

Comparison in Dimethyl Ether Steam Reforming of Conventional Cu-ZnO-Al₂O₃ and Supported Pt Metal Catalysts

Lide Oar-Arteta^{*a}, Florence Epron^b, Nicolas Bion^b, Andrés T. Aguayo^a, Ana G. Gayubo^a

^a Dpto. Ingeniería Química, Universidad del País Vasco, Apto. 644, 48080 Bilbao, Spain

^b Université de Poitiers, CNRS UMR7285, Institut de Chimie des Milieux et Matériaux de Poitiers (IC2MP), 4 rue Michel Brunet, 86073 Poitiers cedex 09, France
 lide.oararteta@ehu.es

The catalytic performance of platinum based catalysts supported on CeO₂/Al₂O₃ (with different proportion of both oxides) was compared to the conventional Cu-ZnO-Al₂O₃ (CZA) catalyst for methanol steam reforming (MeOH-SR), which is the second stage in the dimethyl ether steam reforming (SRD) process for obtaining H₂. The catalytic performances of Pt based catalysts were notably influenced by the addition of CeO₂ to the support: a higher content of CeO₂ improved the catalyst activity and selectivity to H₂, and limited to some extent CO and CH₄ formation. At low temperatures (below 350 °C), the copper based CZA catalyst provided the best results in MeOH-SR, but at high temperature (350-500 °C) Pt/CeO₂ and CZA showed similar catalytic performance. Consequently, Pt/CeO₂ can be envisioned as a proper metallic function to be used in the bifunctional catalyst for SRD together with γ -Al₂O₃ acid function, which requires temperatures above 350 °C for attaining high conversion in dimethyl ether hydrolysis.

1. Introduction

Hydrogen is a suitable fuel to meet the increasing demand of energy as it may be produced from renewable sources (Hočevar and Summers, 2008). Hydrogen fuel cell, which transforms chemical energy into electrical energy by consuming hydrogen and oxidant, is presented as an efficient and environmentally friendly power generator for both mobile and stationary use (Sieniutycz and Póswiata, 2011). Nevertheless, hydrogen is difficult to handle and store, and therefore, a hydrogen vector needs to be used. Methanol is an excellent raw material for on-board H₂ production for proton exchange membrane (PEM) fuel cells, as it can be easily and selectively converted into an H₂-rich gas at low temperature (150 – 300 °C) by steam reforming (Sa et al., 2010), but due to its toxicity and corrosiveness there is interest in the use of alternative H₂ vectors. Amongst them, dimethyl ether (DME) is an alternative of growing interest, since it is relatively inert, non-corrosive, non-carcinogenic, it can be stored and handled as liquefied petroleum gas (LPG) and, consequently, it is more readily used in fuel cells (Semelsberger et al., 2006). Moreover, DME can be synthesized from biomass resources (bio-DME), via the 'syn gas' obtained from biomass gasification (Higo and Dowaki, 2010), and consequently, the DME synthesis by co-feeding CO₂ with syngas in a single reaction step is considered a key process for both CO₂ sequestration and the viability of lignocellulosic biomass gasification (Bulushev and Ross, 2011).

The steam reforming of DME (SRD) proceeds over bifunctional catalysts, via hydrolysis of DME (over an acid function), followed by MeOH-SR (over a metallic function). Additionally, other reactions take place which decrease H₂ production, such as reverse water gas shift (r-WGS), MeOH/DME decomposition and methanation reactions that must be avoided by employing the appropriate catalysts and operating conditions. The Cu/ZnO/Al₂O₃ (CZA) formulation has been extensively used in literature as a catalyst for the MeOH-SR (Sá et al., 2010), but it suffers from sintering at relatively low temperature of 300 °C which is

a handicap for i) its use as metallic function in DME-SR together with γ - Al_2O_3 as acid function (as the latter requires $T > 350^\circ\text{C}$ for high activity in DME hydrolysis) and ii) the regeneration of the bifunctional catalyst by coke combustion (which requires temperature above 500°C). Catalysts based on noble metals, such as Pd and Pt, have also been used in MeOH-SR, and can also act as metallic functions alternative to CZA for SRD because they present some advantages such as higher thermal stability and long-term stability (Sá et al, 2010). Noble metals supported on different ionic oxides such as Al_2O_3 and CeO_2 have been studied and found promising in the reforming of DME (Fukunaga et al., 2008) and other oxygenated compounds such as ethanol (Palma et al., 2012).

This work is focused on the viability of Pt based catalysts (with Al_2O_3 , CeO_2 and mixed $\text{Al}_2\text{O}_3/\text{CeO}_2$ supports) as metallic functions for the bifunctional catalysts in SRD, by comparing their behavior in the MeOH-SR reaction (second step in SRD process) with that corresponding to a commercial CZA catalyst.

2. Experimental

2.1 Catalyst preparation and characterization

The following supports were used for the preparation of the supported Pt catalysts: Al_2O_3 (provided by Axens), CeO_2 (provided by Solvay) and three mixed oxides of Al_2O_3 (80 % wt)- CeO_2 (20 % wt), Al_2O_3 (20 % wt)- CeO_2 (80 % wt) and $\text{Ce}_{0.5}\text{Zr}_{0.5}\text{O}_2$ (90 % wt)- Al_2O_3 (10 % wt) denoted as Al(80)Ce(20), Al(20)Ce(80) and CeZrAl, respectively. Al(80)Ce(20) mixed support was prepared by wet impregnation of Al_2O_3 support with cerium nitrate $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ while Al(20)Ce(80) and CeZrAl were synthesized by the sol-gel method with aluminium isopropoxide, $\text{Al}[\text{OCH}(\text{CH}_3)_2]_3$, and commercial CeO_2 or $\text{Ce}_{0.5}\text{Zr}_{0.5}\text{O}_2$. After preparation all the supports were calcined at 800°C , in order to obtain the alpha phase of the Al_2O_3 , for 5 h in a muffle oven *Nabertherm Controller P3 30*. The 1 wt. % of platinum was deposited on each support by wet impregnation, using H_2PtCl_6 as precursor salt (Gauthard et al., 2003). The Pt catalysts were calcined at 600°C for 4 h in air and pre-reduced in H_2 at 500°C for 1 h. The conventional CZA commercial catalyst employed in this study was provided by Süd Chemie.

The catalysts were characterized employing different techniques. Specific surface area and pore volume measurements were determined by N_2 physisorption in a *TriStar Micromeritics* volumetric device after degassing of the samples at 250°C during 4 h. The metallic species liable to reduction and the temperature triggering the reduction were determined by temperature programmed reduction (TPR) from room temperature to 1050°C at a rate of $5^\circ\text{C}/\text{min}$ in a gas mixture of 1% H_2 in Ar ($30\text{ cm}^3\text{ min}^{-1}$) using an *AutoChem 2920* from *Micromeritics*. Prior to TPR, the sample was oxidised with pure O_2 from room temperature to 500°C (1h) at a rate of $10^\circ\text{C min}^{-1}$. Platinum content in the catalyst was determined by by ICP-OES using a Perkin Elmer Optima 2000 DV. Prior to the analyses, the samples were mineralized with a mixture of nitric and chloridric acids. The metallic dispersion and the metal crystallite size of Pt based catalysts were determined by H_2 chemisorption in an own designed chromatographic device, while the same parameters for CZA catalyst were determined by N_2O pulsed chemisorption in a *Micromeritics AutoChem 2920* coupled to a *Balzers Instruments Omnistar* mass spectrometer. Metal particle size was calculated as indicated in Eq(1).

$$d(\text{nm}) = 5 \cdot 10^5 \frac{M}{\rho \cdot D \cdot S} \quad (1)$$

where M and ρ are the molar mass (g mol^{-1}) and density (g cm^{-3}) of the metal, D is the metal dispersion and S is the surface developed by one mole of metal ($\text{m}^2\text{ mol}^{-1}$).

2.2 Catalytic tests

Figure 1 shows the scheme of the reaction and analysis device, which was already described elsewhere (Rijo Gomes et al (2011)). The MeOH-SR reaction was carried out in a quartz tubular continuous flow reactor ($L=330\text{ mm}$; $\varnothing_{\text{int}}=12\text{ mm}$). Methanol and water were injected with a *Gilson 305* pump and preheated up to 200°C before entering the reaction zone. The reaction products passed through a condenser working at 0°C in order to trap the remaining water and methanol and then gaseous products were analyzed every ten minutes in two gas chromatographs connected on line: a Varian 3800 GC employing a 5A molecular sieve and H_2 as carrier gas was used for detecting CO , CO_2 and CH_4 and a Varian 3900 employing a 13X molecular sieve and Ar as carrier gas for detecting H_2 . Liquid products (MeOH and H_2O) were collected every hour, weighted in a balance and measured in an HPLC pump employing H_2SO_4 as eluent. The catalytic tests were carried out at atmospheric pressure, under increasing temperature steps from 200°C to 500°C , space time of $0.13\text{ g}_{\text{cat}} \cdot \text{h} \cdot \text{g}_{\text{MeOH}}^{-1}$ and steam/MeOH ratio of 1.3. The catalytic bed consisted of 0.2 g of the catalyst and 0.2 g of an inert (SiC). Prior to the reaction, the catalyst was reduced *in situ* with pure H_2 ($100\text{ cm}^3\text{ min}^{-1}$) at the first reaction step temperature (200°C) for 1 h.

The reaction indices employed to quantify the catalytic activity are MeOH conversion, X_{MeOH} , and yield of products (H_2 , CO and CH_4), Y_i , defined by Eq(2) and Eq(3), respectively:

$$X_{\text{MeOH}} = \frac{F_{\text{MeOH},0} - F_{\text{MeOH}}}{F_{\text{MeOH},0}} \cdot 100 \quad (2)$$

$$Y_i = \frac{F_i}{F_{\text{MeOH}} \cdot \nu_i} \cdot 100 \quad (3)$$

where $F_{\text{MeOH},0}$ and F_{MeOH} are the molar flow rate of the MeOH at the inlet and the outlet respectively; F_i is the molar flow rate of product i at the outlet and ν_i is the stoichiometric coefficient for i .

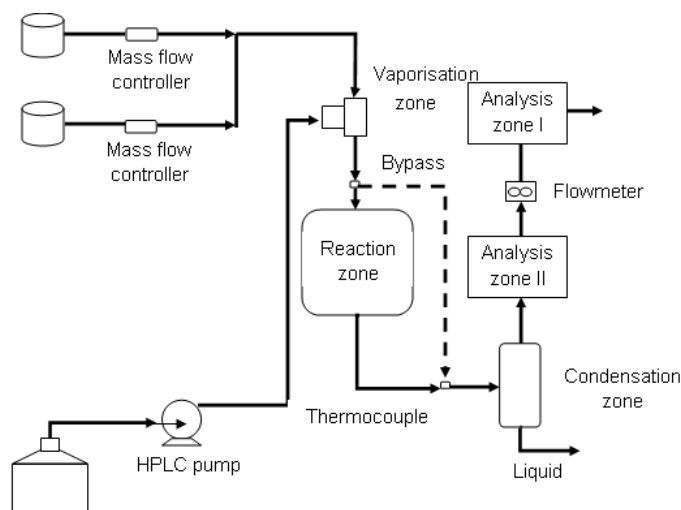


Figure 1: Scheme of the reaction equipment Results

3. Results

3.1 Catalyst characterization

Table 1 shows the values of specific surface area and average pore volume for CZA catalyst, for the different supports and for the Pt based catalysts.

Table 2: Specific surface area measurements for supports, supported platinum catalysts and CZA catalyst

Catalysts	Specific Surface ($\text{m}^2 \text{g}^{-1}$)	Pore Volume ($\text{cm}^3 \text{g}^{-1}$)	Pore size (\AA)
CZA	83	0.35	155
Al_2O_3	184	0.49	108
$\text{Pt}/\text{Al}_2\text{O}_3$	180	-	-
$\text{Al}(80)\text{Ce}(20)$	103	0.32	124
$\text{Pt}/\text{Al}(80)\text{Ce}(20)$	83	-	-
CeZrAl	66	0.2	125
Pt/CeZrAl	44	-	-
$\text{Al}(20)\text{Ce}(80)$	34	0.07	76
$\text{Pt}/\text{Al}(20)\text{Ce}(80)$	25	-	-
CeO_2	256	0.17	147
Pt/CeO_2	221	-	-

All the supports are mesoporous solids, as their average pore size is comprised between 20 and 500 \AA . The commercial CeO_2 support shows higher specific surface area than Al_2O_3 . For all Al_2O_3 - CeO_2 supports, prepared by impregnation and by the sol-gel method, an increase in the CeO_2 content implies a decrease in both specific surface area and the pore volume. The noticeable higher surface area and pore volume of CeO_2 support compared to the rest of CeO_2 containing supports could be due to the fact that this commercial support was not calcined at 800 $^\circ\text{C}$ as was the rest of supports. The addition of platinum to all

the supports involves a decrease in the specific surface area. The metallic properties of the catalysts are summarized in Table 2. Metallic content for CZA catalyst is much higher than for platinum based catalysts, and consequently it shows lower metallic dispersion and higher particle size. It is observed that supported platinum catalysts with high content of CeO₂ in the support (≥ 80 wt%) have dispersion values around 35 % with metallic particle size of 30 Å. As the content of CeO₂ in the support diminishes the dispersion of platinum is enhanced and smaller particle sizes are obtained (with values of 77 % and 12 Å, respectively, for 20 wt% CeO₂ in the support), which could be attributable to the higher surface area of the support.

Table 1: Metal (Cu or Pt) content, dispersion and particle size of the catalysts

Catalysts	Metal content (ICP) (%)	Metal dispersion (%)	Metal particle size (Å)
CZA	45	12	86
Pt/Al ₂ O ₃	0.66	67	14
Pt/Al(80)Ce(20)	1.33	77	12
Pt/CeZrAl	1.04	50	19
Pt/Ce(80)Al(20)	0.96	31	30
Pt/CeO ₂	1.15	36	27

The TPR profile of CZA metallic function contains a peak with a maximum at 190 °C corresponding to the reduction of Cu²⁺ to Cu⁰ (Agrell et al., 2003). Figure 2 shows TPR profiles (graph a) and the evolution of the reduction temperature with CeO₂ content (graph b) for the Pt based catalysts. In the TPR profiles of the catalysts with CeO₂ in the support, two temperature domains can be distinguished. In the first one (T<350 °C) the reduction is due to the reduction of PtO_x and superficial CeO₂ whose reduction at low temperature is promoted by the Pt interaction with the support (Milone et al. 2006), while the second one (T>350 °C) is due to the reduction of the bulk CeO₂ (Sedjame et al, 2014). As it is observed in Figure 2.b, in the first reduction domain, the reduction temperature is in general lower for catalysts with higher content of CeO₂.

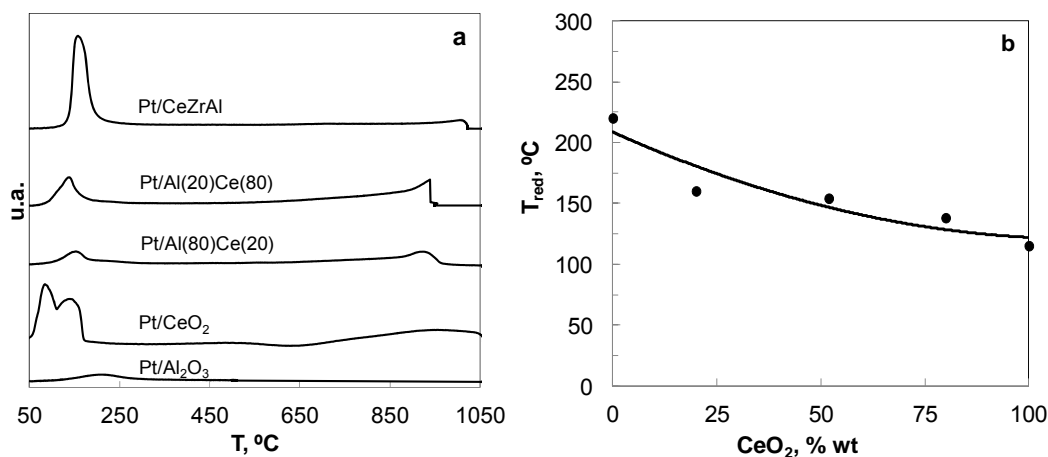


Figure 2: TPR profiles (graph a) and evolution of the reduction temperature with CeO₂ content (graph b) for the Pt based catalysts.

3.2 Catalytic performance

The evolution with temperature of the methanol conversion and H₂ yield for the different catalysts are shown in Figure 3.

These results show that CZA catalyst is highly active at low temperature for MeOH-SR (Kurr et al., 2008), and complete MeOH conversion and maximum H₂ yield (100%) are achieved at 300 °C. Above this temperature MeOH decomposition and reverse WGS reactions take place, which favor CO formation and slightly decrease H₂ yield.

At low temperature, the Pt based catalysts show much lower MeOH conversion and H₂ yield than CZA catalyst (Sá et al., 2010). Both reaction indices increase noticeable with temperature and total conversion (Figure 3a) and H₂ yield of around 100 % (Figure 3b) are reached just with the Pt/CeO₂ catalyst, but at higher temperature than that required with CZA catalyst. Moreover, high yields of by-products CO and CH₄ (especially the former) are obtained with the Pt catalysts even at low temperature (Fukunaga et al., 2008),

especially with that supported on Al_2O_3 , which is consistent with other results of literature that conclude that methanol decomposition is promoted over this type of catalysts (Imamura et al., 1999). The addition of ceria to the Al_2O_3 support slightly increases MeOH conversion and H_2 yield, suppresses to a great extent methanation reactions and significantly decreases CO formation, which can be explained by the high activity of CeO_2 for WGS reaction (Roh et al., 2012). These effects are accentuated as the amount of ceria in the support is increased. The best results in MeOH-SR with Pt based catalysts are obtained with Pt supported on commercial CeO_2 , which shows almost the same catalytic performance at 400 °C than CZA catalyst.

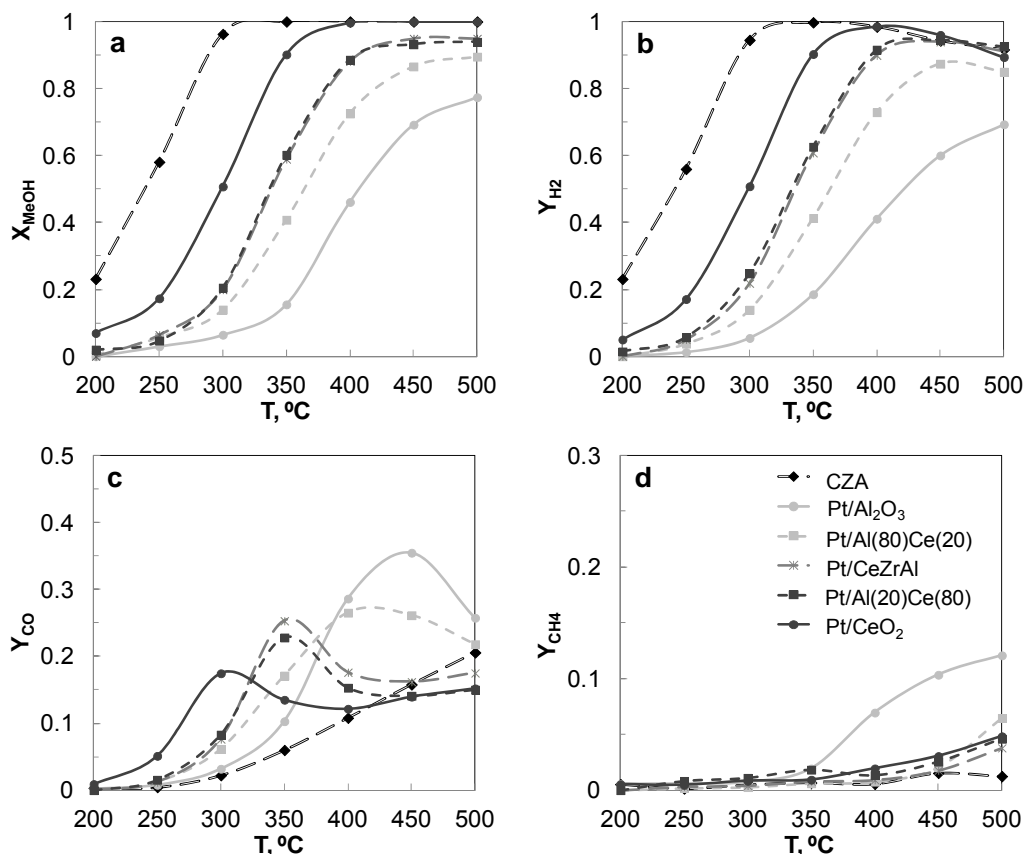


Figure 3: Evolution of MeOH conversion (graph a) and yield of H_2 (graph b), CO (graph c) and CH_4 (graph d) for the different catalysts studied. Operating conditions: $P=1.3$ bar.

4. Conclusions

The copper based CZA catalyst shows better performance than Pt based catalysts in MeOH-SR at low temperature, as it is highly active and selective to H_2 formation, although it promotes CO formation (by reverse-WGS reaction) above 350 °C.

The addition of CeO_2 to the Al_2O_3 support improves the catalytic performance of Pt supported catalysts for MeOH-SR: thus, catalyst activity and selectivity to H_2 increase with the content of CeO_2 in the $\text{Al}_2\text{O}_3/\text{CeO}_2$ support, whereas CO and CH_4 formation are notably suppressed. The best results in MeOH-SR with Pt based catalysts are obtained with Pt/ CeO_2 catalyst, whose catalytic performance at high temperature (350-500 °C) is similar to that obtained with CZA catalyst. Taking into account the well known higher thermal stability of Pt based catalysts compared to Cu based catalysts, it is concluded that Pt/ CeO_2 can be envisioned as a proper metallic function to be used in the preparation of a bifunctional catalyst for dimethyl ether steam reforming together with $\gamma\text{-Al}_2\text{O}_3$ as acid function, which requires temperatures above 350 °C for attaining high conversion in DME hydrolysis (the first step in SRD). At this high temperatures, CZA metallic function is likely to sinterize, whereas Pt/ CeO_2 metallic function shows higher thermal stability, with a presumably lower deactivation (both by coke deposition or sintering).

References

- Agrell J., Boutonnet M., Melián-Cabrera I., Fierro J.L.G., 2003, Production of hydrogen from Methanol over Binary Cu/ZnO Catalysts: Part I. Catalyst preparation and Characterisation. *Appl. Catal. A Gen.*, 253, 201-211.
- Bulushev D.A., Ross J.R.H., 2011, Catalysis for Conversion of Biomass to Fuels via Pyrolysis and Gasification: A Review. *Catal. Today*, 171, 1-13.
- Fukunaga T., Ryumon N., Shimazu S., 2008, The Influence of Metals and Acidic Oxide Species on the Steam Reforming of Dimethyl Ether. *Appl. Catal. A-Gen.*, 348, 193-200.
- Gauthard F., Epron F., Barbier J., 2003, Palladium and Platinum-based Catalysts in the Catalytic Reduction of Nitrate in Water: Effect of Copper, Silver, or Gold Addition. *J. Catal.*, 220, 182-191
- Higo M., Dowaki K., 2010, A Life Cycle Analysis on a Bio-DME Production System considering the Species of Biomass Feedstock in Japan and Papua New Guinea. *Appl. Energy*, 87, 58-67.
- Hočevar S., Summers W., 2008, *Hydrogen Technology: Hydrogen Production*, Ed. Léon A., Springer-Verlag, Berlin/Heidelberg, Germany.
- Imamura S., Higashihara T., Saito Y., Aritani H., Kanai H., Matsumura Y., Tsuda N., 1999, Decomposition of Methanol on Pt-loaded Ceria. *Catal. Today*, 50, 369-380.
- Kolb G., Keller S., Pecov S., Pennemann H., Zapf R., 2011, Development of Micro-Structured Catalytic Wall Reactors for Hydrogen Production by Methanol Steam Reforming over Novel Pt/In₂O₃/Al₂O₃ Catalysts, *Chemical Engineering Transactions*, 24, 133-138, DOI: 10.3303/CET1124023
- Kurr P., Kasatkin I., Girgsdies F., Trunschke A., Schlög R., Ressler T. 2008, Microstructural characterization of Cu/ZnO/Al₂O₃ Catalysts for Methanol Steam Reforming- A Comparative study. *Appl. Catal. A-Gen.*, 348, 153-164.
- Milone C., Fazio M., Pistone A., Galvagno S., 2006, Catalytic Wet Air Oxidation of p-Coumaric Acid on CeO₂, Platinum and Gold Supported on CeO₂ Catalysts, *Appl. Catal. B-Environ.*, 68, 28-37.
- Palma V., Castaldo F., Ciambelli P., Iaquaniello G., 2012, Bio-Ethanol Steam Reforming Reaction over Bimetallic Ceria-Supported Catalysts, *Chemical Engineering Transactions*, 29, 109-114, DOI: 10.3303/CET1229019
- Rijo Gomes S., Bion N., Blanchard G., Rousseau S., Bellière-Baca V., Harlé V., Duprez D., Epron F., 2011, Thermodynamic and Experimental Studies of Catalytic Reforming of Exhaust Gas Recirculation in Gasoline Engines, *Appl. Catal. B-Environ.*, 102, 44-53.
- Roh H.S., Potdar H.S., Jeong D.W., Kim K.S., Shim J.O., Jang W.J., Koo K.Y., Yoon W.L., 2012, Synthesis of Highly Active Nano-Sized (1 wt.% Pt/CeO₂) Catalyst for Water Gas Shift Reaction in Medium Temperature Application. *Catal. Today*, 185, 113-118.
- Sá S., Silva H., Brandao L., Sousa J.M., Mendes A., 2010, Catalysts for Methanol Steam Reforming - A Review. *Appl. Catal. B-Environ.*, 99, 43-57.
- Sedjame H.J., Fontaine C., Lafaye G., Barbier Jr J., 2014, On the Promoting Effect of the Addition of Ceria to Platinum based Catalysts for VOCs Oxidation. *Appl. Catal. B-Environ.*, 144, 233-242.
- Semelsberger T.A., Borup R.L., Greene H.L., 2006, Dimethyl Ether (DME) as an Alternative Fuel. *J. Power Sources*, 156, 497-511.
- Sieniutycz S., Póswiata A., 2011, Basic Thermodynamic Properties of Fuel Cell Systems, *Chemical Engineering Transactions*, 24, 547-552, DOI: 10.3303/CET1124092