



Ethanol steam reforming for hydrogen production over cobalt catalyst supported on the cerium oxide prepared *via* the one-step hard template method

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Highlights

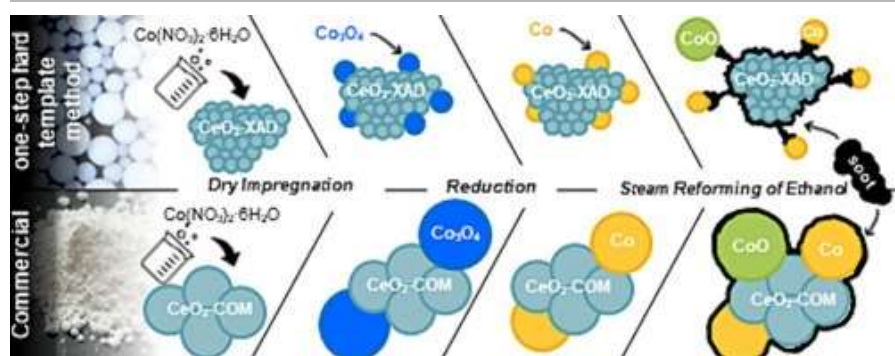
- Templated CeO₂ works perfectly as cobalt catalyst carrier in ethanol steam reforming.
- Templated highly porous CeO₂ enables the formation of tiny Co₃O₄ crystallites.
- Fine, homogeneously dispersed Co particles strongly interact with templated CeO₂.
- Filamentous carbon deposit is formed on Co catalyst supported on templated CeO₂.
- Cobalt catalyst supported on templated cerium oxide resists deactivation in SRE.

Abstract

This study describes a cobalt catalyst supported on highly porous cerium oxide beads (CeO₂-XAD) prepared *via* the one-step hard template method (using resin Amberlite® XAD7HP as a template) for catalytic steam reforming of ethanol (SRE) for hydrogen production. For comparative purposes, Co

catalyst supported on a commercial CeO_2 is discussed ($\text{Co}/\text{CeO}_2\text{-COM}$). Comprehensive studies, including TEM, XPS and $\text{H}_2\text{-TPR}$ analysis, reveal that the bare $\text{CeO}_2\text{-XAD}$ consists of tiny particles with highly damaged surfaces, which contain various forms of oxygen. The hierarchical structure of the support beads, fixed after calcination, ensures high mesoporosity favouring the formation of small, evenly dispersed Co_3O_4 crystallites on $\text{CeO}_2\text{-XAD}$ (~ 3 times smaller than in $\text{Co}/\text{CeO}_2\text{-COM}$), which then, after reduction, transformed into fine, homogeneously dispersed Co particles that strongly interact with the support. Consequently, the Co catalyst supported on $\text{CeO}_2\text{-XAD}$ exhibits high catalytic activity in SRE (much higher than $\text{Co}/\text{CeO}_2\text{-COM}$). Although both catalysts deactivate during SRE due to carbon deposition the process is less severe for the catalyst with smaller Co crystallites and nanostructured support. This study reveals the huge role played by the appropriate morphology and nanostructure of the catalyst support in SRE since they affect not only the ethanol conversion efficiency but also increase the selectivity of the process and thus limit the deactivation of the catalyst.

Graphical abstract



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Introduction

The catalytic steam reforming of ethanol (SRE, $\text{C}_2\text{H}_5\text{OH} + 3\text{H}_2\text{O} \leftrightarrow 6\text{H}_2 + 3\text{CO}_2$) is one of the most promising processes for hydrogen production, especially when renewable bio-ethanol is used [1]. The hydrogen obtained in SRE can then be applied to generate energy in fuel cell systems. This is an attractive solution that may be a response to the growing demand for energy. Therefore, many national strategies of European countries include developing hydrogen technologies and aiming to improve their efficiency and reduce costs towards economic viability [2].

Over the past decade, significant progress has been made in identifying the reaction pathways in ethanol conversion towards hydrogen [3], [4], [5], [6], [7]. Many heterogeneous catalysts based on noble metals (Pt, Pd, Ir, Ru and, particularly, Rh [5], [8], [9]) have been thoroughly investigated and evidenced as having the highest activity and stability in the SRE process with negligible or no coke formation [3]. However, the relatively inexpensive and industrial hydrogen production requires widely available and low-cost catalysts. Both conditions may be fulfilled when using catalysts based on non-noble metals, such as Co, Ni, and Cu [3], [4], [10], [11], [12], [13], [14], since they exhibit high activity towards C–C bond cleavage, which is a crucial characteristic of catalysts in the SRE process.

Admittedly, using catalysts based on non-noble metals poses several difficulties, mainly due to their low resistance to deactivation caused by coke formation or sintering of the metal active phase as a result of high-temperature SRE operations, but there are various possibilities for minimising or eliminating them. One of the effective strategies is to optimise the conditions for steam reforming of ethanol (e.g., temperature, space-time (W/Q), water-to-ethanol ratio at the SRE reactor inlet, etc.) [9], [15], [16], [17]. The second one is to design alternative materials as SRE catalysts [18], [19], [20] or to continuously improve existing systems by developing new methods of their synthesis and modifications. A perfect example of such an approach is doping catalysts with alkali metals (e.g. K, Na, Li) [21], [22]. The alkali dopants affect various catalyst properties, not only the resistance to coke formation but also the activity, selectivity, strength and the number of surface Lewis acidic sites, depressing of metal active phase sintering, as well as the porosity of catalysts [23], [24], [25]. However, the impact of the presence of alkalis is not unambiguous and strongly depends on the type of dopant, the composition of the support and the active phase [22], [26], [27]. Another approach to overcoming the disadvantages of SRE catalysts based on non-noble metals is to optimise the chemical composition and the structural parameters of supports of the catalysts to ensure, among others, high dispersion of active phase nanoparticles, resistance to sintering of the active phase, and active suppression of coke formation. For this purpose, redox-active oxides are frequently used as supports [4], [28]. They actively constrain the deactivation of the catalyst caused by the coke deposition by participating in the oxidation of coke and/or adsorbed CH_x species [3]. Among various redox-active oxides, cerium oxide is very interesting support due to its uniquely high catalytic activity, recognised not only in the SRE process [29], [30], [31] but also in such catalytic processes as oxidation of carbon monoxide (e.g. in gas sensors and catalytic converters) [32], water-gas shift reaction (WGSR) [33], direct dimethyl carbonate synthesis from CO_2 and methanol with 2-cyanopyridine as an organic dehydrating agent [34], soot oxidation [35], [36], and many others. This is attributed to the high oxygen mobility in cerium oxide and the unique ability of cerium to shuttle between Ce^{3+} and Ce^{4+} states (called oxygen storage capacity, OSC) [37], [38], [39]. With changes in the cerium oxidation state, oxygen vacancies or defects are formed in the lattice structure by losing oxygen and/or electrons. They may change spontaneously or in response to various factors such as surface stresses, oxygen partial pressure, electric field, presence of dopants or temperature, without modifying the crystal structure of ceria [32], [38]. Decreasing ceria particle size towards nanoparticles leads to a huge increase of oxygen vacancies in its lattice, facilitates the formation of extra defects on the external surfaces, as well as makes it possible to have a superior surface-to-volume ratio [32], [40], [41]. Therefore, the synthesis of cerium oxide, particularly with the controlled surface/interface and particle size and morphology, has attracted much attention. Moreover, it has been previously presented that the pore diameter of the supports, regardless of their type, significantly impacts the active phase's average crystallite size [42], [43]. Thus, the employment of the cerium oxide with a well-developed mesoporous structure as the support for the active phase is highly promising and should facilitate the formation of tiny, well-dispersed crystallites of the active phase within the pores. This is of particular importance in the case of the preparation of cobalt catalysts *via* incipient wetness impregnation also known as the dry impregnation method.

Dry impregnation is a commonly used method for producing heterogeneous catalysts, including cobalt catalysts, due to its technical simplicity, low costs, high availability of the required metal precursors, and low post-reaction waste [44], [45]. However, it has been reported that the preparation of cobalt catalysts *via* incipient wetness impregnation by using cobalt nitrate solution as

the precursor of cobalt (one of the most popular and cheapest precursors) yields poorly dispersed metal crystallites [46], [47]; this, in turn, is highly undesirable due to possibility of reducing catalytic activity [30].

This study aims to investigate the effect of the structure of cerium oxide supports on the size and dispersion of cobalt particles deposited on it and, consequently, on the reducibility of cobalt catalysts and their activity and stability in SRE. Highly porous cerium oxide, synthesised *via* a one-step hard template method, was used as the support of cobalt particles. It is an easy method which involves the application of polymer resin as the template and the widely used and easily accessible cerium(III) nitrate hexahydrate as a precursor [48]. In general, this method enables the synthesis of various inorganic oxides, such as SiO₂ [49], [50], manganese oxides [51], and ceria [48], but also nickel catalysts supported on silica [52]. The cerium oxide produced by this method is in the form of easy-to-handle, relatively homogeneous grains (microspheres). Moreover, properties such as the high specific surface area, the high Ce³⁺ concentration on the surface even before reduction and fine crystalline structure [53] are favourable and promising, especially when the Co catalyst synthesis is performed by dry impregnation using cobalt nitrate solution as the precursor. However, to our knowledge, neither this cerium oxide microspheres nor the cobalt catalyst prepared by doping this cerium oxide *via* dry impregnation has so far been the subject of catalytic research in general, and in particular, catalytic steam reforming of ethanol. The properties of Co catalyst supported on microspheres have been compared to those supported on the commercial nano-dispersed CeO₂.

Section snippets

Cobalt catalyst preparation

The cobalt catalysts were synthesised *via* the dry impregnation method, and as supports, two cerium oxides were selected, i.e. CeO₂-XAD and CeO₂-COM. The CeO₂-XAD sample was prepared according to the procedure given in Ref. [48] *via* the one-step hard template method. Porous resin Amberlite® XAD7HP (Sigma Aldrich, beads ranging in diameter from 500µm to 840µm, XAD7) was employed as a hard template, while aqueous solution of cerium(III) nitrate hexahydrate (99%, Sigma Aldrich) of concentration

Characterisation of fresh supports

Two different cerium oxides, namely CeO₂-XAD and CeO₂-COM, were used as supports. CeO₂-XAD was produced according to the one-step hard template method using resin Amberlite® XAD7HP as a template [48], [50], [51], [57]. In general, CeO₂-XAD is in the form of beads (Fig. 1a), but the presence of fragments of various sizes resulting from the fragmentation of beads is also characteristic. The SEM micrographs at high magnification reveal the complex pattern of the CeO₂-XAD interior, suggesting that

Conclusions

The paper has presented the high suitability of cerium oxide (prepared *via* the one-step hard template method using resin Amberlite® XAD7HP as a template) as support for the preparation of

cobalt catalysts *via* dry impregnation by using inexpensive cobalt nitrate as the precursor of cobalt. XPS and H₂-TPR results prove that this bare support consists of fine and highly surface-defective particles on the surface, of which there are a multiplicity of different surface oxygen species with different

Author contributions

J.L., M.G. and A.K. conceived the research project; J.L., M.R., G.S. and A.S. performed the experiments and prepared the data; J.L. and A.S. performed the figures, and J.L., A.K. and M.G. wrote an original draft. All authors contributed to the interpretation of the data.

CRedit authorship contribution statement

Joanna Lupa: Writing – review & editing, Writing – original draft, Visualization, Validation, Resources, Project administration, Investigation, Funding acquisition, Conceptualization. **Magdalena Greluk:** Writing – review & editing, Writing – original draft, Investigation, Conceptualization. **Marek Rotko:** Resources, Investigation, Formal analysis. **Grzegorz Słowik:** Visualization, Resources, Investigation, Formal analysis. **Andrzej Sienkiewicz:** Visualization, Investigation. **Agnieszka Kierys:** Writing –

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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References (129)

M. Ni *et al.*

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Int. J. Hydrogen Energy (2007)

S. Ogo *et al.*

[Recent progress in ethanol steam reforming using non-noble transition metal catalysts: A review](#)

Fuel Process. Technol. (2020)

S. Anil *et al.*

A review on ethanol steam reforming for hydrogen production over Ni/Al₂O₃ and Ni/CeO₂ based catalyst powders

Int. J. Hydrogen Energy (2022)

X. Feng *et al.*

A mini review on recent progress of steam reforming of ethanol

RSC Adv. (2023)

Z. Liu *et al.*

Chapter 5 - catalysts for the steam reforming of ethanol and other alcohols

Y.C. Sharma *et al.*

Ethanol steam reforming for hydrogen production: Latest and effective catalyst modification strategies to minimize carbonaceous deactivation

Renew. Sustain. Energy Rev. (2017)

A.K. Seriyala *et al.*

Tin and lanthanum modified Ni/CeO₂ catalyst systems for low temperature steam reforming of ethanol

Int. J. Hydrogen Energy (2024)

M. Wang *et al.*

Metal-support interactions over Ni/CeO₂-ZrO₂ catalysts for ethanol steam reforming and their effects on the coke gasification

Catal. Today (2024)

R. Li *et al.*

Regulating cobalt chemical state by CeO₂ facets preferred exposure for improved ethanol steam reforming

Fuel (2023)

V. Palma *et al.*

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Appl Catal B (2014)



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