

Transformation of Carbon Dioxide to Diethyl Carbonate over Ceria and Ceria-supported Catalysts

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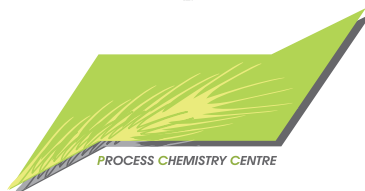
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Preface

This research work was carried out at the Laboratory of Industrial Chemistry and Reaction Engineering at Åbo Akademi University as a part of the activities of the Johan Gadolin Process Chemistry Centre. The financial support from the Academy of Finland and Doctoral Education Network in Materials Research is gratefully acknowledged.

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Turku/Åbo, March, 2015

Ewelina Leino

Abstract

Transformation of Carbon Dioxide to Diethyl Carbonate over Ceria and Ceria-supported Catalysts

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Keywords: diethyl carbonate, carbon dioxide utilisation, butylene oxide, ethanol, cerium oxide, ceria-supported materials

Carbon dioxide is regarded, nowadays, as a primary anthropogenic greenhouse gas leading to global warming. Hence, chemical fixation of CO₂ has attracted much attention as a possible way to manufacture useful chemicals. One of the most interesting approaches of CO₂ transformations is the synthesis of organic carbonates. Since conventional production technologies of these compounds involve poisonous phosgene and carbon monoxide, there is a need to develop novel synthetic methods that would better match the principles of "Green Chemistry" towards protection of the environment and human health.

Over the years, synthesis of dimethyl carbonate was under intensive investigation in the academia and industry. Therefore, this study was entirely directed towards equally important homologue of carbonic esters family namely diethyl carbonate (DEC). Novel synthesis method of DEC starting from ethanol and CO₂ over heterogeneous catalysts based on ceria (CeO₂) was studied in the batch reactor. However, the plausible drawback of the reaction is thermodynamic limitations. The calculated values revealed that the reaction is exothermic ($\Delta_r H^\ominus_{298K} = -16.6$ kJ/mol) and does not occur spontaneously at room temperature ($\Delta_r G^\ominus_{298K} = 35.85$ kJ/mol). Moreover, co-produced water easily shifts the reaction equilibrium towards reactants excluding achievement of high yields of the carbonate. Therefore, *in-situ* dehydration has been applied using butylene oxide as a chemical water trap. A 9-fold enhancement in the amount of DEC was observed upon introduction of butylene oxide to the reaction media in comparison to the synthetic method without any water removal. This result confirms that reaction equilibrium was shifted in favour of the desired product and thermodynamic boundaries of the reaction were suppressed by using butylene oxide as a water scavenger.

In order to obtain insight into the reaction network, the kinetic experiments were performed over commercial cerium oxide. On the basis of the selectivity/conversion profile it could be concluded that the one-pot synthesis of diethyl carbonate from ethanol, CO₂ and butylene oxide occurs via a consecutive route involving cyclic carbonate as an intermediate.

Since commercial cerium oxide suffers from the deactivation problems already after first reaction cycle, in-house CeO₂ was prepared applying room temperature precipitation technique. Variation of the synthesis parameters such as synthesis time, calcination temperature and pH of the reaction solution turned to have considerable influence on the physico-chemical and catalytic properties of CeO₂. The increase of the synthesis time resulted in high specific surface area of cerium oxide and catalyst prepared within 50 h exhibited the highest amount of basic sites on its surface. Furthermore, synthesis under pH 11 yielded cerium oxide with the highest specific surface area, 139 m²/g, among all prepared catalysts. Moreover, CeO₂-pH11 catalyst demonstrated the best catalytic activity and 2 mmol of DEC was produced at 180 °C and 9 MPa of the final reaction pressure.

In addition, ceria-supported onto high specific surface area silicas MCM-41, SBA-15 and silica gel were synthesized and tested for the first time as catalysts in the synthesis of DEC. Deposition of cerium oxide on MCM-41 and SiO₂ supports resulted in a substantial increase of the alkalinity of the carrier materials. Hexagonal SBA-15 modified with 20 wt % of ceria exhibited the second highest basicity in the series of supported catalysts. Evaluation of the catalytic activity of ceria-supported catalysts showed that reaction carried out over 20 wt % CeO₂-SBA-15 generated the highest amount of DEC.

Referat

Omvandling av koldioxid till dietylkarbonat på katalysatorer innehållande ceriumoxid samt ceriumoxid på bärarmaterial

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Nyckelord: dietylkarbonat, utnyttjande av koldioxid, butylenoxid, etanol, ceriumoxid, bärarmaterial

Koldioxid anses nuförtiden vara en primär, antropogen växthusgas som förorsakar global uppvärmning. Kemisk fixering av koldioxid (CO₂) har väckt mycket uppmärksamhet som en potentiell väg att framställa användbara kemikalier. Ett av de mest intressanta förhållningssätten för CO₂-omvandlingar är syntes av organiska karbonater. Eftersom de konventionella framställningsteknologierna av dessa komponenter innehåller giftiga kemikalier, ss. fosgen och kolmonoxid, finns det ett behov att utveckla nya syntetiska metoder vilka bättre följer principerna för grön kemi för att skydda miljön och människornas hälsa.

Under många års tid har syntes av dimetylkarbonat undersökts intensivt vid universiteten och i industrin. Denna undersökning ägnades totalt åt framställning av viktiga homologer av karbonestrar, nämligen dietylkarbonat (DEC). Den nya syntesmetoden för DEC utgående från etanol och CO₂ på heterogena ceriumoxidbaserade katalysatorer undersöktes i en satsreaktor. Termodynamiska begränsningar bromsar reaktionen. Beräknade värden på termodynamiska storheter avslöjade att reaktionen är exotermisk ($\Delta_r H^\ominus_{298K} = -16.6$ kJ/mol) och icke-spontan vid rumstemperatur ($\Delta_r G^\ominus_{298K} = 35.85$ kJ/mol). I reaktionen bildas vatten och det bildade vattnet förskjuter jämvikten mot reaktanter varvid höga utbyten av karbonater utesluts. Därför tillämpades in situ -avvattning tillämpats med hjälp av butylenoxid som en kemisk vattenfälla. DEC-mängden ökade nio gånger då butylenoxid användes jämfört med experiment utan avvattningssteget. Detta resultat bekräftade att reaktionsjämvikten förskjöts mot de önskade produkterna och inverkan av reaktionens termodynamiska gränser på utbytet minimerades genom att använda butylenoxid som vattenfälla.

Reaktionsnätverket undersöktes genom att utföra kinetiska experiment med en kommersiell ceriumoxidkatalysator. På basis av selektivitet/omsättningsgradprofilen kan sammanfattas att

syntes av dietylkarbonat från etanol, CO₂ och butylenoxid i ett steg sker via en konsekutiv rutt innehållande en cyklisk karbonat som reaktionsintermediär.

Kommersiell ceriumoxid (CeO₂) lider av deaktiveringsproblem redan efter den första reaktionscykeln och därför framställdes en CeO₂-katalysator genom att tillämpa utfällningsteknik vid rumstemperatur. Förändring av syntesparametrar, ss. syntestid, kalcineringsstemperatur och pH av reaktionslösningen visade sig ha en stor inverkan på fysikalisk-kemiska och katalytiska egenskaper av CeO₂. En ökning av syntestiden resulterade i en hög specifik ytareal av ceriumoxid och katalysatorn, som var framställd under 50 timmars tid innehöll den största mängden basiska säten på ytan. Ytterligare gav en syntes vid pH 11 ceriumoxid med den högsta specifika ytarean, 139 m²/g bland alla framställda katalysatorer. Denna CeO₂-katalysator hade den största katalytiska aktiviteten och 2 mmol av DEC framställdes vid 180°C och det slutliga reaktionstrycket 9 var MPa.

Ytterligare syntetiserades och testades ceriumoxidkatalysatorer på bärrmaterial med höga specifika ytareor, ss. kisel-MCM-41, SBA-15 och kiseldioxid för första gången som katalysatorer i syntes av DEC. Deponering av ceriumoxid på MCM-41 och SiO₂ bärrmaterial resulterade i en stor ökning av alkalinitet för bärrmaterialet. Hexagonal SBA-15 modifierad med 20 v% ceriumoxid hade den nästhögsta basiciteten i serien för de framställda katalysatorerna på bärrmaterial. Utvärdering av den katalytiska aktiviteten för ceriumoxidkatalysatorer på bärrmaterial visade att reaktionen genomförd med 20 v% CeO₂-SBA-15 bildade den högsta mängden DEC.

List of Publications

- I. Ewelina Leino, Päivi Mäki-Arvela, Valerie Eta, Dmitry Murzin, Tapio Salmi, Jyri-Pekka Mikkola "Conventional synthesis methods of short-chain dialkylcarbonate and novel production technology via direct route from alcohol and waste CO₂" *Applied Catalysis A: General* 2010, 383, 1-13 Contribution: wrote and edited the article manuscript
- II. Ewelina Leino, Päivi Mäki-Arvela, Kari Eranen, Dmitry Yu. Murzin, Tapio Salmi, Jyri-Pekka Mikkola "Enhanced yields of diethyl carbonate via direct route from CO₂ and ethanol: shifting of the equilibrium by means of chemical water trap" *Chemical Engineering Journal* 2011, 176-177, 124-133 Contribution: performed the experiments, wrote and edited the article manuscript
- III. Narendra Kumar, Ewelina Leino, Päivi Mäki-Arvela, Atte Aho, Mats Källdström, Kari Eränen, Jyri-Pekka Mikkola, Tapio Salmi, Dmitry Yu. Murzin "Synthesis and characterization of solid base mesoporous and microporous catalysts: Influence of the support, structure and type of base metal" *Microporous and Mesoporous Materials* 2012, 152, 71-77 Contribution: performed most of the experiments, contributed to writing of the article manuscript
- IV. Ewelina Leino, Narendra Kumar, Päivi Mäki-Arvela, Atte Aho, Krisztián Kordás, Anne-Riikka Leino, Andrey Shchukarev, Dmitry Yu. Murzin, Jyri-Pekka Mikkola "Influence of the synthesis parameters on the physico-chemical and catalytic properties of cerium oxide for application in the synthesis of diethyl carbonate" *Materials Chemistry and Physics* 2013, 143, 65-75 Contribution: performed the experiments, wrote and edited the article manuscript
- V. Ewelina Leino, Päivi Mäki-Arvela, Valerie Eta, Narendra Kumar, Frederic Demoisson, Ajaikumar Samikannu, Anne-Riikka Leino, Andrey Shchukarev, Dmitry Yu. Murzin, Jyri-Pekka Mikkola "The influence of various synthesis methods on the catalytic activity of cerium oxide in one-pot synthesis of diethyl carbonate starting from CO₂, ethanol and butylenes oxide" *Catalysis Today* 2013, 210, 47-54 Contribution: performed the experiments, wrote and edited the article manuscript

List of Other Contributions Related to the Topic

1. Ewelina Leino, Narendra Kumar, Paivi Maki-Arvela, Jorma Roine, Johnny Dahl, Dmitry Yu. Murzin, Jyri-Pekka Mikkola, "Synthesis of ceria-supported catalysts for the application in carbon dioxide transformation to diethyl carbonate" (in preparation)
2. Sari Hyvärinen, Ewelina Leino, Valerie Eta, Elena Privalova, Eero Salminen, John Gräsvik, Pasi Virtanen, Päivi Mäki-Arvela, Jyri-Pekka Mikkola "Heterogeneous catalysis in biomass to chemicals and fuels" – "Ionic liquids as catalytic medium for biomass transformations" Book Chapter; (Kubicka, D., Kubicková, I. (eds.)), Research Signpost, India (2011), ISBN: 978-81-308-0462-0
3. Ewelina Leino, Päivi Mäki-Arvela, Dmitry Yu. Murzin, Tapio Salmi, Jyri-Pekka Mikkola "Utilization of carbon dioxide for the synthesis of organic carbonates" – The 7th European Congress of Chemical Engineering ECCE-7, Prague, Czech Rep., August 28 – September 01, 2010 (oral presentation)
4. Ewelina Leino, Päivi Mäki-Arvela, Dmitry Yu. Murzin, Tapio Salmi, Jyri-Pekka Mikkola "Enhanced yield of diethyl carbonate via catalytic route from CO₂ and ethanol: shifting the equilibrium by chemical water trap" The 19th International Conference on Chemical Reactors, Vienna, Austria, September 05-09, 2010 (poster presentation)
5. Ewelina Leino, Päivi Mäki-Arvela, Dmitry Yu. Murzin, Tapio Salmi, Jyri-Pekka Mikkola "Carbon dioxide as a renewable feedstock for producing diethyl carbonate via direct route over heterogeneous catalysts" The 3rd International IUPAC Conference on Green Chemistry, Ottawa, Canada, August 15-18, 2010 (poster presentation)
6. Ewelina Leino, Päivi Mäki-Arvela, Dmitry Yu. Murzin, Jyri-Pekka Mikkola "Utilization of carbon dioxide for the synthesis of diethyl carbonate" The 11th International Conference on Carbon Dioxide Utilization, Dijon, France, June 27-30, 2011 (poster presentation)
7. Ewelina Leino, Päivi Mäki-Arvela, Dmitry Yu. Murzin, Tapio Salmi, Jyri-Pekka Mikkola "Kinetics of the synthesis of diethyl carbonate from CO₂ and ethanol over

- heterogeneous catalysts” The EuropaCat X Congress, Glasgow, Scotland, August 27 – September 02, 2011 (oral presentation)
8. Ewelina Leino, Narendra Kumar, Päivi Mäki-Arvela, Dmitry Yu. Murzin, Tapio Salmi, Jyri-Pekka Mikkola ”Catalytic synthesis of diethyl carbonate starting from ethanol and carbon dioxide over cerium oxide” The 16th IUPAC International Symposium on Organometallic Chemistry Directed Towards Organic Synthesis, Shanghai, China, July 24-28, 2011 (poster presentation)
 9. Ewelina Leino, Narendra Kumar, Päivi Mäki-Arvela, Dmitry Yu. Murzin, Jyri-Pekka Mikkola ”Utilization of carbon dioxide to diethyl carbonate via one-pot synthesis starting from ethanol, CO₂ and butylene oxide over cerium oxide catalyst” The 15th International Congress on Catalysis, Munich, Germany, July 01-06, 2012 (oral presentation)
 10. Ewelina Leino, Narendra Kumar, Päivi Mäki-Arvela, Anne-Riikka Leino, Andrey Shchukarev, Dmitry Yu. Murzin, Jyri-Pekka Mikkola ”One-pot synthesis of diethyl carbonate starting from CO₂, ethanol and butylene oxide over cerium (IV) oxide prepared via a precipitation technique” The 15th Nordic Symposium on Catalysis, Åland, Finland, June 10-12, 2012 (oral presentation)
 11. Ewelina Leino, Valerie Eta, Narendra Kumar, Päivi Mäki-Arvela, Frédéric Demoisson, Ajaikumar Samikannu, Dmitry Yu. Murzin, Jyri-Pekka Mikkola ”Effect of different synthesis methods of cerium (IV) oxide on its catalytic activity in the synthesis of diethyl carbonate” International Symposium on Catalysis for Clean Energy and Sustainable Chemistry, Madrid, Spain, June 27-29, 2012 (oral presentation)

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1. Introduction

1.1. Carbon dioxide

As early as in the 19th century scientists realized that accumulation of gases in the Earth's atmosphere may cause "green-house effect" which, consequently, might affect the planet's temperature. Among several green-house gases such as water vapour, methane, nitrous oxide, chlorofluorocarbons and ozone, carbon dioxide (CO₂) is the most prominent one. Its long life-time and ability to absorb and re-emit infrared energy makes it an effective heat-trapping gas. The levels of carbon dioxide alone in the atmosphere have risen more than 30 % since the Industrial Revolution in the 1700's. Natural sources of CO₂ include respiration processes of aerobic organisms, volcanic outgasing and/or wildfires and are nearly balanced by natural physical and biological processes as solubility in water forming carbonic acid and photosynthesis. As a matter of fact, the recent rise of carbon dioxide concentration in the atmosphere is known to be mainly due to human activity. Next to deforestation and worldwide cement production, combustion of fossil fuels is the leading cause of CO₂ emissions yielding 36 Gt of CO₂ released in 2013, compared to 6.15 Gt in 1990.¹ Recently, the idea that accumulation of carbon dioxide in the Earth's atmosphere may result in global warming and irreversible climate change for hundreds of thousands of years has reached the public awareness and became a cause of primary concern. Therefore, numerous researches have been targeted at improving the current technologies or developing new approaches of waste carbon dioxide capture and storage (CCS).² There are several methodologies for carbon dioxide capture and sequestration such as absorption in amine and ammonium solutions,^{3,4} adsorption via molecular sieves and activated carbon,⁵ membrane separation, application of solid imidazolium-based poly(ionic liquids) with variable molecular weights for CO₂ capture,⁶ sequestration in deep saline aquifers and coal beds,⁷ as well as relatively novel method of CO₂ injection into cold geologic formations resulting in clathrate hydrates formation.^{8,9} Another powerful tool to reduced carbon dioxide concentration and mitigate global warming is its utilization to value-added chemicals. The application of CO₂ in the synthesis of chemicals is known already since the second half of 1800's when the process of the synthesis of salicylic acid from phenol salts and carbon dioxide was discovered in 1869¹⁰ followed by conversion of ammonia and CO₂ into urea and synthesis of methanol from syngas enriched with CO₂.¹¹ About 200 Mt of carbon dioxide yearly is, nowadays, converted to chemicals which make two orders of magnitude larger amount than carbon capture and sequestration.

Undoubtedly, conversion of CO₂ to useful products will also allow it to be viewed as a valuable feedstock rather than a waste.

CO₂ is recognized as a non-toxic, inexpensive, renewable and widely abundant carbon source and attractive C1 building block for organic synthesis that can replace poisonous chemicals such as phosgene, isocyanates or carbon monoxide.^{12,13} Nevertheless, the problem of CO₂ activation is a continuous challenge for synthetic chemists to "force" this molecule into selective reactions under mild enough conditions. CO₂ is a thermodynamically stable and kinetically inert, therefore a substantial input of energy, appropriate reaction conditions and active catalysts are necessary for its chemical fixation.

The conversion of CO₂ into fuels and polymeric/construction materials is at present in significant demand^{14,15} including the conversion of CO₂ to formic acid,¹⁶ methanol,¹⁷ methyl formate¹⁸ and higher hydrocarbons¹⁹ which are all of great interest. From the energetic point of view, the most favourable process of carbon dioxide conversion is a transformation in which carbon atom maintains its +4 oxidation state. Based on this concept, synthesis of such compounds as carbamates, ureas, polycarbonates, polyurethanes and organic carbonates using CO₂ as a raw material is of essential importance.

1.2. Organic carbonates

The carbon atom in carbon dioxide molecule is an electrophile, thus reactions of CO₂ are dominated by nucleophilic attacks on C-atom resulting in production of carboxyl groups. Further reactions of these species with electrophiles lead to the formation of organic carbonates. Organic carbonates can be categorized into cyclic and linear carbonates from which ethylene carbonate (EC), propylene carbonate (PC), diphenyl carbonate (DPC) and dimethyl carbonate (DMC) are industrially important compounds due to their excellent properties.²⁰ They find commercial application as polar aprotic solvents, selective reagents, intermediates and substituents for phosgene in the manufacture of polycarbonates and polyurethanes.²¹ Since polycarbonates are durable materials, they are extensively used as electronic components, data storage (Compact Discs, DVDs, Blue-ray Discs) and construction materials. Polyurethanes, in turn, are applied in the manufacture of flexible, high-resilience foam seatings, insulation panels, print rollers, synthetic fibers, elastomeric wheels and tyres. Over the years, the need for safer and more selective processes applying biodegradable and non-toxic materials caused the growing interest for DMC production proven by substantial number of literature reports. In contrast, diethyl carbonate (DEC) the second homologue in short-chain dialkylcarbonate family played only a marginal role.

1.2.1. Properties and applications of diethyl carbonate

Diethyl carbonate is one of the most important green chemicals of carbonate esters also called ethyl carbonate, carbonic acid diethyl ester or Eufin. It is a colourless, transparent liquid under the normal conditions and has a mild toxicology profile.²⁰ The physical properties of DEC are summarized in Table 1.

Table 1. Physical properties of diethyl carbonate.

Molar mass (g/mol)	118.13
Boiling point (°C)	126 - 128
Melting point (°C)	- 43
Flash point (°C)	25
Density (g/cm ³)	0.975
Toxicology	Mildly toxic

The fact that DEC can be prepared from bioethanol and its biodegradability when released to the environment proves eco-friendly character of diethyl carbonate and provides a “bio-derived” label to all processes in which it is used. The presence of two ethyl groups and one carbonyl group in DEC structure represents a viable alternative to both ethyl halides and phosgene for ethylation and carbonylation processes. High oxygen content of DEC (40.6 wt %) when compared to methyl *tert*-butyl ether (MTBE) (18.2 wt %) and ready solubility in fuels without any phase separation allows considering it as a replacement for MTBE as an attractive oxygen containing gasoline additive. Additionally, the gasoline/water distribution coefficients are more favourable for DEC than for dimethyl carbonate and ethanol potentially opening a large market for DEC as a fuel component.²¹ It has been shown, that introduction of 5 wt % of diethyl carbonate into diesel fuel could reduce the emissions of particulate matter by 50 %.²² DEC finds also an application as a raw material for manufacturing of polycarbonates,²³ as an excellent solvent and an intermediate for various pharmaceuticals such as antibiotics and phenobarbital.^{24,25} Furthermore, DEC is applied as a solvent of polyamide, polyacrylonitrile and diphenol resin in the synthetic fibre industry, as solvents of cellulose ether, synthetic and natural resin in the textile printing and dyeing industry, as a paint remover and it is widely used as an electrolyte in lithium ion batteries.

1.2.2. Production technologies of diethyl carbonate

1.2.2.1. Phosgenation of ethanol

The great majority of phosgene (COCl_2) called also carbon dichloride oxide, carbon oxychloride and/or chloroformyl chloride is used in production of isocyanates such as toluene diisocyanate and methylene diphenyl diisocyanate being the precursors for polyurethanes. Another significant application of phosgene is the production of organic carbonates. Phosgenation of ethanol is the oldest known and currently applied method for manufacturing of diethyl carbonate proposed by Muskat already in 1941.²⁶ It should be, however, noted that in 1970's, a non-phosgene technology for dimethyl carbonate synthesis was developed by EniChem (Italy) which is based on liquid-phase methanol oxidative carbonylation. Later on in 1980's, a process based on the carbonylation of methyl nitrite was patented by UBE (Japan).^{27,28}

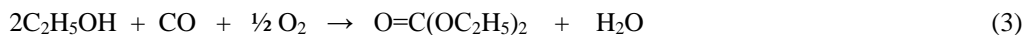
The majority of the production processes for dialkylcarbonates follow a similar route, according to equations (1) and (2)



COCl_2 reacts with an alcohol to form chloroformates which react further with another molecule of alcohol to form carbonate. The process occurs in anhydrous solvents such as toluene, dichloromethane or benzene with excess of pyridine, which acts as a hydrochloric acid trap in order to shift the equilibrium of the reaction towards formation of dialkylcarbonates.²⁶ The main drawback of this method is the employment of phosgene that has been identified as an extremely poisonous compound for human health and environment. Inhalation of COCl_2 results in adverse respiratory effects such as pulmonary edema and pulmonary emphysema finally leading to the death. Additionally, it causes ocular irritation and dermal burns. Thus, the toxicity of this process and expensive post-synthesis purification as well as readiness to match the principles of "Green Chemistry" command industry to target for less restrictive and much more safe for human health and the environment technologies of diethyl carbonate synthesis.

1.2.2.2. Oxidative carbonylation of ethanol

Nowadays, ethanol is attracting considerable attention for its potential in realizing the strategy of energy diversification and producing other valuable chemicals. Together with carbon monoxide ethanol is a reagent for synthesis of diethyl carbonate via oxidative carbonylation route (Eq. (3)).



Similarly to DMC, high quantities of diethyl carbonate have been produced over homogenous copper chloride catalyst in excess of carbon monoxide.²⁹ The disadvantage of this method is highly corrosive effect of CuCl or CuCl₂ catalysts on metallic or alloy reactor due to existence of Cl⁻ and the redox reaction between Cu(II)/Cu(I) and Cu(0).

The catalytic activities of various non-corrosive Co-Schiff base complexes were tested and salophen type cobalt complex (Fig. 1) displayed high DEC yield 15.8 % with selectivity equal to 97 % at 140 °C and 5 MPa.³⁰ Phenyl ring of diimine bridge in the structure of salophen-type ligand is conjugated with two phenyl rings of salicyl moieties which consequently improved the stability of the formed Co(salophen) complex and increased the electron density of the center Co(II) cation so that the complex catalyst favoured the formation of reaction intermediates.

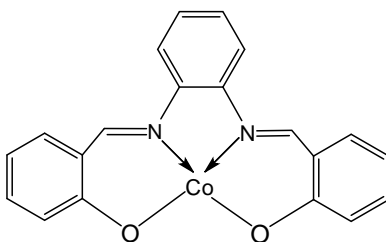


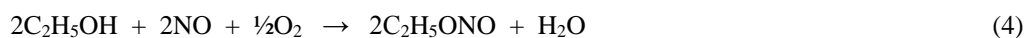
Figure 1. Co-Schiff base complex.

Subsequently, a number of supported heterogeneous catalysts was investigated. A vapour-phase reaction over copper/palladium chloride supported on activated carbon resulted in 100 % selectivity to DEC at temperature below 120 °C.³¹ However, the catalyst was easily deactivated due to sintering of the cuprous chloride and the decomposition of palladium chloride. The effect of various potassium salts (potassium acetate, potassium citrate tribasic monohydrate, potassium sorbic, potassium chloride) in CuCl₂/PdCl₂/activated carbon catalyst

using a continuous reactor system was studied and it was shown that introduction of KCl improved catalyst activity and stability.³² A certain interest has been also devoted to the development of catalysts supported on other materials than activated carbon. Cu-substituted hexagonal mesoporous silica (HMS) for DEC formation via oxidative carbonylation of ethanol was reported for the first time in 2007.³³ No conversion of ethanol to DEC was observed over pure Cu-HMS and PdCl₂/HMS catalysts, while PdCl₂/Cu-HMS exhibited excellent catalytic performance at 150 °C and 0.64 MPa. Further studies revealed that an optimized Si/Cu ratio about 50/1 had a remarkable effect on catalyst performance and simultaneously a favourable amount of Pd loading was found to be 0.25 wt %.³⁴

1.2.2.3. Carbonylation of ethyl nitrite

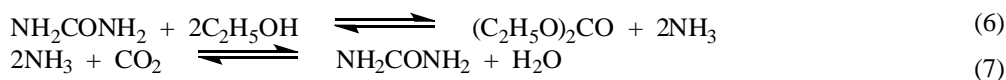
Another promising method for manufacturing of diethyl carbonate is carbonylation of ethyl nitrite in which ethanol is first converted into ethyl nitrite (Eq.(4)) and, afterwards, into diethyl carbonate via a reaction with carbon monoxide (Eq.(5)).



Mesoporous aluminosilicate MCM-41 due to its high specific surface area, thermal and hydrothermal stability as well as a possibility to control pore size and hydrophobicity has been chosen as a support for palladium in carbonylation of ethyl nitrite.³⁵ It was found that Pd, Pd-Cu and Pd-Ti deposited on Si-MCM-41 demonstrated higher catalytic activities than the catalysts supported on Ti-MCM-41. An interesting observation was that the 1.5 wt % Pd-0.5 wt % Ti/Si-MCM-41 catalyst was favourable for DEC synthesis, while for the 1.5 wt % Pd-0.5 wt % Cu/Ti-MCM-41 catalyst diethyl oxalate (DEO) was the dominant product. Several other carrier materials such as activated carbon, silica, alumina and HMS were studied for Wacker-type catalysts and PdCl₂-CuCl₂ supported on activated carbon turned to be the most efficient catalyst for DEC synthesis from carbon monoxide and ethyl nitrite.³⁶ The catalytic activity of the catalyst was still greatly enhanced by chemical pretreatment with hydrogen and optimum Pd/Cu mole ratio was found to be 1/2 considering both DEC yield and selectivity.

1.2.2.4. Catalytic ethanolysis of urea and ethyl carbamate

Synthesis of urea has been a traditional industrial process for carbon dioxide utilization. As a CO₂ carrier, urea is cheap and widely available and, therefore, it was thought that alcoholysis of urea could be a potential route for the synthesis of organic carbonates. Apparent advantages of this process, i.e. abundant resources, low cost of raw materials, no azeotrope formation between alcohol and water as well as an easy product separation and purification makes it an interesting approach. Diethyl carbonate is prepared by reacting ethanol with urea in the presence of the catalyst (Eq. (6)). In this process, urea plays a role as a carbonylation agent. Furthermore, the co-product ammonia can be recycled to urea (Eq. (7)).

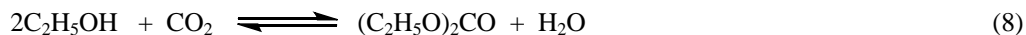


Zinc oxide (ZnO), calcium oxide (CaO), zirconium dioxide (ZrO₂), titanium dioxide (TiO₂), tin dioxide (SnO₂), magnesium oxide (MgO) and γ -aluminum oxide (γ -Al₂O₃) have been used as catalysts for DEC synthesis from urea.³⁷ Among these catalysts, ZnO and ZrO₂ exhibited the best catalytic performance while γ -Al₂O₃ was the least active catalyst, probably due to stronger acidity compared to CaO or MgO. It was proposed that high activity of ZnO and ZrO₂ is attributed to their acidic and basic properties. Additionally, reaction carried out in the absence of the catalyst resulted in 84 % yield of ethyl carbamate (EC) and no DEC generation, indicating that EC is the intermediate for DEC formation from urea and ethanol. Since the consecutive reaction of ethyl carbamate and ethanol to form DEC is the rate-controlling step, an effort has been devoted to further investigation of this reaction. Lead oxide (PbO) showed a good catalytic activity yielding 16 % of DEC at 180 °C and 2 MPa.³⁸ The yield was even more enhanced to 21 % over ZnO-PbO mixed oxides.³⁹ Interestingly, waste slag generated from steel production was found to be an excellent source for solid base catalyst applied in the reaction of ethylene carbamate and ethanol resulting in 33 % yield of DEC with over 74 % selectivity to the desired product.⁴⁰

1.2.2.5. Direct reaction starting from ethanol and carbon dioxide

The development of innovative reaction methodologies based on carbon dioxide as a feedstock is of considerable importance in academia and industry boosted by Sustainable Chemistry and Engineering challenge. Among all synthesis methods of diethyl carbonate the

straightforward synthesis starting from ethanol and CO₂ (Eq. (8)) is the most promising and eco-friendly one producing only water as a by-product and is presently regarded as a green chemical process.



It has received much attention due to a number of reasons such as carbon recycling, high atom economy, phosgene-free technology and a possibility to replace multistep processes with a more direct synthetic procedure which consequently enable waste reduction. Although the utilization of CO₂ to diethyl carbonate will not have, at least in the near future, a major impact on mitigation of greenhouse gases, undoubtedly, it is a potential pathway that could contribute to a complete (balance) global carbon dioxide cycle.

As previously mentioned all the reactions aimed to use carbon dioxide need an applicable catalytic system. Hence, the catalyst development is next to the reaction thermodynamics and kinetics one of the key parameters in CO₂ chemical fixation that could promote the accomplishment of the significant selective carbon dioxide utilization.

Over the past few decades, rare-earth oxides have gained enormous attention and have been widely investigated as structural and electronic promoters to improve the activity, selectivity and thermal stability of catalysts. Assuredly, cerium oxide (CeO₂) is the most feasible of the oxides of rare-earth elements in industrial catalysis owing to its unique structural, redox and acid-base properties.⁴¹ Due to a high oxygen storage capacity arising from the ability to be easily and reversibly reduced ceria became a crucial component of the three way catalysts (TWC),^{42,43} simultaneously, providing the most efficient method to reduce pollutants released from automotive exhaust gases. Moreover, cerium oxide finds a wide range of applications as UV absorbents and filters,⁴⁴ glass polishing material,⁴⁵ oxygen ion conductor in solid oxide fuel cells (SOFCs),⁴⁶ catalytic wet oxidation,⁴⁷ NO removal catalyst,⁴⁸ a catalyst support and promoter.⁴⁹⁻⁵¹

Catalytic activity of ceria-zirconia mixed oxides (Ce/(Ce + Zr) = 0.2) in the direct carboxylation of ethanol has been reported for the first time in year 2002.⁵² Diethyl carbonate was selectively formed under 110 °C and 6 MPa with the yield of 0.4 mmol irrespectively on the amount of the catalyst used in the reaction. Other studies on the same catalytic system with tuned Ce/Zr ratio showed that Ce_xZr_{1-x}O₂ (x=1) exhibited the highest activity towards DEC followed by Ce_xZr_{1-x}O₂ (x=0.7) which could be attributed to a strong dependence of catalytic properties of Ce_xZr_{1-x}O₂ on the crystal structures and the acid-base sites on the

surface with varied Ce/Zr ratios.⁵³ In spite of high selectivities (90-100 %) of the process, the yield of dialkylcarbonates produced via the direct route remains far from satisfactory due to the unfavourable thermodynamics of the reaction. Additionally, rapid hydrolysis of dialkylcarbonate with co-produced water exclude formation of high amounts of the desired product. Therefore, several physical and chemical means of improving the productivity of the reaction by water elimination such as the use of molecular sieves,⁵⁴ 2,2-dimethoxypropane,⁵² trimethyl orthoformate and/or dimethoxymethane⁵⁵ have been attempted at first in the synthesis of dimethyl carbonate starting from methanol and CO₂. For diethyl carbonate, in turn, *in situ* dehydration with acetonitrile acting as a chemical water trap resulted in the enhanced yields of DEC over cerium oxide catalyst.⁵⁶ A CO₂-based yield of DEC equal to 42 % was achieved after 24 h reaction time at 150 °C and 0.2 MPa of CO₂ pressure. Furthermore, pervaporation membranes namely a polymeric organic membrane and inorganic ceramic membrane were used in order to decrease the water content in the direct synthesis of DEC.⁵⁷ The conversion of ethanol increased from 0.9 up to 2.3 % and relatively pure diethyl carbonate (> 90 %) has been isolated via distillation. It has been also found that Nb₂O₅-loaded ceria exhibited even 50 % higher catalytic activity than the corresponding Al₂O₃-loaded ceria at 135 °C and 5 MPa.

Based on aforementioned findings it could be concluded that *in situ* dehydration in direct carboxylation of ethanol is a powerful methodology to shift the reaction to the carbonate side. Moreover, the application of the catalyst possessing specific for the reaction properties and suitable reaction conditions combined with the efficient water removal may be conclusive to solve the drawbacks of the process.

1.3. Aims and scope of the thesis

Since the 1970's, the development of non-phosgene synthetic methodologies of dimethyl carbonate such as oxidative carbonylation and straightforward synthesis starting from methanol and CO₂ has played a crucial role in the academic and industrial investigations. Therefore, this thesis has been entirely devoted to the synthesis of diethyl carbonate, an equally important homologue of carbonic esters family.

Conventionally, hazardous carbon monoxide and phosgene are the preferred C1 feedstock for DEC production owing to their reactivity. Thus, this work was focused on the advancement of novel and eco-friendly technology of DEC synthesis applying a direct route that provides a possibility for the utilization of abundant and non-toxic CO₂.

Cerium oxide has been found to be an active catalyst in the direct synthesis of diethyl carbonate. Nevertheless, up to now, the research has been mainly concerned on the use of commercial cerium oxide which suffers from deactivation issues. Thus, in this study a special effort was devoted to the development of a more stable CeO₂ via in-house synthesis involving different preparation techniques. Furthermore, a particular focus was put on better understanding of the influence of CeO₂ synthesis method and synthesis parameters on physico-chemical and catalytic properties of the resulting material. Moreover, several ceria-modified silica materials were prepared, characterized and for the first time used as catalysts in the synthesis of diethyl carbonate.

In the thesis, a succinct report on the thermodynamic calculations of direct synthesis of diethyl carbonate starting from ethanol and CO₂ is provided (**II**), the employment of a dehydrating agent to increase the yields of DEC is described (**II**), preparation of ceria and ceria-supported catalysts via different synthesis methods and variation of synthesis parameters including in-depth catalyst characterization and activity testing is addressed (**III, IV, V**).

2. Materials and Methods

2.1. Materials

Cerium (IV) oxide, cerium (III) nitrate hexahydrate ($\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$), aqueous ammonium hydroxide (28-30 %), ethanol (Etax, Aa, 99.5 %), butylene oxide (99 %), diethyl carbonate (99 %), diethyl ether (99.5 %), 1,2-butanediol (99 %) were purchased from Sigma Aldrich. Carbon dioxide (99.99 %) and gas mixture (ethane 1 %, propene 0.983 %, butene-1 0.961 %, butane –ISO 0.977 %, helium 96.1 %) were purchased from AGA. All chemicals were used as received.

2.2. Catalyst preparation

2.2.1. Room temperature precipitation method

Synthesis of cerium (IV) oxide was carried out by slowly adding 1M aqueous solution of cerium (III) nitrate hexahydrate into a well-stirred precipitating solution of ammonium hydroxide. The pH of the solution was carefully controlled throughout the synthesis process at the desired value. The colour of the solution changed from light red indicating a precipitate of $\text{Ce}(\text{OH})_3$ to purple which characterized the oxidation of $\text{Ce}(\text{OH})_3$ to $\text{Ce}(\text{OH})_4$. Eventually, it became a light yellow suspension of CeO_2 . The resulting precipitate was filtrated, washed with deionized water, dried overnight at 100 ° C and calcined at specified temperature for 3 h in air.

2.2.2. Supercritical water hydrothermal method

The CeO_2 powder has been synthesized with a continuous hydrothermal production process under supercritical conditions allowing a productivity of 10 g h⁻¹. The key feature of this process is the tailor-made patented reactor.⁵⁸ It is a counter-current flow reactor that allows the metallic salt precursor to be rapidly heated up to the desired temperature.⁵⁹ In the continuous hydrothermal experimental set-up reactive solution of $\text{Ce}(\text{NO}_3)_3$ 0.05 M and demineralized water are fed to the reactor using high-pressure pumps. Pressure is regulated due to a back pressure regulator, located at the outlet and kept constant at 30 MPa in the whole apparatus. Demineralized water is preheated to a temperature higher than the expected temperature in the pre-heater keep up at 400 °C. Consequently, the three streams are then injected in the patented reactor made of Inconel 625. The residence time in the reactor depends on pump flow rates and has been fixed at 4 s. Once leaving the reactor, the suspension is rapidly quenched in a cold bath. Two filters made of 7 µm and 2 µm porous stainless steel remove agglomerated nanoparticles. Then, the suspension is centrifuged and

washed with demineralized water under ultrasonication. The suspension is freeze-dried to keep well-dispersed nano-powder. Supercritical conditions lead to instantaneous formation of a large number of hydroxide nuclei, therefore short residence times are required to reduce the particle growth. Therefore, nano-powder is synthesized with a production rate of around 10 g h⁻¹.

2.2.3. Preparation of ceria-supported catalyst

Preparation of ceria supported on SBA-15 mesoporous material

CeO₂ modified SBA-15 was prepared by the deposition-precipitation method. Calcined Si-SBA-15 was dispersed in 150 ml of urea (0.372 M) aqueous solution. Under stirring conditions, an appropriate amount of cerium nitrate hexahydrate dissolved in deionized water was added to the above suspension. In the next step, the temperature of the suspension was raised to 70 °C and stirred for 5 h to enable slow decomposition of urea to ammonia giving rise to an increased pH and, consequently, a slow precipitation of metal precursors. In order to ensure complete precipitation, pH of the suspension was increased to 9 by adding aqueous ammonia with stirring continuing for an hour. Then, the solids were recovered by filtration and washed thoroughly with deionized water. Thereafter, the solids were dried overnight in an oven at 100 °C and calcined at 600 °C for 3 h in air.

Preparation of ceria supported on MCM-41 and silica gel

Ceria modification of MCM-41 and silica gel materials was carried out using evaporation impregnation method in a rotator evaporator. Cerium nitrate hexahydrate was used as a precursor. After modification, the catalysts were dried at 100 °C and calcined at 550 °C in a muffle oven.

2.3. Catalyst characterisation

2.3.1. Surface and structural analyses of catalysts (II, III, IV, V)

The structural properties of ceria and ceria modified catalysts were investigated by X-ray powder diffraction (XRD) (Philips, X'Pert Pro MPD) using CuK α (40 kV, 50 mA) radiation with 2θ ranging from 23 ° to 83 ° at a scanning speed 0.04 °/3s.

X-ray photoelectron spectroscopy (XPS) was used to determine the state of Ce. All XPS spectra were recorded with Kratos Axis Ultra DLD electron spectrometer. A monochromated Al K α source operated at 150 W, hybrid lens system with magnetic lens, providing an analysis area of 0.3 x 0.7 mm² and a charge neutralizer were used for the measurements. The

survey spectrum and high resolution spectra of Ce 3d, O 1s and C 1s photoelectron lines were collected at 160 eV and 20 eV pass energy, respectively. The binding energy (BE) scale was referenced to the C 1s component of aliphatic carbon, set at 285.0 eV. Processing of the spectra was accomplished with the Kratos software. Powder samples for XPS measurements were hand-pressed into a special powder holder (without any adhesive tape or other artificial binders).

The electron microphotographs of the cerium oxide samples were taken by a LEO 912 OMEGA energy-filtered transmission electron microscope by using 120 kV acceleration voltage. Scanning electron microscopy (SEM) analysis was conducted by Zeiss Leo 1530 Gemini.

2.3.2. Specific surface area of catalysts (II, III, IV, V)

The specific surface area of the catalyst was determined by measuring the nitrogen adsorption-desorption isotherms (Sorptomatic 1900, Carlo Erba Instruments). Prior to the measurement, the samples were outgassed for 3 h at 150 °C to a residual pressure below 0.01 Pa. The total surface area was calculated according to the B.E.T. (Brunauer-Emmett-Teller) equation.

2.3.3. Basicity and acidity of catalysts (III, IV, V)

Basicity of the catalysts was studied by performing temperature programme desorption of CO₂ (CO₂-TPD, Micromeritics Instrument AutoChem 290) using a conventional flow-through reactor with CO₂ as a probe molecule. The catalyst was first dried under helium flow, followed by adsorption of CO₂, flushing of physisorbed CO₂ and temperature programmed desorption up to the temperature of 900 °C. The eluent from the reactor was analyzed by a thermal conductivity detector. Carbon dioxide calibration was performed by pulse injection of 1 ml CO₂ and compared with the actual amount of CO₂ desorbed from the catalyst.

The acidic properties of the catalysts were determined with infrared spectroscopy (ATI Mattson FTIR) using pyridine as a probe molecule. A thin, self supported wafer of the catalyst was pressed and then placed into the FTIR-cell. The cell was evacuated and the temperature was raised to 450 °C and kept constant for 1 h. Thereafter, the temperature was decreased to 373 K and the background spectra of the sample were recorded. Pyridine was adsorbed on the sample for 30 min at 100 °C followed by desorption at 250, 350 and 450 °C for 1 h and the spectra of the sample were recorded in between every temperature ramp. The scanning was performed under vacuum at 100 °C. Spectral bands at 1545 cm⁻¹ and at 1450 cm⁻¹ were used to identify Brønsted (BAS) and Lewis (LAS) acid sites, respectively.

2.4. Activity testing

All experiments were carried out in a laboratory scale stainless steel autoclave (Parr Inc) with an inner volume of 300 ml equipped with a stirrer and an electric heater. In a standard procedure a known amount of catalyst was introduced into the reactor followed by the addition of ethanol and butylene oxide. The reactor was purged and pressurized to 4.5 MPa with CO₂ at room temperature. Subsequently, the reactor was heated and mechanically stirred constantly at the desired temperature during the reaction. After the reaction, the reactor was cooled to about 5 °C and depressurized.

For the kinetic experiments, the autoclave setup was modified by addition of a sampling line made of stainless steel equipped with a system of valves at the inlet and outlet. The sample (ca. 100 µl) trapped in the sampling line was cooled and collected slowly in a glass tube. The products in the liquid phase were analyzed by gas chromatography (Agilent Technologies, 6890N) using a capillary columns (HP-Wax 30 m x 250 µm x 0.25 µm and DB-Petro 100 m x 250 µm x 0.5 µm) and the products in the gas phase using a capillary column (HP-Plot Q + HP-Molsiv 5A 60 m x 530 µm x 33 µm) equipped with a flame ionization detector (FID). Reliability of the results has been confirmed by analysing each sample twice. The products were also indentified by means of GC-MS (Agilent Technologies, 6890N) using capillary column (DB-Petro 50 m x 200 µm x 0.5 µm).

3. Results and Discussion

3.1. Thermodynamics of direct synthesis of diethyl carbonate (II)

Thermodynamics constitutes a central branch of science that plays an important role in chemistry, physics, biology and engineering. It describes how the systems respond to the variation in their surroundings through the effects of heat, work and energy on the system. Thermodynamics allows to assess the spontaneity of each process by the Gibbs function (G) which combines enthalpy (H) and entropy (S) into a single value (Eq. (9)) and determines if chemical reaction is thermodynamically possible.

$$G(p,T) = H - TS \quad (9)$$

The understanding of the reaction thermodynamics of diethyl carbonate formation via direct route is, therefore, highly important in seeking of novel synthesis ideas both in academic investigations and practical applications.

The thermodynamic data of various substances such as ethanol, carbon dioxide, DEC and water involved in the synthesis of DEC is tabulated in Table 2.

Table 2. Thermodynamic data of various substances in the reaction (8).⁶⁰

Substance	$\Delta_f H^\theta$ (kJ/mol)	S^θ (J/mol*K)	C_p^a (J/mol* K)
DEC	-637.9	^b 412.21	^b 152.1
H ₂ O	-241.8	188.8	33.6
CO ₂	-393.5	213.8	37.1
C ₂ H ₅ OH	-234.8	281.6	65.6

^a C_p is assumed independent of temperature at 273 - 473 K; ^b value as reported in [61]

Hence, the enthalpy and the entropy of the reaction at 25 °C estimated from the $\Delta_f H^\theta$ and S^θ values amounted to:

$$\Delta_r H^\theta_{298 K} = - 16.60 \text{ kJ/mol}$$

$$\Delta_r S^\theta_{298 K} = - 175.99 \text{ J/molK}$$

Based on the obtained values free Gibbs energy can be calculated and is equal to $\Delta_r G^\theta_{298 K} = + 35.84 \text{ kJ/mol}$. Thus, it can be concluded that the reaction is exothermic and does not occur spontaneously at room temperature, meaning that the reaction towards products formation is

not favoured likewise in the case of the synthesis of dimethyl carbonate from methanol and carbon dioxide. The relative pattern of the reaction heat with the temperature is expressed by the Kirchhoff's law (Eq. (10)), whereas Gibbs energy of the reaction, at different temperatures, can be given by Gibbs – Helmholtz equation (Eq. (12)). Integration of both sides of the equation (12) transforms it to equation (13) and reveals that the value of $\Delta_r G_f^\theta$ increases with the reaction temperature. For instance, if the reaction temperature attains 100 °C (373 K), $\Delta_r G_{353\text{ K}}^\theta$ amounts to 48.89 kJ/mol, clearly indicating that the increase in the temperature is disadvantageous to the formation of DEC.

$$\Delta H_r^\theta = \Delta_r H_{298\text{ K}}^\theta + \Delta C_p(T - 298) = -21.78 + 0.0174T \quad (10)$$

for ΔC_p :

$$\Delta C_p = (152.1 + 33.6) - (2 \times 65.6 + 37.1) = 17.4 \text{ J/mol} = 0.0174 \text{ kJ/mol} \quad (11)$$

$$d\left(\frac{\Delta_r G^\theta}{T}\right) = \left[\frac{21.78 - 0.0174T}{T^2}\right]dT \quad (12)$$

$$\Delta_r G_T^\theta = \frac{T\Delta_r G_{298\text{ K}}^\theta}{298} - 21.78\left(\frac{1}{T} - \frac{1}{298}\right)T - 0.0174T \ln\left(\frac{T}{298}\right) \quad (13)$$

Considering carbon dioxide as an ideal gas, the Gibbs free energy can be also related to the pressure at constant temperature and written as follows:

$$d\Delta_r G = \Delta V dP = (V_1 - V_g) dP = -V_g dP = -\left(\frac{RT}{P}\right) dP \quad (14)$$

$$\Delta_r G_P = \Delta_r G^\theta - RT \ln\left(\frac{P}{P^\theta}\right) \quad (15)$$

Calculations on the basis of equation (15) indicate that the reaction transforms to a spontaneous one at 100 °C when the pressure of the reaction system exceeds 7.25×10^5 MPa. However, such an enormous pressure is not technically feasible and synthesis cannot occur under conventional industrial conditions. Consequently, further engineering of the reaction employing chemical or physical means is needed in order to shift the equilibrium towards the formation of products. Moreover, as can be seen from Table 3, the thermodynamic limitations in the direct DEC synthesis exclude achieving a substantial amount of diethyl carbonate with increasing temperature. The equilibrium constant K was determined from the Gibbs energy according to Equation (16).

$$\Delta_r G_T^o = -RT \ln K \quad (16)$$

$$\text{where } K = \frac{[DEC][H_2O]}{[C_2H_5OH]^2[CO_2]} \quad (17)$$

The formed amounts of DEC were calculated thereafter from Equation (17).

Table 3. Thermodynamic properties of diethyl carbonate synthesis via direct route starting from ethanol and carbon dioxide.

T (K)	353	373	423	443	473
$\Delta_r G_T^o$ (kJ/mol)	45.44	48.90	57.47	60.84	65.89
K	1.89×10^{-7}	1.42×10^{-7}	8.04×10^{-8}	6.70×10^{-8}	5.29×10^{-8}
^a DEC (mmol)	1.02	0.89	0.61	0.55	0.47

^a at constant pressure (9.3 MPa)

3.2. Effect of the dehydrating agent (II)

DEC was not formed in the reaction carried out without the catalyst concluding that direct synthesis of diethyl carbonate requires a catalyst. The reactions performed over commercial cerium oxide in the absence of butylene oxide as a dehydrating agent resulted in low yields of DEC due to the establishment of the reaction equilibrium and thermodynamic limitations (Fig. 2). Selectivity of the process can be considered 100 % since no other by-products were observed within the detection limits during the analysis of the liquid phase.

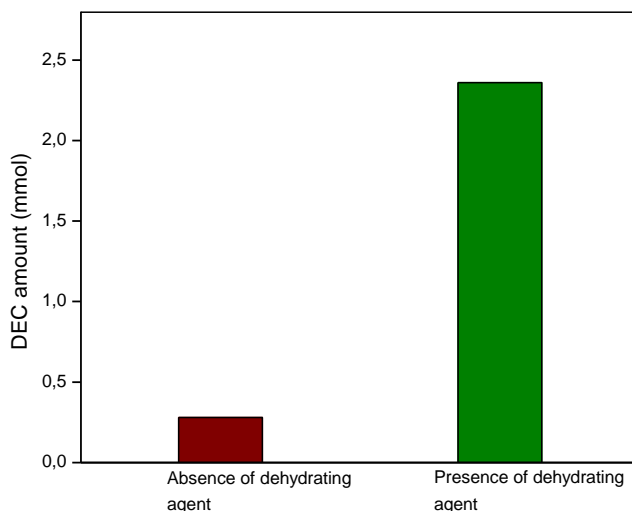


Figure 2. Product yields obtained over commercial cerium (IV) oxide catalyst. Conditions: 1g catalyst, 170 °C, 314 mmol of ethanol, 19 mmol of butylene oxide, 4.5 MPa initial CO₂ pressure, 23 h.

The performance of butylene oxide (1,2-epoxybutane) as a chemical water trap has been investigated. The apparent advantages of this high molecular weight epoxide are lower toxicity and reactivity towards ethanol and carbon dioxide in comparison to ethylene and propylene oxides, respectively. The introduction of dehydrating agent to the reaction system led to 4-fold enhancement of DEC amount than that calculated under thermodynamic limitations (0.55 mmol) in the same reaction conditions and 9-fold enhancement in the comparison to DEC amount obtained without any water removal. This indicates that water produced during the reaction reacted *in situ* with butylene oxide, simultaneously, shifting the reaction equilibrium in favour of DEC formation and suppressing thermodynamic limitations.

3.3. Kinetics and reaction network of DEC synthesis (II)

Kinetic studies of diethyl carbonate synthesis starting from ethanol and CO₂ have been carried out in the presence of butylene oxide over commercial CeO₂ to facilitate better understanding of the reaction network. A typical concentration curve of DEC reaction synthesis is depicted in Fig 3a.

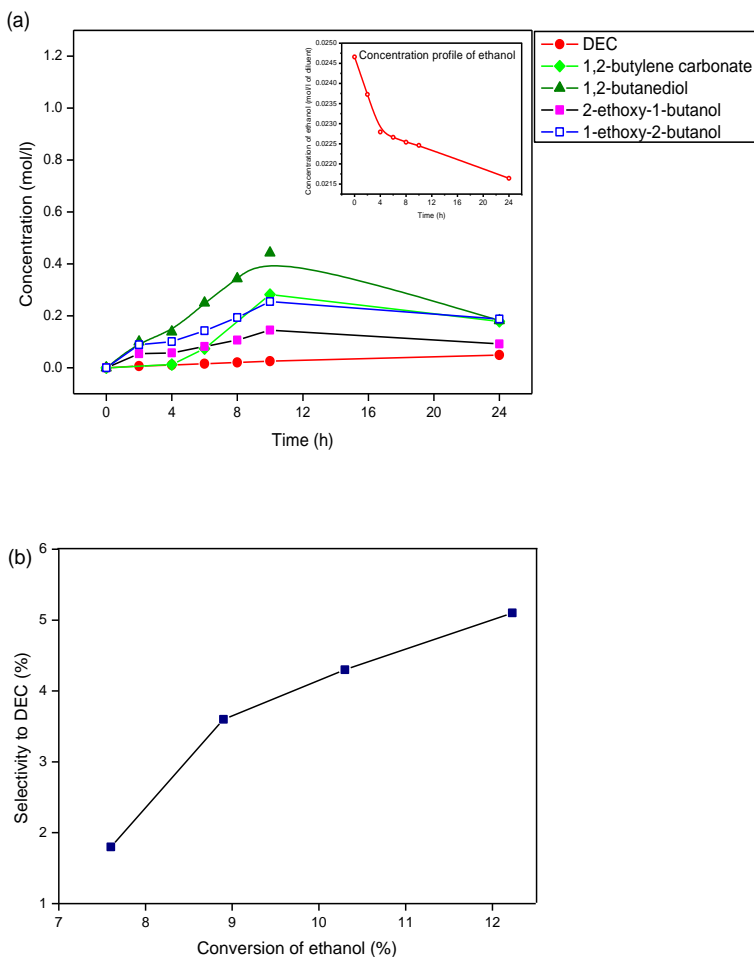


Figure 3: a) Concentration profiles of various species obtained during the synthesis of DEC from ethanol and carbon dioxide using butylene oxide as a dehydrating agent. b) Selectivity to DEC based on ethanol plotted against conversion of ethanol. Conditions: 0.5 g catalyst, 170 °C, 4.5 MPa initial CO₂ pressure, 314 mmol ethanol, 19 mmol butylene oxide.

The conversions of butylene oxide and ethanol were 98.8 % and 12.2 %, respectively. The yield of diethyl carbonate was 1 mmol after 24 h of reaction time at 170 °C and 4.5 MPa of initial CO₂ pressure. While the yield of DEC and conversion of ethanol considerably increased due to the introduction of butylene oxide into the reaction system, the selectivity of ethanol towards DEC decreased compared to the reaction carried out without water scavenger. It can be seen that 1,2-butanediol generated from the reaction between butylene oxide and water is the most dominating product after 10 h of reaction. Moreover, butylene oxide reacts with ethanol and carbon dioxide resulting in the formation of ethoxy-species (1-ethoxy-2-

butanol and 2-ethoxy-1-butanol) and cyclic butylene carbonate, respectively. Since the selectivity to DEC increases with increasing ethanol conversion (Fig. 3b) and the amount of butylene carbonate declines with time it can be concluded that diethyl carbonate synthesis proceeds via consecutive route including the cyclic butylene carbonate as an intermediate (pathway II, Fig. 4). First, butylene oxide reacts with CO₂ to produce the intermediate butylene carbonate which subsequently undergoes trans-esterification with ethanol to yield diethyl carbonate accompanied with 1,2-butanediol. Most probably this is the primary reaction that leads to DEC formation and not the reaction between ethanol and CO₂. It should also be mentioned that the high molecular weight compounds were noticeable during the analysis of the reaction mixture. It can be presumed that these compounds are formed simultaneously from dehydration of alcohols e.g. ethanol and 1,2-butanediol. The kinetic results showed also that the amount of 1,2-butanediol decreases with time. Probably, the reason for that is the formation of dibutylene glycol which was detected during the analysis by means of GC-MS. The ether is formed via dehydration of two molecules of 1,2-butanediol accompanied with water release.

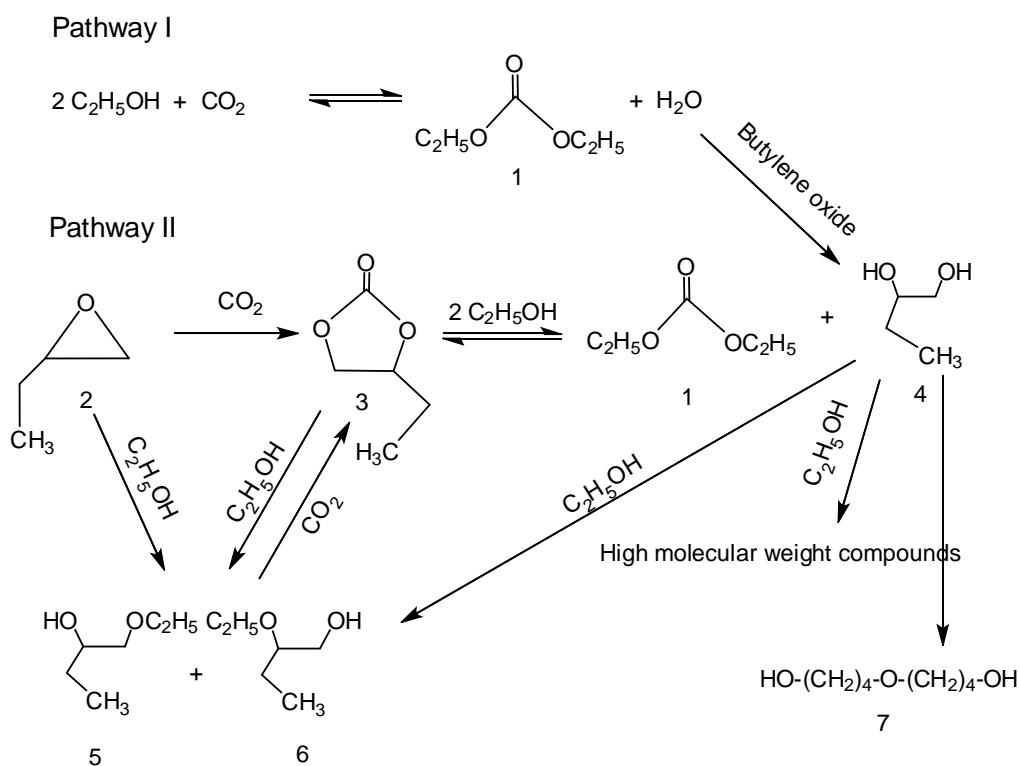


Figure 4. The reaction pathway in the synthesis of diethyl carbonate from ethanol and CO₂ using butylene oxide as the dehydrating agent. Notation: 1, DEC; 2, butylene oxide; 3, butylene carbonate; 4, 1,2-butanediol; 5, 1-ethoxy-2-butanol; 6, 2-ethoxy-1-butanol; 7, dibutylene glycol

3.4. In-house preparation and characterization of ceria and ceria-supported catalysts

3.4.1. Influence of the synthesis parameters and synthesis method on physico-chemical properties of cerium oxide (IV, V)

Loss of catalytic activity during the reaction is one of the major issues related to the operation of heterogeneous catalysis. A number of different mechanisms, both of chemical and physical nature can cause catalyst deactivation. The most common ones are catalyst poisoning, coking or fouling, sintering and phase transformation. It has been shown that commercial cerium oxide is not stable in the synthesis of DMC via direct methanol carboxylation and significantly loses catalytic activity already after the first reaction cycle.⁴⁹ The reasons for that was the reduction of specific surface area of CeO₂ during the catalysis as well as involvement of surface of CeO₂ in red-ox process with Ce⁴⁺ reduction to Ce³⁺ and concomitant methanol oxidation. Ceria synthesized applying the precipitation method, however, preserved its stability over a numerous reaction cycles yielding equal amounts of DMC.

A scientific insight to the synthesis of the catalysts via precipitation route was provided by Marcilly in 1984.⁶² The method is of significant interest since it combines the advantages of generating very pure material in an inexpensive manner as well as possesses high flexibility of the process with respect to the final product quality. Nevertheless, up to now only minor attention has been paid to the influence of the synthesis parameters during the precipitation on the physico-chemical properties of obtained cerium oxide. It is known that even subtle variations in the preparative details may result in appreciable alteration in the properties of the final catalyst. Thus, the effect of synthesis time, calcination temperature and pH of the solution on characteristics and stability of CeO₂ prepared via homogeneous precipitation was examined. It should also be noted that CeO₂ samples were prepared by varying systematically one variable at a time while maintaining all the others constant. Table 4 summarises all parameter values that have been varied during the preparation of ceria catalysts. Finally, hydrothermal synthesis of CeO₂ using supercritical water as a medium has also been applied to investigate influence of the synthesis method on resulting material.

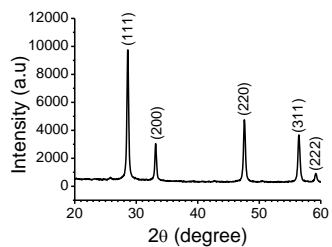
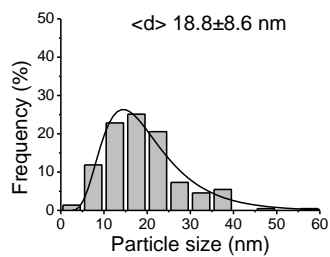
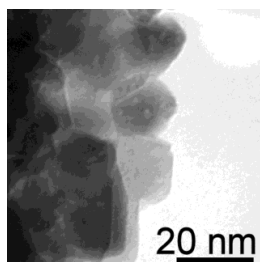
Table 4. Parameter values used during the synthesis of CeO₂ catalysts via room temperature precipitation technique.

Catalyst	Synthesis parameters										
	Synthesis time (h)					Calcination temperature (°C)			pH of the solution		
	0.5	24	50	90	144	400	600	800	9	10	11
CeO ₂ -0.5 h	×						×				×
CeO ₂ -24 h		×					×				×
CeO ₂ -50 h			×				×				×
CeO ₂ -90 h				×			×				×
CeO ₂ -144 h					×		×				×
CeO ₂ -400 °C			×			×					×
CeO ₂ -600 °C			×				×				×
CeO ₂ -800 °C			×					×			×
CeO ₂ -pH 9			×				×		×		
CeO ₂ -pH 10			×				×				×
CeO ₂ -pH 11			×				×				×

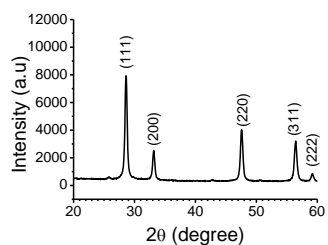
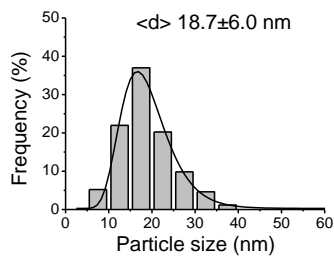
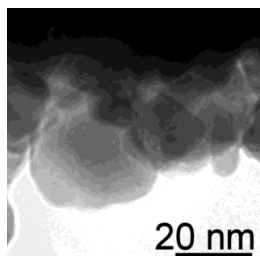
3.4.1.1. Synthesis time

A series of CeO₂ samples were synthesized at room temperature at pH of precipitation equal to 10 in a range of synthesis time between 0.5 h to 144 h and calcined at 600 °C in air for 3 h. The obtained XRD patterns and TEM images are presented in Fig. 5, where d denotes the average particle size. The XRD results show in all cases the phase pure product consisted of well-crystallized CeO₂ exhibiting in accordance with the literature^{63,64} two characteristic XRD peaks for the cubic fluorite phase at 2 theta 28.6 and 33 degrees. The particle size distribution histograms exhibit maxima for all samples, however, increase of the synthesis time of CeO₂ causes a slight decrease of the average particle size and the width of histograms become narrower in the range of 10 to 20 nm (Fig. 5e).

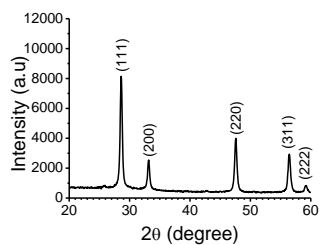
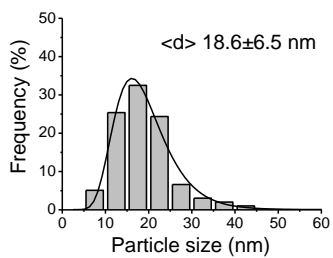
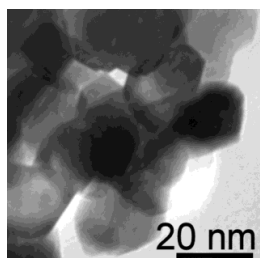
(a) CeO₂ – 0.5 h



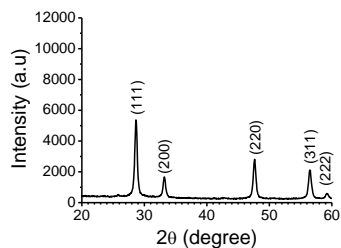
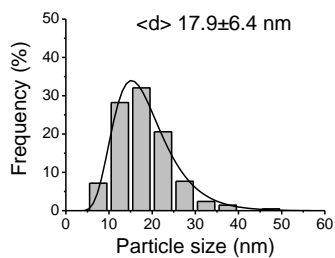
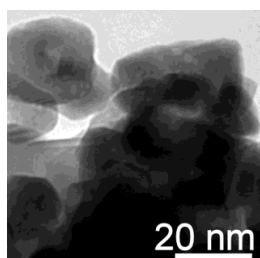
(b) CeO₂ – 24 h



(c) CeO₂ – 50 h



(d) CeO₂ – 90 h



(e) CeO₂ – 144 h

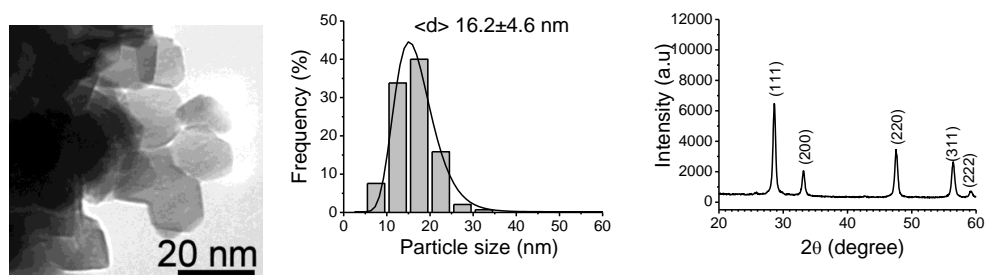


Figure 5. TEM images and XRD patterns of the CeO₂ catalysts prepared within different synthesis time: (a) CeO₂–0.5 h; (b) CeO₂–24 h; (c) CeO₂–50 h; (d) CeO₂–90 h; (e) CeO₂–144 h

In heterogeneous catalysis high specific surface area of the produced catalyst is an essential requirement for the successful implementation in commercial applications. From Table 5 it can be observed that prolonged synthesis time resulted in high specific surface area cerium oxide for samples prepared over 50 h, 90 h and 144 h, respectively. Pore size distribution of prepared powders revealed that the pore volume of CeO₂ increased substantially with the increase of the synthesis time. Additionally, preliminary results of the cluster size distribution obtained for CeO₂–0.5 h and CeO₂–144 h catalysts revealed 3-fold enhancement of the cluster size with the increase of the crystallization time. Thus, it can be speculated that high specific surface area of cerium oxide prepared at longer time is attributed to the increase of the specific pore volume of the catalysts rather than to the decrease of their particle size.

Table 5. Specific surface area and basicity of cerium oxide prepared varying synthesis time.

Catalyst	Basic sites (mmol/g)				Specific surface area (m ² /g)
	Weak (320 K–500 K)	Medium (500 K–750 K)	Strong (> 750 K)	Total basicity	
CeO ₂ -0.5 h	0.6	0.9	1.9	3.4	14
CeO ₂ - 24 h	1.6	1.9	3.8	7.3	69
CeO ₂ - 50 h	2.1	2.2	4.8	9.1	113
CeO ₂ - 90 h	1.9	2.1	3.6	7.6	123
CeO ₂ - 144 h	1.6	1.9	2.6	6.1	126

As already discussed above based on kinetic studies, the primary route of diethyl carbonate synthesis occurs via trans-esterification of butylene carbonate with ethanol (Fig. 4). It has also been reported in the open literature⁶⁵⁻⁶⁷ that solid base catalysts are preferred over acid

catalysts owing to the high yields of linear carbonate produced and reduction of side reactions. Therefore, during this work special consideration has been paid on the basicity of in-house synthesized cerium oxide. The amount of basic sites present on the surface of CeO_2 prepared varying synthesis time was determined by means of temperature programme desorption (TPD) using carbon dioxide as a probe molecule and results are tabulated in Table 5. The amount of weak, medium and strong basic sites was estimated from the area under their TPD curves for the temperature range of 320 K – 500 K, 500 K – 750 K and > 750 K, respectively. The total amount of CO_2 desorption from CeO_2 with 0.5 h synthesis time is very low indicating a lack of basic sites on its surface. This can be ascribed to very low specific surface area of this material. As expected, increase of the specific surface area of cerium oxide prepared within prolonged synthesis time (24 h, 50 h, 90 h and 144 h) is accompanied with the enlargement of the basicity of the materials with respect to CeO_2 -0.5 h. It should be mentioned that pH of the precipitate was manually adjusted throughout the cerium oxide preparation and during the long-term synthesis a number of pH declines were observed which could, in turn, have an effect on the surface basicity of the cerium oxide catalysts prepared in 90 h and 144 h synthesis time. Among all prepared samples, CeO_2 -50 h exhibited the highest amount of total basic sites, hence 50 h was chosen as an optimum synthesis time of cerium oxide in this group of the prepared materials.

Another important characteristics of each catalyst is its surface chemistry. Therefore, in order to determine the surface chemical state of Ce in cerium oxide samples synthesized by varying the synthesis time, X-ray photoelectron spectroscopy (XPS) analysis was conducted. The Ce 3d spectra collected for CeO_2 -0.5 h and CeO_2 -144 h samples are shown in Fig. 6. Similar spectra have been observed for cerium oxide samples with 24 h, 50 h and 90 h of synthesis time as well as for CeO_2 prepared at different pH of precipitation and calcined at various temperatures.

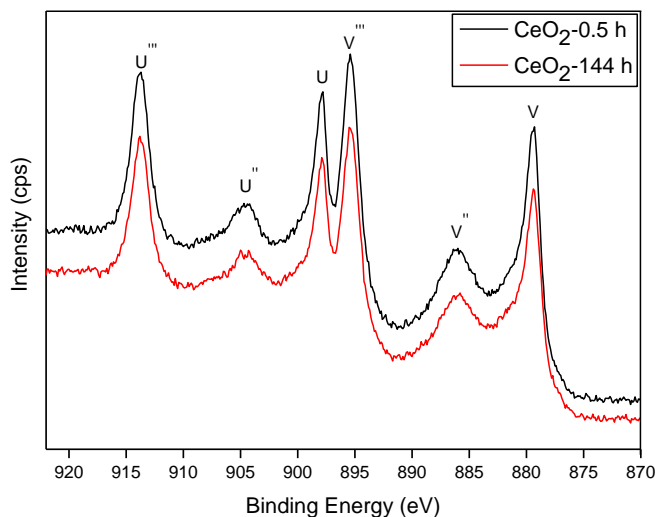


Figure 6. XPS analysis spectra Ce 3d of CeO₂–0.5 h and CeO₂–144 h samples.

The labels follow the convention established in ref. [68] where V and U indicate the spin-orbit coupling 3d_{5/2} and 3d_{3/2}, respectively. The satellite peak U''' associated to the Ce 3d_{3/2} is a characteristic of the presence of tetravalent Ce (Ce⁴⁺ ions) in ceria compounds which is in good agreement with other literature reports.⁶⁹⁻⁷¹ The highest binding energy peaks, U''' and V''' located at about 915 eV and 895 eV, respectively, are the result of a Ce 3d⁹ 4f⁰ O 2p⁶ final state. The peaks with the lowest binding energy U, V, U'', V'' located at about 898 eV, 878 eV, 904 eV and 885 eV, respectively, can be ascribed to Ce 3d⁹4f² O 2p⁴ and Ce 3d⁹4f¹ O 2p⁵ final states.

3.4.1.2. Calcination temperature

CeO₂ powder with 50 h synthesis time was calcined at three different temperatures 400 °C, 600 °C and 800 °C for 3 h in air. Analogously to the literature^{72,73} increase of the calcination temperature enhanced the crystallinity which was evidenced by the substantial growth of the crystal size of cerium oxide calcined at 600 °C and 800 °C (Table 6). Furthermore, it can be noticed that the average crystal size obtained by XRD is in good agreement with TEM particle size which indicates that the presence of agglomerates in CeO₂ particles can be neglected. Cerium oxide calcined at 400 °C exhibited the highest total amount of basic sites on its surface, whereas for CeO₂–600 °C and CeO₂–800 °C the total amount of

basic sites notably declined. It can be attributed to the decrease of the specific surface area of cerium oxide during the calcination at higher temperatures.

Table 6. Specific surface area, crystal sizes and total amount of basic sites of cerium oxide calcined at various temperatures.

Catalyst	Specific surface area BET (m ² /g)	Particle size TEM (nm)	Crystal size XRD (nm)	Total basicity (mmol/g)
CeO ₂ —400 °C	143	10	14	12
CeO ₂ —600 °C	113	19	22	9
CeO ₂ —800 °C	103	33	36	4

3.4.1.3. The pH of the reaction solution

The synthesis of cerium oxide at different pH of alkaline solution such as pH 9, 10 and 11 within 50 h of synthesis time was performed. Afterwards, the materials underwent calcination at 600 °C for 3 h. No significant difference in morphology of the prepared cerium oxide catalysts with varying solution pH was observed and spherical crystals of CeO₂ were obtained. All cerium oxide materials prepared within this series exhibited high specific surface area (Table 7). Precipitation carried out at pH 11 resulted in cerium oxide possessing the highest specific surface area, 139 m²/g, among all CeO₂ catalysts prepared within this work.

Table 7. Specific surface area, total amount of Brønsted and Lewis acid sites and total amount of basic sites of cerium oxide powders prepared at different pH of the reaction solution.

Catalyst	Specific surface area (m ² /g)	Total Brønsted acid sites (μmol/g)	Total Lewis acid sites (μmol/g)	Total basicity (mmol/g)
CeO ₂ —pH 9	123	110	14	6
CeO ₂ —pH 10	113	n.d.	n.d.	9
CeO ₂ —pH 11	139	84	17	8

n.d. - not determined

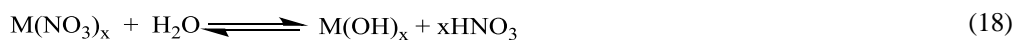
It is well-recognized that both acid and basic sites are simultaneously present on the solid surfaces which consist of coordinatively unsaturated cations (Mⁿ⁺), oxide (O²⁻) ions and residual OH-groups that often remain even after the surface purification. The amount and nature of basic and acid sites of cerium oxide synthesized under different pH was investigated, respectively, by means of CO₂-TPD and Fourier transform infrared spectroscopy (FTIR) using pyridine as a probe molecule. As previously, weak, medium and strong type of

basic sites were determined. The total amount of basic sites passes through a maximum at pH 10 and slightly decreases for CeO₂ prepared at pH 11 of the precipitate (Table 7). Concerning the analysis of surface acid sites, coordination of pyridine molecules to the surface and formation of Lewis acid sites is the indication of exposure of coordinatively unsaturated metal atoms of the surface. The protonation of pyridine into pyridinium ions results, in turn, in the creation of Brønsted acid sites which are indicative of the availability of the surface OH-groups and coordinated H₂O molecules. The comparison of two powders prepared under final pH 9 and pH 11 of the reaction solution shows a very weak acidic character of cerium oxide in agreement with other literature reports.^{74,75} The total amount of Brønsted acid sites decreased with an increase in the pH obviously due to a higher concentration of the hydroxyl groups present on the surface of the material synthesized at pH 11. The Lewis acidity, in turn, appeared to be weaker than the Brønsted as also reported elsewhere.⁷⁶

3.4.1.4. Effect of the synthesis method

The continuous hydrothermal synthesis method using supercritical water as a medium was employed to prepare cerium oxide. Supercritical water allows controlling of the crystal phase, morphology and particle size by variation of solvent properties such as density of water and dielectric constant with a change of pressure and temperature. Lower density and dielectric constant of water promotes the nucleation and crystal growth of inorganic nanoparticles.^{77,78} It gives as well a beneficial reaction field for particle formation due to enhancement of the reaction rate and large super-saturation.

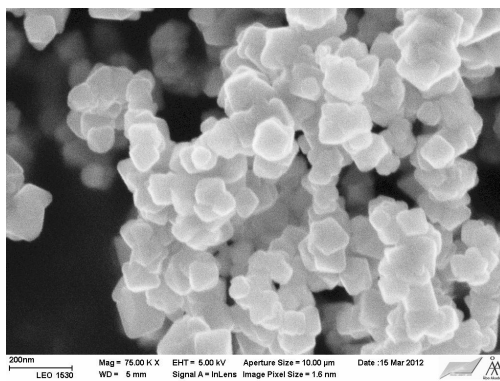
Hydrothermal synthesis mechanism consists of two steps of metal oxide generation from metal nitrate solution. First hydrated metal ions are hydrolyzed to metal hydroxide (Eq. (18)) and afterwards through a dehydration step metal hydroxide proceeds to precipitate as metal oxide (Eq.(19)).



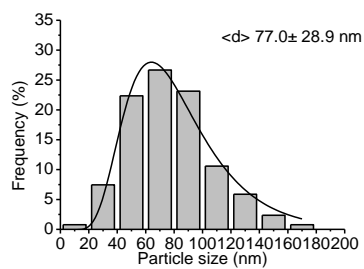
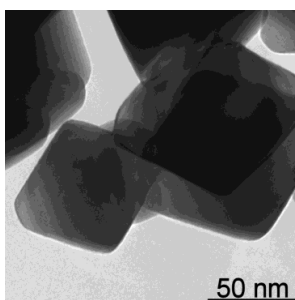
Thus, it was thought to be valuable to compare the morphology and surface properties of CeO₂ catalysts produced via the hydrothermal method and the conventional precipitation technique. Among CeO₂ powders synthesized by homogeneous precipitation the one with the highest specific surface area has been selected as a reference for the comparison. SEM and

TEM images as well as particle size distributions of cerium oxide materials are shown in Figure 7.

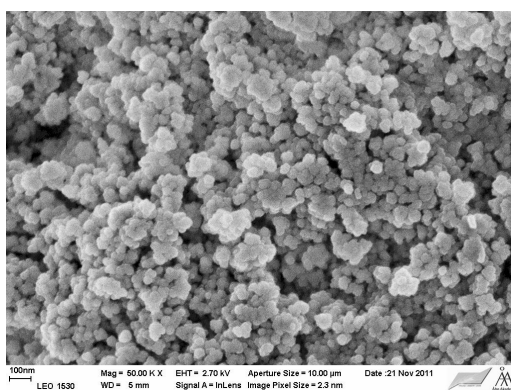
(a)



(b)



(c)



(d)

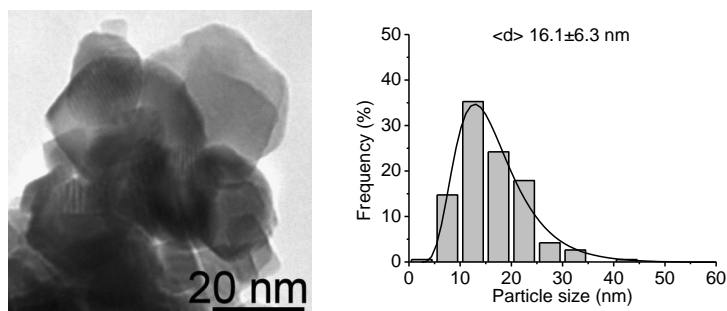


Figure 7. Comparison of the morphology of cerium oxide prepared using various methods.(a) SEM image, (b) TEM image and particle size distribution of CeO₂ prepared via hydrothermal method; (c) SEM image, (d) TEM image and particle size distribution of CeO₂ prepared via precipitation method.

A distinct difference in the morphology and shape of crystals can be observed from the comparison of two samples obtained applying various synthesis methods. Cerium oxide prepared by continuous hydrothermal method exhibits particles with well-developed crystal faces for non-spherical octahedral-like shapes (Fig. 7a) whereas CeO₂ prepared by means of precipitation technique consists of uniform spherical particles (Fig. 7c). The particle size distribution histograms exhibit maxima in both cases (Fig. 7b and d). Nevertheless, it can be clearly seen that cerium oxide synthesized via precipitation represents a more homogeneous material than the corresponding one prepared on hydrothermal way since the width of the histogram is narrower and majority of the particles are in a range of 10 to 20 nm. Besides, crystallite sizes of CeO₂ catalysts determined by X-ray broadening according to the Scherrer equation confirm the presence of larger crystals in hydrothermally obtained cerium oxide (Table 8). As expected, consequently this fact had a direct effect on the specific surface area of the catalyst, hence CeO₂ prepared via hydrothermal synthesis shows a very low surface area. Analogously, basicity of the catalyst follows the same trend and subsequently a low amount of basic sites can be found on its surface.

Table 8. Specific surface area, crystal size and basicity of cerium oxide catalysts prepared by various synthesis methods.

Catalyst	Total basicity (mmol/g)	Crystal size determined by XRD (nm)	Specific surface area (m ² /g)
CeO ₂ (hydrothermal method)	1.5	130	6
CeO ₂ (precipitation method)	8	18	139

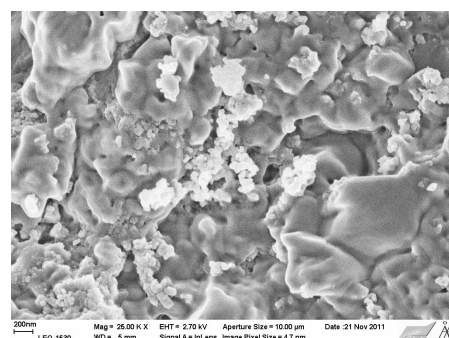
3.4.2. Physico-chemical properties of ceria-supported catalysts (III, V)

Supported catalysts constitute a widespread type of heterogeneous catalysts wherein a highly dispersed component is located on the surface of a porous support. Particularly in terms of costly materials such as noble metals it is an important approach since small particles represent a larger surface-to-volume ratio and therefore better utilization of the metal in terms of catalytic performance can be achieved. Following this trail the interest has arisen in dispersing ceria onto high surface area support in order to combine its catalytic properties with high surface area and thermo-mechanical stability of a support. Furthermore, the aim was to establish the role of the base metal on the surface characteristics of a support. Mesoporous silicas MCM-41 and SBA-15 as well as silica gel powder (SiO_2) were used as the supports. 16 and 32 wt % ceria were deposited over MCM-41 and SiO_2 whereas SBA-15 was modified with 20 wt % ceria. SEM images of as-prepared materials are shown in Figure 8. Relatively well-dispersed ceria can be observed on 16 wt % CeO_2 -MCM-41 material in contrast to its 32 wt % counterpart where no clear ceria particles can be distinguished and certain destruction likely due to high loading of CeO_2 is apparent. In turn, ceria supported on SiO_2 in both cases exhibits uniform morphology. Long tube shaped particles of SBA-15 can be seen in Figure 8e, however turned to be very challenging to differentiate separate cerium oxide particles although EDX analysis (Fig. 8f) results confirmed the presence of ceria in 20 wt % CeO_2 -SBA-15. Most probably cerium oxide particles are very small and well dispersed or alternatively locating inside the SBA-15 matrix. It is noteworthy, Ce-O bond length is longer than that of Si-O which may apply incorporation of cerium ions into silicate framework and creation of cerium oxide high-disparity species on the surface of SBA-15.⁷⁹

(a)



(b)



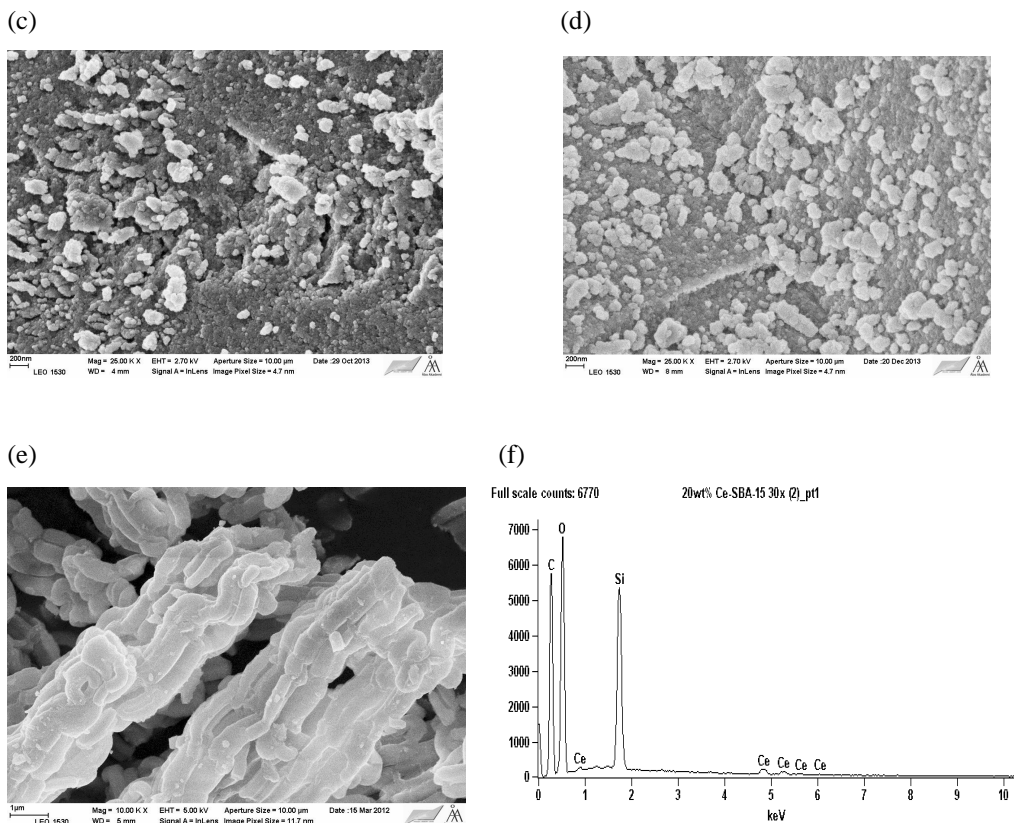


Figure 8. SEM images of ceria-supported catalysts. (a) 16 wt % CeO₂-MCM-41, (b) 32 wt % CeO₂-MCM-41, (c) 16 wt % CeO₂-SiO₂, (d) 32 wt % CeO₂-SiO₂, (e) 20 wt % CeO₂-SBA-15, (f) EDX analysis of 20 wt % CeO₂-SBA-15

X-ray powder diffraction analysis conducted on ceria-supported catalysts provided information on crystallinity of cerium oxide deposited on the porous supports (Fig. 9). The major peak of MCM-41 mesoporous material at 2 theta value of 0.2 to 11 degrees together with characteristic for ceria cubic structure peaks at 2 theta values of 28.6 and 33 degrees⁸⁰ are observable for 16 wt % CeO₂-MCM-41 catalyst. For 32 wt % CeO₂-MCM-41 material, in turn, ceria was not observable most likely due to partial distortion of the MCM-41 mesoporous structure as already seen in the SEM image.

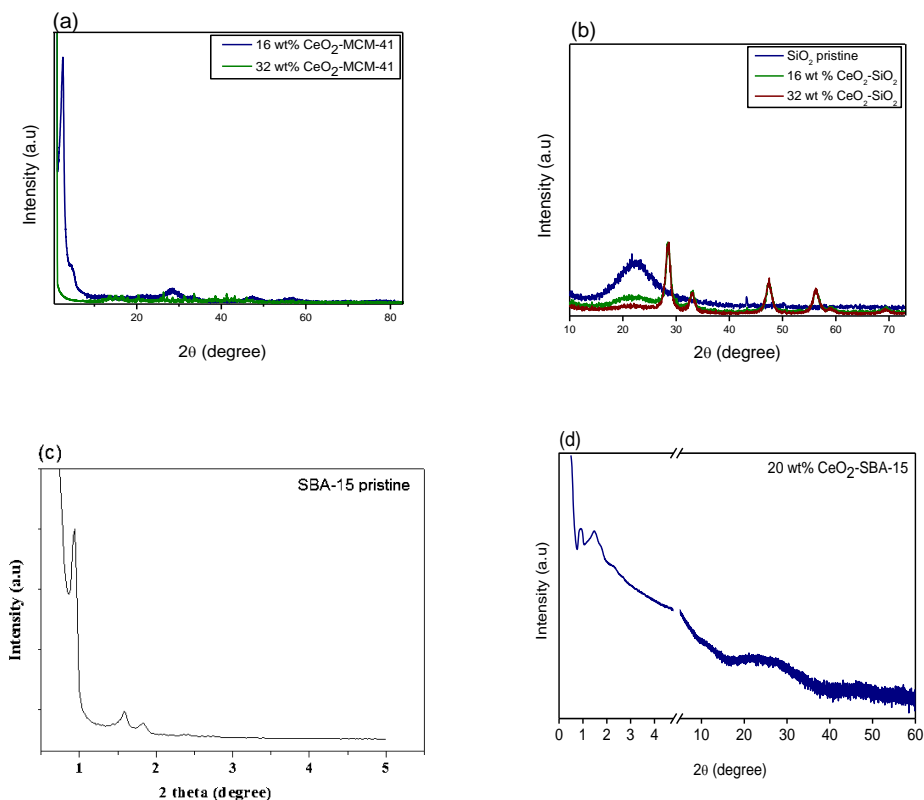


Figure 9. XRD patterns of ceria-supported catalysts. (a) 16 wt % CeO₂-MCM-41 and 32 wt % CeO₂-MCM-41; (b) SiO₂ pristine, 16 wt % CeO₂-SiO₂ and 32 wt % CeO₂-SiO₂; (c) SBA-15 pristine; (d) 20 wt% CeO₂-SBA-15

Diffraction patterns specific to cubic CeO₂ crystalline phase can be identified in both ceria-SiO₂ catalysts. The diffraction intensities of 16 wt % CeO₂-SiO₂ and 32 wt % CeO₂-SiO₂ are similar indicating comparable average crystal size and/or crystallinity of samples. In addition, a broad peak of pure silica at around 2 theta value 23 degree confirms an amorphous character of SiO₂ support. It can be noticed that silica peak intensity of as-synthesized composite particles is much weaker than that of the pure SiO₂. In correspondence to the literature this is because SiO₂ particles may be well coated with ceria and the outer CeO₂ particles may prevent the diffraction of inner SiO₂ to some degree.⁸¹ XRD pattern of pure SBA-15 (Fig. 9c) shows the diffraction peaks characteristic for *p6mm* hexagonal lattice symmetry of SBA-15 at 2 theta values 0.99, 1.63 and 1.86 degree confirming ordered mesoporous structure of SBA-15.^{80,82} It can be seen from Figure 9d that mesoporous structure of SBA-15 is retained upon deposition of ceria, however, cerium oxide peaks are not visible in XRD pattern of 20 wt%

CeO₂-SBA-15. Nonetheless, as mentioned above the presence of ceria was confirmed by EDX analysis as well as indirectly shown by the decrease of the specific surface area of CeO₂-SBA-15 compared to that of parent material, since the BET specific surface area of pure SBA-15 material was 845 m²/g and it dropped after ceria loading to 598 m²/g.

The temperature programmed desorption profiles of CO₂ for the supported-ceria catalysts are depicted in Figure 10 and quantified in Table 9. As previously, three types of basic sites can be differentiated depending on the strength of carbon dioxide bonding to the surface of the catalysts.

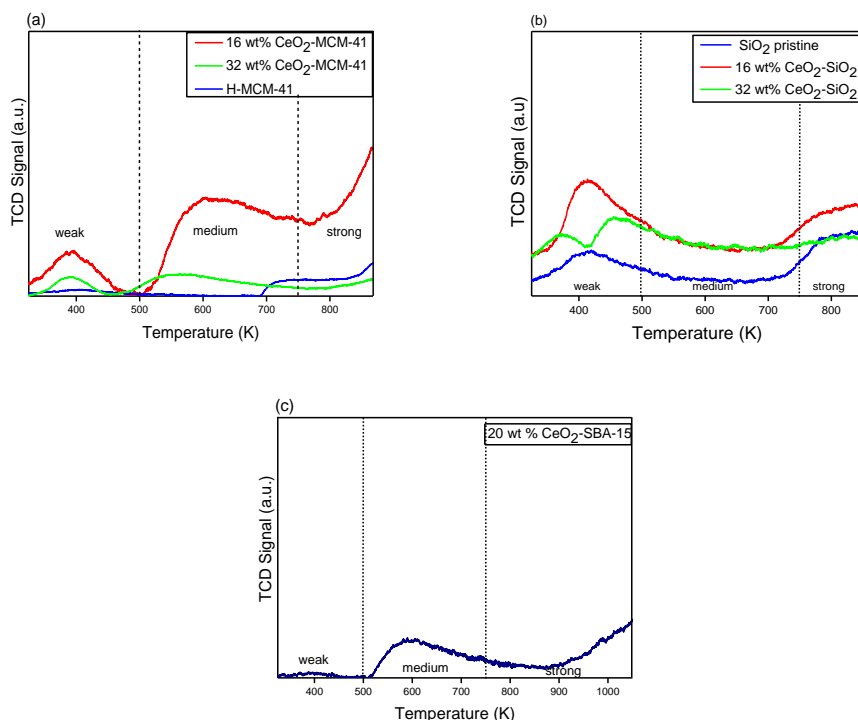


Figure 10. CO₂-TPD profiles of ceria-supported catalysts.

It can be seen from Figure 10a that the total amount of CO₂ desorption from H-MCM-41 is very low, indicating the lack of basic sites on its surface. Likewise SiO₂ exhibited low total alkalinity. The reason for higher total amount of basic sites of pure H-MCM-41 comparing to SiO₂ is undoubtedly notable variation in the specific surface area of these materials (Table 9).

Table 9. Specific surface area and total basicity of the ceria-supported catalysts.

Catalyst	Specific surface area (m ² /g)	Total basicity (mmol/g)
H-MCM-41	904	1.3
16 wt% CeO ₂ -MCM-41	852	16
32 wt% CeO ₂ -MCM-41	384	2.5
SiO ₂	389	0.7
16 wt% CeO ₂ -SiO ₂	325	2.9
32 wt% CeO ₂ -SiO ₂	211	2.2
20 wt% CeO ₂ -SBA-15	598	4.4

Incorporation of ceria into MCM-41 and SiO₂ supports resulted in the considerable increase of the total basicity of carrier materials. Noteworthy, 32 wt % CeO₂-MCM-41 showed much lower amount of basic sites than 16 wt % CeO₂-MCM-41 most probably, as discussed above, due to high ceria loading. It has been reported that when La₂O₃ loading on mesoporous Si-MCM-41 was above 10 wt % the specific surface area decreased followed by the decrease in the basicity of the material.⁸³ The same trend can be observed in the case of CeO₂ supported on silica gel powder where 32 wt % loading of ceria resulted in lowering of the surface area and alkalinity of the catalyst. The second highest basicity among this series of ceria based catalysts is represented by 20 wt % CeO₂-SBA-15. From CO₂-TPD profile (Fig. 10c) the occurrence of medium and strong basic sites with the lack of weak strength basicity is apparent. XPS analysis was performed in order to obtain additional information about the structural properties of cerium oxide deposited on silicate supports (Figure 11). The results confirmed presence of Ce⁴⁺ ions alone in 20 wt % CeO₂-SBA-15 and concurrently the majority of tetravalent Ce ions (79 %) was observed in 16 wt % CeO₂-SiO₂. In ceria modified MCM-41 mesoporous materials, 66 % of trivalent Ce was determined in 32 wt % CeO₂-MCM-41 and 46 % in its 16 wt % counterpart. The presence of only Ce⁴⁺ in SBA-15 supported ceria may be attributed to the thicker pore walls and larger pore size of SBA-15 in comparison to MCM-41.⁸⁴

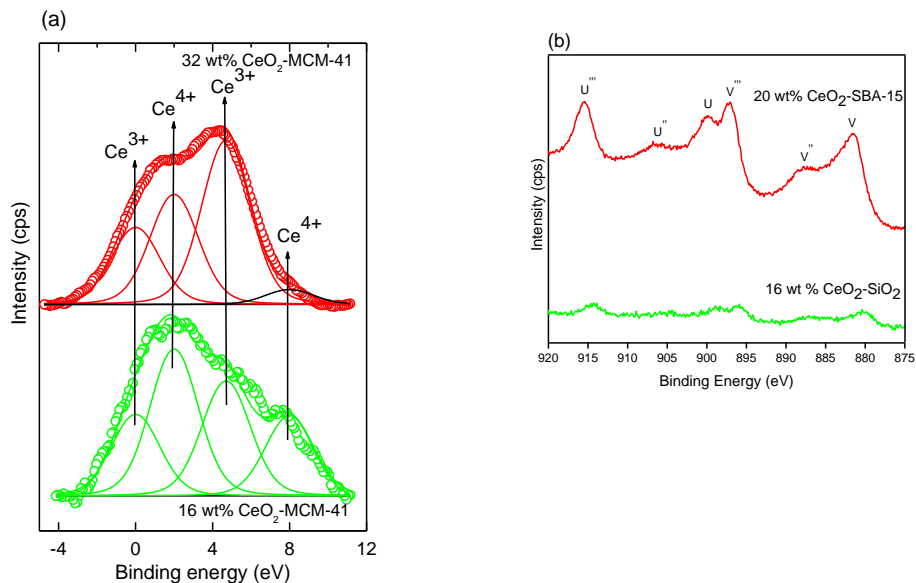


Figure 11. XPS analysis spectra Ce 3d of ceria modified MCM-41 catalysts (a) and 16 wt % CeO₂-SiO₂ and 20 wt % CeO₂-SBA-15 (b) samples.

3.5. Comparison of the catalytic activities of ceria and ceria-supported catalysts

Catalytic properties of in-house synthesized ceria and ceria-modified silica catalysts have been evaluated in the synthesis of diethyl carbonate starting from inexpensive and renewable resources CO₂ and ethanol with the aid of butylene oxide as a water trap. It is worth to mention that no research on the influence of the synthesis method and preparation parameters during CeO₂ synthesis on its catalytic properties in DEC formation has been found in the open literature. Moreover, ceria-supported on porous MCM-41, SBA-15 and silica gel catalysts with varied ceria loading were applied for the first time in CO₂ transformation to diethyl carbonate.

3.5.1. Influence of the synthesis parameters and synthesis method on catalytic activity of cerium oxide (IV, V)

Appreciable variations of CeO₂ catalytic properties were observed upon changes of the synthesis time, calcination temperature and pH of the media (Fig. 12). As already described above, the basicity of the catalyst seems to have a straightforward effect on the catalytic

activity of the material. Moreover, tuning the catalyst properties towards an enhancement of its basicity could be a key for the increase of diethyl carbonate yield and selectivity.

Figure 12 shows the dependence of CeO₂ catalytic activity and the amount of basic sites as a function of the selected synthesis parameter.

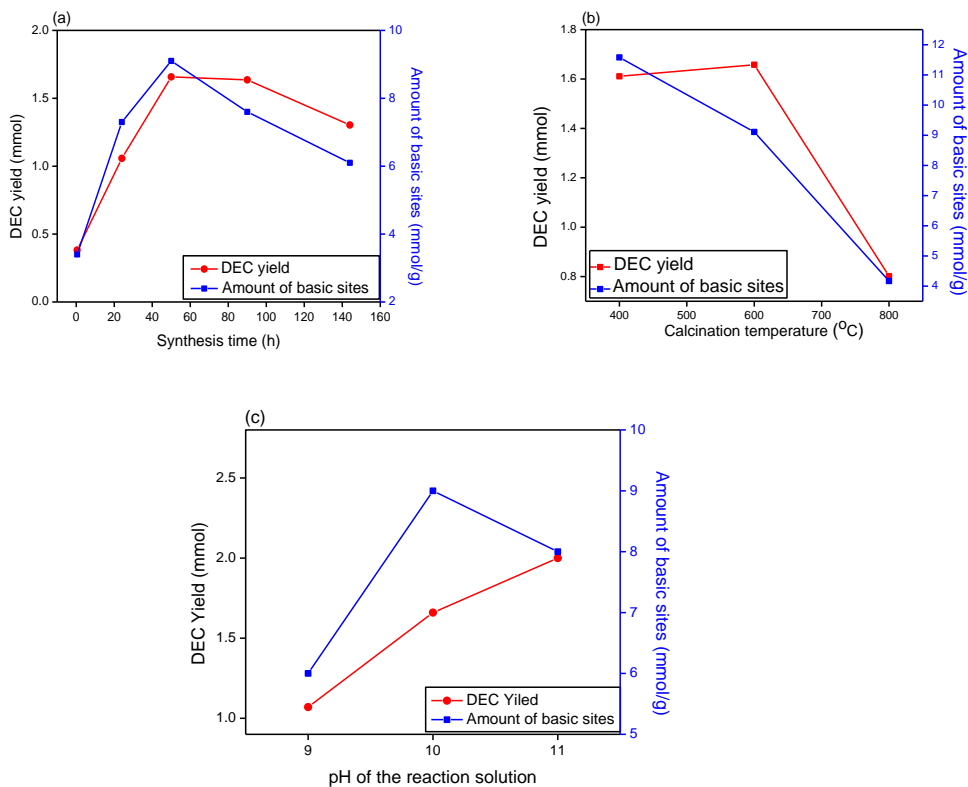


Figure 12. Diethyl carbonate yield as a function of cerium oxide preparation variables (a) synthesis time, (b) calcination temperature, (c) pH of the reaction solution. Reaction conditions: 1 g CeO₂ catalyst, 4.5 MPa initial CO₂ pressure, 314 mmol ethanol, 19 mmol butylene oxide, 25 h, 180 °C, *ca.* 700 rpm.

CeO₂ prepared within 0.5 h demonstrated the lowest activity towards DEC among ceria catalysts prepared via homogeneous precipitation which can be attributed to the very low specific surface area (Table 5, Section 3.4.1.1.) of the material. Concurrently, as can be seen from Fig. 12a surface basicity of CeO₂–0.5 h is the lowest compared to other powders synthesized within this series which subsequently had an impact on its low catalytic activity. Prolonged synthesis time of CeO₂ yielded in the enhanced amount of DEC produced due to the enlargement of the catalyst basicity. The reaction performed over cerium oxide prepared within 50 h resulted in the highest yield of DEC formed. It can be noted that CeO₂–50 h

exhibits the highest number of basic sites present on its surface that are the active sites of DEC synthesis. Thereafter, a slight decline can be observed for CeO₂–90 h and CeO₂–144 h, respectively. The reason of such behaviour can be explained by the decrease of the amount of basic sites in comparison to CeO₂–50 h. In accordance to the literature,^{49,85} an increase in the calcination temperature (Fig. 12b) initially resulted in the increased amount of diethyl carbonate formed followed by a distinct decrease of DEC yield for the catalyst calcined at 800 °C. The obvious cause of catalytic activity loss for CeO₂–800 °C was the decline in the number of basic sites with the increase of the calcination temperature. Similarly, noticeable differences in cerium oxide catalytic activity could be seen for the catalysts prepared under different pH of the reaction solution (Fig. 12c). The amount of DEC increased with the increase of the reaction pH, eventually resulting in the highest yield of DEC (2 mmol) obtained over CeO₂–pH 11 at reaction temperature 180 °C, 9 MPa of total final pressure and 25 h reaction time. The conversion of ethanol was 25 %. Despite a slightly lower amount of basic sites present on CeO₂–pH 11 surface in comparison to CeO₂–pH 10 catalyst, catalytic activity of CeO₂–pH 11 was high which can be evidently attributed to the uncommon for cerium oxide high specific surface area (139 m²/g). No substantial change in the selectivity of ethanol was observed upon variation of ceria properties applying different synthesis parameters. It has been reported that modification of zirconium oxide with KCl and K₂CO₃ improved selectivity of methanol conversion towards dimethyl carbonate in one-pot synthesis starting from menthol, CO₂ and butylene oxide.^{55,86} Therefore, addition of promoters to cerium oxide could be considered as a subsequent approach in diethyl carbonate synthesis for achieving high DEC selectivity.

Stability of each heterogeneous catalyst is a crucial characteristic that has a direct effect on its successful implementation. As discussed above, it has been proven that the catalytic performance of a commercial cerium oxide substantially declines already after the first reaction cycle. Hence, stability tests of the best performing CeO₂–pH 11 were conducted. The catalyst was recovered by filtration, dried at room temperature and reused in a new reaction system fed with anhydrous ethanol. In two consecutive runs the amount of diethyl carbonate produced was the same as over fresh CeO₂–pH 11 meaning that the catalyst can be efficiently recycled preserving its catalytic activity. Moreover, prolonged reaction time up to 94 h did not reveal any catalyst deactivation since the yield of DEC continuously increased throughout the experiment.

Influence of the synthesis method on the catalytic activity of cerium oxide was evaluated based on CeO₂ prepared applying continuous hydrothermal synthesis using supercritical

water. As expected, a low specific surface area and basicity of the catalyst (Table 8, Section 3.4.1.4.) affected its catalytic performance and only 0.3 mmol of DEC was generated under 180 °C, 25 h and 9 MPa of the total final pressure. The conversion of ethanol was 10 %. This implies that hydrothermally prepared CeO₂ yielded merely 15 % of DEC which was obtained using the precipitated catalyst.

3.5.2. Catalytic activities of ceria-supported catalysts (V)

Application of the parent mesoporous material MCM-41 and silica gel did not exhibit any catalytic activity towards DEC indicating a lack of active sites necessary for its generation and emphasising importance of these materials to be functionalized mostly as supports in the heterogeneous catalysis. Surface modification of mesoporous silicas and silica gel with cerium oxide resulted in creation of active sites for synthesis of the desired product and different catalytic properties of the catalysts could be observed (Fig. 13). Catalytic tests carried out over 32 wt % CeO₂-MCM-41 and 32 wt % CeO₂-SiO₂ yielded the least amount of DEC 0.06 and 0.08 mmol per mmol of cerium oxide, respectively. Presumably, the reason for that is the high ceria loading which consequently led to the decrease of specific surface area and basicity of the catalysts and in the case of 32 wt % CeO₂-MCM-41 to certain destruction of the structure of MCM-41 composite material. In turn, 16 wt % CeO₂-MCM-41 and 16 wt % CeO₂-SiO₂ showed higher catalytic activity than their counterparts with 32 wt % CeO₂ loading and the latter one appeared to be the second most active after 20 wt % CeO₂-SBA-15 among all ceria-supported catalysts.

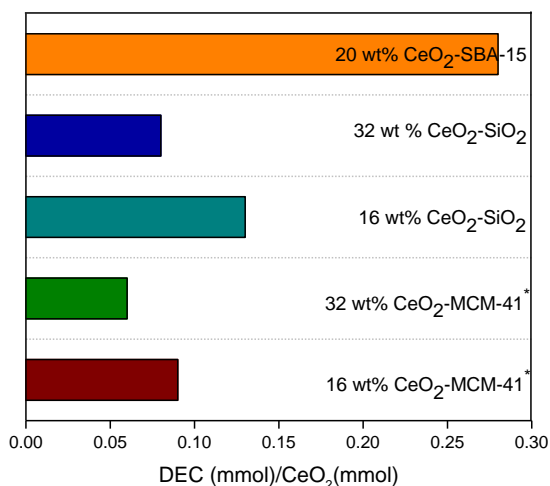


Figure 13. Comparison of catalytic activities of ceria-supported catalysts in diethyl carbonate synthesis. Reaction condition: 1 g CeO₂ catalyst, 4.5 MPa initial CO₂ pressure, 314 mmol ethanol, 19 mmol butylene oxide, 25 h, 180 °C, *ca.* 700 rpm. *For ceria-supported on MCM-41 catalysts reaction temperature 170 °C and reaction time 23 h.

Improved catalytic performance of 20 wt % ceria immobilized on mesoporous SBA-15 comparing to 16 wt % ceria supported on silica gel is obviously due to higher ceria loading on SBA-15 as well as greater specific surface area and basicity of the catalyst (Table 9, Section 3.4.2.). On the other hand, although 16 wt % CeO₂-MCM-41 possesses 3.6 times higher amount of basic sites and over 1.4 times higher specific surface area than 20 wt % CeO₂-SBA-15 the amount of DEC produced is lower than over ceria-supported on SBA-15. This demonstrates that both basicity and dispersion of ceria on the support are very important factors applying this type of materials in one-pot synthesis of DEC starting from ethanol, CO₂ and butylene oxide. The average crystal size of 16 wt % ceria deposited onto MCM-41 surface determined from the Scherrer's formula was 2.7 nm. Therefore, most probably particles of this size were unable to fit into the pores of MCM-41, which have average pore diameter 1.8-2 nm.⁸⁷ This implies that majority of cerium oxide must be located on the outer surface of the mesoporous silica support and as can be seen from Figure 8a agglomerating in a variable size aggregates. Instead, for 20 wt % CeO₂-SBA-15 no indication for the presence of ceria in SEM and TEM images as well as no evidence of crystalline CeO₂ in XRD analysis suggests that ceria is well dispersed over the support surface which accordingly might have an influence on high catalytic activity of the material. Furthermore, comparison of 20 wt % CeO₂-SBA-15 and the best performing CeO₂ catalyst prepared applying the precipitation technique shows that CeO₂-pH 11 produces 0.34 mmol of diethyl carbonate per mmol of CeO₂ which constitutes to 18 % more DEC formed than over 20 wt % CeO₂-SBA-15 under the same reaction conditions. This implies that SBA-15 modified with cerium oxide has a great potential to be implemented as a highly active catalyst in the one-pot synthesis of DEC, thus further studies on this material ceria material should be carried out.

4. Conclusions

The subject of this study was carbon dioxide transformation to diethyl carbonate via novel synthesis method starting from inexpensive, renewable and non-toxic ethanol and CO₂. Detailed thermodynamic calculations revealed that the reaction is exothermic and non-spontaneous at room temperature. Further, the co-produced water easily shifts the reaction equilibrium towards reactants. Therefore, a new method of *in-situ* dehydration was proposed by introduction of butylene oxide to the reaction system as a chemical water trap. A 9-fold enhancement of DEC yield was achieved over butylene oxide when compared to the synthetic method without any water removal. This result showed that butylene oxide exhibits water-capturing properties under employed reaction conditions which subsequently resulted in the suppression of the thermodynamic limitations, thereby shifting the reaction equilibrium towards the desired product. Cerium oxide exhibited catalytic activity in one-pot synthesis of DEC starting from ethanol, CO₂ and butylene oxide.

For the first time, kinetic studies were conducted for the synthesis of diethyl carbonate starting from CO₂ and ethanol using butylene oxide as the water scavenger over commercial CeO₂ in order to facilitate better understanding of the reaction network. It has been observed that the reaction proceeds via a consecutive route involving cyclic butylene carbonate as an intermediate that is formed from the reaction between carbon dioxide and butylene oxide. Subsequently butylene carbonate undergoes trans-esterification with ethanol to produce diethyl carbonate accompanied with 1,2-butanediol formation.

Room temperature precipitation technique was applied for the in-house synthesis of CeO₂. The emphasis was put on the determination of the influence of the synthesis parameters on the properties of the resulting materials, which up to date has not been intensively studied and reported in the open literature. In particular, the influence of the synthesis time, calcination temperature and pH of the solution on the physico-chemical and catalytic characteristics of CeO₂ catalysts was carefully examined. X-ray powder diffraction results revealed that in all cases phase-pure catalysts were obtained, exhibiting characteristic peaks for cerium oxide fluorite cubic structure. In addition, Ce 3d spectra collected using X-ray photoelectron spectroscopy showed the occurrence of tetravalent Ce ions in all synthesized ceria compounds. Noticeably, synthesis time appeared to have a considerable effect on the specific surface area and basicity of the powders. An increase in the synthesis time resulted in high specific surface area catalysts demonstrating high basicity. Furthermore, the variation of the

pH of the precipitate yielded cerium oxide with uncommonly high specific surface area, 139 m²/g, for the catalyst prepared under pH 11. From the comparison of the catalytic activities of the synthesized cerium oxide catalysts, as expected, the one with the highest surface area yielded the highest amount of diethyl carbonate (2 mmol) at 180 °C and 9 MPa of total final pressure. The amount of DEC produced over CeO₂-pH 11 represents the highest value of DEC yield ever reported in the open literature over synthesized cerium oxide applying this reaction system. In addition, stability tests revealed that in-house prepared cerium oxide preserved its catalytic activity in contrast to the commercial catalyst.

Furthermore, in-house prepared ceria-supported materials were applied for the first time as catalysts in carbon dioxide transformation to diethyl carbonate. High specific surface area silicas such as MCM-41, SBA-15 and silica gel were used as supports for cerium oxide deposition. Phase pure cubic fluorite cerium oxide was observed for both 16 and 32 wt % ceria loaded on silica gel, whereas certain destruction of the composite material was noticeable for 32 wt % CeO₂-MCM-41, respectively. In turn, modification of SBA-15 material with 20 wt % ceria retained an ordered mesoporous structure of SBA-15. However, ceria could not be determined by means of XRD studies on SBA-15 surface although its presence was confirmed directly by EDX analysis and indirectly by a decrease of specific surface area of the parent material upon CeO₂ dispersion. Most probably, cerium oxide particles were very small and well dispersed or alternatively located inside the SBA-15 matrix. This material among all ceria-supported catalysts showed the highest catalytic activity towards ceria resulting in 0.28 mmol of DEC formed per mmol of cerium oxide.

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