in the energy production landscape	3
1.1.2 Global Energy and Climate Model (GEC) scenarios	6
1.1.3 Current context of renewable energy resources (RES)	8
1.2. STRATEGIES FOR ENERGY TRANSITION: DEFOSSILIZATION OF THE CHEMICAL INDUSTRY	11
1.2.2 Direct electrification	13
1.2.2.1 <i>Resistive heating</i>	13
1.2.2.2 <i>Induction heating</i>	14
1.2.2.3 <i>Non-thermal plasma heating</i>	16
1.3 SYNGAS PRODUCTION TECHNOLOGIES: A PLATFORM FOR CHEMICALS OBTENTION	17
1.3.1 Syngas production from natural gas	17
1.3.1.1 <i>Steam reforming</i>	18
1.3.1.2 <i>Partial oxidation</i>	18
1.3.1.3 <i>Autothermal reforming (ATR)</i>	19
1.3.2 Syngas production through coal and biomass gasification	19
1.3.3 Power-to-Syngas technology (PtS)	29
1.3.3.1 <i>Role of Hydrogen in the chemical industry</i>	29
1.3.3.2 <i>Syngas production form CO₂ and water co-electrolysis</i>	32
1.4 SYNGAS CONVERSION ROUTES	37
1.4.1 Syngas valorisation with no C-chain propagation: Methanol and dimethyl ether (DME) synthesis	39

1.4.2 Syngas conversion through unselective C-chain propagation: The Fischer-TropschSynthesis (FTS)	42
1.4.3 Syngas conversion <i>via</i> selective C-chain propagation into C ₂ oxygenates	45
1.4.3.1 <i>Synthesis of acetyls from C₁ compounds: Acetic acid and methyl acetate</i>	45
1.4.3.2 <i>Synthesis of ethanol from C₁ compounds</i>	49
1.5 TANDEM CATALYTIC PROCESSES FOR SYNGAS CONVERSION	56
1.5.1 Syngas to dimethyl ether, DME (STD)	57
1.5.2 Syngas to light olefins (STO)	60
1.5.3 Syngas to aromatics (STA)	62
1.5.4 Syngas to higher alcohols (HAS)	64
1.6 REFERENCES	68
CHAPTER 2. OBJECTIVES	84
CHAPTER 3. EXPERIMENTAL METHODS	89
3.1 MATERIALS SYNTHESIS METHODS	91
3.1.1 General description of synthesis methods	91
3.1.1.1 <i>Hydrothermal synthesis of zeolitic materials: general consideration</i>	91
3.1.1.2 <i>Impregnation methods</i>	91
3.1.1.3 <i>Coprecipitation</i>	93
3.1.1.4 <i>Direct salt thermal decomposition</i>	93
3.1.2 Synthesis of zeolite-based DME carbonylation catalysts	94
3.1.2.1 <i>Hydrothermal synthesis of H-ETL zeolite</i>	94
3.1.2.2 <i>Hydrothermal synthesis of H-FER zeolite</i>	95

<i>3.1.2.3 Post-synthesis modification of NH₄-MOR: synthesis of H-MOR, Ag/MOR and sel-Ag/MOR</i>	95
3.1.3 Synthesis of ketonisation catalysts	96
3.1.3.1 <i>Synthesis of Pr_yCe_(1-y)O_x based materials</i>	96
3.1.3.2 <i>Synthesis of Pd/ZrCeO_x</i>	97
3.1.3.3 <i>Synthesis of Pr₂O₃/SiO₂</i>	98
3.1.3.4 <i>Synthesis of Ce_{0.1}Mg₃Al_{0.9}O_x</i>	98
3.1.4 Synthesis of hydrogenation and hydrodehydration catalysts	99
3.1.4.1 <i>Silica-supported Ag-based catalysts</i>	100
3.1.4.2 <i>Alumina-supported Ag-based catalysts</i>	102
3.1.4.3 <i>Ag catalysts supported on chemically inert carrier materials (Ag/C-Norit®, Ag/C-DARCO® and Ag/SiC)</i>	103
3.1.4.4 <i>Synthesis of other mixed-metal supported catalysts (Pd-In/α-Al₂O₃, Pd-Sn/α-Al₂O₃ and Pt-Sn/α-Al₂O₃)</i>	104
3.1.4.5 <i>Synthesis of nickel-molybdenum-zinc catalyst supported on alumina (Ni-Mo-ZnO_x/γ-Al₂O₃)</i>	105
3.1.5 Synthesis of ester hydrolysis zeolite catalysts	106
3.1.5.1 <i>H-ERI zeolite</i>	106
3.1.5.2 <i>H-ZSM-5 zeolite (MFI structure)</i>	106
3.1.5.3 <i>H-MCM-22 zeolite (MWW structure)</i>	106
3.1.5.4 <i>H-BEA zeolite</i>	107
3.1.5.5 <i>H-USY zeolite (FAU structure)</i>	107
3.2 CHARACTERIZATION METHODS	107
3.2.1 Nitrogen physisorption	107
3.2.2 Powder X-Ray diffraction (XRD)	109
3.2.3 Inductively Coupled Plasma Optical Emission spectroscopy (ICP-OES)	110
3.2.4 Microscopy techniques	110

<i>3.2.4.1 Field Emission Scanning Electron microscopy (FESEM) and Chemical analysis by Energy-dispersive X-ray spectroscopy (EDS)</i>	111
<i>3.2.4.2 (Scanning-)transmission electron microscopy ((S)TEM)</i>	112
<i>3.2.5 X-Ray Absorption Spectroscopy (XAS)</i>	113
<i>3.2.6 Infrared spectroscopy (IR)</i>	116
<i>3.2.6.1 In-situ Fourier Transform Infrared spectroscopy (<i>in situ</i>-FTIR)</i>	116
<i>3.2.6.2 Infrared spectroscopy coupled to the adsorption of pyridine as a probe molecule (Py-IR)</i>	117
<i>3.2.7 Solid state nuclear magnetic resonance (NMR)</i>	120
<i>3.2.8 Themogravimetric analysis (TGA)</i>	123
3.3 CATALYTIC TESTING	123
<i>3.3.1 Reaction setup</i>	123
<i>3.3.1.1 General tandem carbonylation-ketonisation and carbonylation-ketonisation-hydrogenation experiments</i>	123
<i>3.3.1.2 Tandem carbonylation-ketonisation-hydrodehydration experiments</i>	127
<i>3.3.1.3 C₂ carboxylic compound hydrolysis and ketonisation conversion tests</i>	127
<i>3.3.2 General methods for catalytic testing</i>	128
<i>3.3.2.1 Catalytic functionalities arrangement</i>	128
<i>3.3.2.2 Activation treatments prior to catalytic reaction tests</i>	131
<i>3.3.2.3 Catalytic testing starting from DME/syngas mixtures</i>	132
<i>3.3.2.4 Catalytic testing starting from C₂ carboxylic compounds</i>	132
<i>3.3.2.5 Analysis by gas chromatography (GC)</i>	133
<i>3.3.3 Calculation of catalysis performance descriptor parameters</i>	137
<i>3.3.3.1 Experiments starting from DME/syngas mixtures</i>	137
<i>3.3.3.2 Conversion of C₂ carboxylic compounds</i>	139
3.4 REFERENCES	141

CHAPTER 4. TANDEM CATALYSIS FOR THE DIRECT SYNTHESIS OF C₃ OXYGENATES FROM C₁ BUILDING BLOCKS	145
4.1 BACKGROUND	147
4.1.1 Acetone production routes	147
4.1.2 2-propanol (isopropanol, IPA) production routes	154
4.2 TANDEM INTEGRATION OF DME CARBONYLATION AND KETONISATION REACTIONS FOR DIRECT ACETONE PRODUCTION	156
4.2.1 Catalysts design	157
4.2.1.1 <i>Design of the carbonylation functionality</i>	157
4.2.1.2 <i>Design of the ketonisation functionality</i>	166
4.2.2 Design and optimization of a tandem DME carbonylation-ketonisation system	171
4.2.3 Effect of pressure and feed composition on the tandem carbonylation-ketonisation system	186
4.2.4 Stability of the tandem DME carbonylation/ketonisation process for direct acetone production	193
4.3 TANDEM INTEGRATION OF DME CARBONYLATION, KETONISATION AND SELECTIVE HYDROGENATION REACTIONS FOR DIRECT 2-PROPANOL PRODUCTION	195
4.4. CONCLUSIONS	200
4.5 REFERENCES	202
CHAPTER 5. TANDEM CATALYSIS FOR A DIRECT SYNTHESIS OF PROPYLENE FROM C₁ BUILDING BLOCKS	208
5.1 PROPYLENE PRODUCTION PROCESSES	210
5.1.1 Steam naphtha cracking	210
5.1.2 Catalytic cracking of hydrocarbons	212
5.1.3 Propane dehydrogenation (PDH) to propylene	214

5.1.4 Propylene production through olefin metathesis	215
5.1.5 Methanol to olefins (MTO) and methanol to propylene (MTP) processes	217
5.2 MULTIFUNCTIONAL CARBONYLATION-KETONISATION-HYDRODEHYDRATION SYNTHESIS OF PROPYLENE FROM DME/SYNGAS MIXTURES	224
5.2.1 Acetone hydrodehydration catalyst design for the tandem conversion of syngas/DME mixtures	226
5.3 CATALYTIC RESULTS	229
5.3.1 Influence of Ag metal loading	229
5.3.2 Optimization of reaction conditions	232
5.3.3 Exploring promotion effects on the chemo-selective hydrodehydration catalyst	235
5.3.4 Stability of the optimal tandem conversion system	241
5.4 CONCLUSIONS	246
5.5 REFERENCES	249
 CHAPTER 6. GENERAL CONCLUSIONS	 257
 APPENDIXES	 262
APPENDIX I. LIST OF FIGURES AND TABLES	264
APPENDIX II. LIST OF SYMBOLS AND ACRONYMS	276
APPENDIX III. CHROMATOGRAPHIC RESPONSE FACTORS UTILIZED FOR CATALYTIC PERFORMANCE PARAMETERS CALCULATION	280
APPENDIX IV. THERMODYNAMIC CONSIDERATIONS: ASPEN-HYSYS SIMULATION OF THE TANDEM CATALYTIC SYSTEMS DEVELOPED	281

