

CO₂ Conversion over Supported Ni Nanoparticles

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To accelerate the reduction of global greenhouse gas emissions represents an urgent response to the climate change and to its devastating effects on human society and planet. The 2030 Agenda for sustainable development written during the last global meeting on climate change (COP 21) requires that greenhouse gas emissions begin to decline within the next two decades, holding the increase in the global average temperature below 2 °C above preindustrial levels. Apart water vapor, the major greenhouse gases present in our atmosphere are CO₂ and CH₄. Consequently, there is much interest in the scientific world towards new and more efficient methods to use carbon dioxide and methane. Therefore, the password for the humanity future is *Decarbonation*. The main source of CH₄ is from natural gas and its main uses are in the combustion processes, power generation and chemical production from syngas. Syngas represents an important intermediate for ultra-clean liquid fuel production and it is a valid raw chemical as alternative source to petroleum. There are numerous processes for syngas production, such as partial oxidation, steam reforming, auto-thermal reforming, dry reforming and oxy-reforming. Among these, dry reforming (e.g. reforming of methane with CO₂), is currently attracting great interest since it utilizes, with respect to the other processes, carbon containing feedstocks. Recently, the CO₂ methanation has become of interest as renewable energy storage system based on a Power-to-Gas conversion. The conversion of electricity into methane takes place into two steps: hydrogen is produced by electrolysis and converted into methane by CO₂ methanation. Active, selective and stable catalyst is the core of the above-mentioned processes (dry-reforming and CO₂ methanation) to produce green fuels. For these reasons, in the last decades several researchers have deeply studied the critical issues in the catalysts preparation for dry reforming and CO₂-methanation reactions. Transition metals (Ni, Pd, Pt, Co, Ru, Rh, etc.) are active species in both catalytic processes. Among these metals, Ni, Ru and Rh are the most effective. Ni has been the most studied because it presents a peculiarity that makes it interesting from a commercial point of view: it is the cheapest. To preserve and improve metal activity, technology focused on the development of metal-supported catalysts. Alumina, silica, zeolites, zirconia, ceria and carbon nanotubes are supports largely investigated. In this work we summarize the fundamental properties of supported Ni nanoparticles that make it the most suitable catalyst for conversion of CO₂ in the sustainable energy production.

1. Introduction

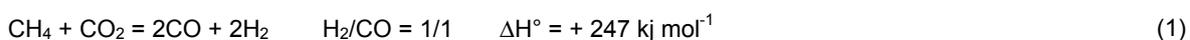
The presence of CO₂ in the atmosphere and its greenhouse effect are the primary causes of the planet life. On the other hand, the anthropic activity has strongly modified, over the centuries, the natural equilibrium between atmospheric gases concentration and greenhouse effect. Carbon dioxide is a very stable molecule, so its atmospheric levels, without any change in human life-style, can only increase with the time. The extent of its increase depends on natural events, on technological and sociological growth and it is strictly connected to the use of fossil fuel as primary energy source. CH₄ is considered the second greenhouse gas for its chemical stability and atmospheric concentration but, simultaneously, is one of main energy sources with low carbon content. Methane can be used directly as fuel, for power generation and as reactant for syngas production.

Dry-reforming of methane, as well as CO₂ methanation, are two processes that represent promising solutions for CO₂ mitigation and for alternative energy production by low-carbon fuels. Catalysts based on Ni, Pd, Pt, Co, Ru, Rh, etc. are differently active in both the catalytic processes. This brief review has the objective to report research results from the author's laboratories on catalysts for dry-reforming of methane and CO₂ methanation, focusing on the metal-support interactions as peculiarity for the productivity and life-time with the aim of improving of the catalytic activity.

1.1 Dry-reforming of methane

The catalytic reforming of CH₄ with CO₂ (Eq(1)) makes use of methane as a feedstock for converting it to syngas (mixture of CO and H₂) which is utilized for several carbonylation and hydrogenation reactions, as well as for methanol synthesis, oxygenated compounds and Fischer-Tropsch synthesis for liquid hydrocarbons production (Rajaram et al., 2014).

This process is actually attracting great interest by scientific community because, compared to steam reforming or partial oxidation, it is industrially advantageous since the H₂/CO ratio produced is close to 1/1 (Rostrupnielsen et al., 1993; Candamano et al., 2015;).



Main drawback of dry-reforming is the high endothermicity of the reaction.

This means that to reach high conversion levels, high operating temperature are required (650-700 °C). Apart the high energy consumption, severe operating conditions result in limited catalyst lifetime due to deactivation phenomena caused by coke deposition and metal sintering. From an economic point of view, catalyst should be based on an inexpensive active metal. For this reason, even if noble metals result in very active species, they are not suitable for development of an industrially acceptable catalyst. Therefore, researchers focused their activity to demonstrate the good performance of supported nickel catalyst in dry-reforming of methane (Frontera et al., 2011; de Caprariis et al. 2015). All researchers agree on the fundamental role of the support on the nickel activity and its deactivation. Moreover, the presence of promoters, such as alkali metals or metal oxides reduces the coke formation and modifies the reforming activity of nickel (Juan-Juan et al., 2004).

1.2 CO₂ methanation

CO₂ methanation, or better known as Sabatier reaction (Sabatier et al., 1903), represents a process in which methane is produced by an exothermic reaction (Eq(2)) with a favourable thermodynamics ($\Delta G^\circ = - 114 \text{ kJ mol}^{-1}$).



Actually, this process is considered a key technology able to solve the problems related to the storage and transportation of renewable hydrogen. In fact, the methane produced by this process, called *Substitute or Synthetic Natural Gas* (SNG), not only contributes to the CO₂ mitigation but also represents a valid solution to the storage of renewable energy, based on *Power-to-Gas* technology (P2G) (Meylan et al., 2016).

CO₂ methanation mechanisms currently accepted can be divided in two types. The former considers an associative mechanism, in which the CO₂ associatively adsorbed with the hydrogen adatom, H_{ad}, forms oxygenate intermediates and, subsequently, is hydrogenated to methane. In the latter a dissociative mechanism occurs: the CO₂ is firstly dissociated in (CO)_{ad} and O_{ad} species and, in turn, the carbonyl hydrogenation to CH₄ take place (Miao et al., 2016). Due to the exothermicity of the reaction, typically operating temperature ranges from 200 °C to 450 °C, depending on the catalyst used. All the group VIII metals the have been studied over different supports, including Ni-based and noble metal-based catalysts (Frontera et al., 2017). Even if Ni-based catalysts are more sensible to coke deactivation and require higher operating temperature with respect to the noble-based catalysts, it represents the most studied catalytic system due to the low cost of the metal. The activity and stability of nickel catalyst in CO₂ methanation, as well as for the dry-reforming of methane, vary significantly with support materials, promoters and preparation methods (Frontera et al., 2011; Frontera et al., 2017). Moreover, the design of a suitable catalyst surface constituted by a combination of more than one metal is another approach in attempting to enhance the catalytic activity (Kang et al., 2011).

2. Catalyst design and characterization

The nature of the support plays a crucial role in the nickel activity and selectivity due to metal-support interactions with nanoparticles. Suitable catalysts should have high metal dispersion, easy to reduced and preserved from sintering. These are aspects in common for catalysts design and optimization, both for dry-

reforming and CO₂ methanation. Oxides such as SiO₂, Al₂O₃, TiO₂, ZrO₂ and CeO₂, are the most studied supports for nickel. Zeolites, mesoporous materials and delaminated structures represent synthetic materials with surface properties tunable to improve nickel catalytic performance. Hydrothermal synthesis is the main procedure to obtain zeolites and related materials, such as Silicalite-1, Ferrierite, MCM-41 and ITQ-6. In order to affect the support surface, post-synthesis treatments have been applied to the obtained materials, such as silylation, ionic-exchange and swelling techniques (Frontera et al., 2011; Frontera et al., 2013; Corma et al., 2000). A thermal treatment, (e.g. calcination), is the final step to recover active support. One of the most popular methods to deposit a metal on a support is the incipient wetness impregnation XRD, SEM/EDX, CHNS, XPS, N₂ Ads-Des, TG-DSC, TPR-H₂, HR-TEM, ¹³³Cs-NMR, ²⁹SiNMR, AFM and CO₂-TPD are employed for a detailed characterization of catalysts. Our results, carried out during the last years, are focused on the synthesis, characterization and optimization of several nickel-supported catalysts.

3. CO₂ conversion results

3.1 Dry-reforming experiments discussion

All CO₂ reforming experiments have been carried out at 1 atm and 700°C, with a stoichiometric mixture of CH₄ and CO₂ and a total flow rate of 100 ml/min, using a continuous flow quartz tube reactor. 0.2 g of catalyst have been used for each catalytic test. Reaction products have been analyzed by an on-line gas chromatograph, equipped with FID and TCD detectors. Catalytic tests results, for all investigated Ni-supported catalysts are summarized in the Table 1. Regarding the H₂/CO ratio values, the performance of selected materials, during the 10 hours of catalytic test, can be considered comparable (the ratio ranging from 1.15 to 1.40). Instead, the coke deposition on spent catalyst, changes dramatically with the type of the support (from 6 wt% to 0.52 wt%). Silicalite-1 type material, a pure silica MFI zeolite structure, brings about the greatest amount of coke formation. High defective all-silica mesoporous structure (MCM-41) allows to reduce the amount of deposited coke of about 30% with respect to Silicalite-1. This suggests that a more defective structure could favor the Ni nanoparticle deposition and dispersion. Silylated support (HMDS-Silicalite-1) and the very high defective surface of delaminated ITQ-6 support performance confirm this supposition. The coke deposited on Ni-ITQ-6 is almost 1/3 of that deposited on Ni-Silicalite-1. Our previous studies demonstrated that a more defective structure of the support allows a fine dispersion of nickel particles (smaller than 20 nm), leading also to the formation of nickel silicate species with stronger metal-support interaction. The nanoparticles of nickel dispersed inside the heterogeneous surface of ITQ-6 material are preserved from sintering phenomena and remain free of carbon along all the time on stream. Following this insight, pure silica lamellar structure FER, precursor of delaminated ITQ-6, has been prepared, characterized and tested as nickel support in dry-reforming of methane. SEM image of this material, after calcination, clearly shows the lamellar structure of the support (Figure 1A). The AFM analysis results, carried out on Ni-FER catalyst, have allowed to observe as the lamellar structure of the FER material affects the nickel dispersion during metal impregnation (Figure 1B). Highly dispersed nickel nanoparticles on FER lamellar surface strongly preserve the catalyst from coke deposition: only 0.88 wt% carbon is deposited on the catalyst after 10 hours of time of stream (Table 1). High stability of Ni-FER and Ni-ITQ-6 catalysts could be again improved combining the support surface role with the promoter effect. Promoters are substances that, when added to a catalyst as minor components, improve one or more property of the catalyst, achieving optimized catalytic performance. It is well known that the basicity of alkali metals or metal oxides strongly avoid carbon deposition on dry-reforming catalysts (Juan-Juan et al., 2004). At present, potassium is one of the most investigated promoters; on the contrary, to the best of our knowledge, cesium has been less investigated. In catalysts cesium-promoted, Ni-Cs-ITQ-6 and Ni-Cs-FER, a shift of the reduction signals to lower temperature, in the TPR-H₂ profile, is observed; this means that more reducible Ni species are present on the support (results not shown).

Table 1: CH₄ and CO₂ conversion, H₂/CO ratio and coke amount values for tested catalyst, after 10 hour of time on stream at 700°C.

Sample	X _{CH4}	X _{CO2}	H ₂ /CO	Coke [wt%]	Ref.
Ni-Silicalite-1	63	83	1.23	6.00	Frontera et al., 2013
Ni-MCM-41	75	86	1.03	4.40	Frontera et al., 2013
Ni-HMDS-Silicalite-1	77	82	1.02	4.20	Frontera et al., 2013
Ni-ITQ-6	77	90	1.39	2.10	Frontera et al., 2013
Ni-FER	75	90	1.40	0.88	Unpublished results
Ni-Cs-ITQ-6	75	92	1.24	0.76	Unpublished results
Ni-Cs-FER	73	91	1.23	0.52	Unpublished results

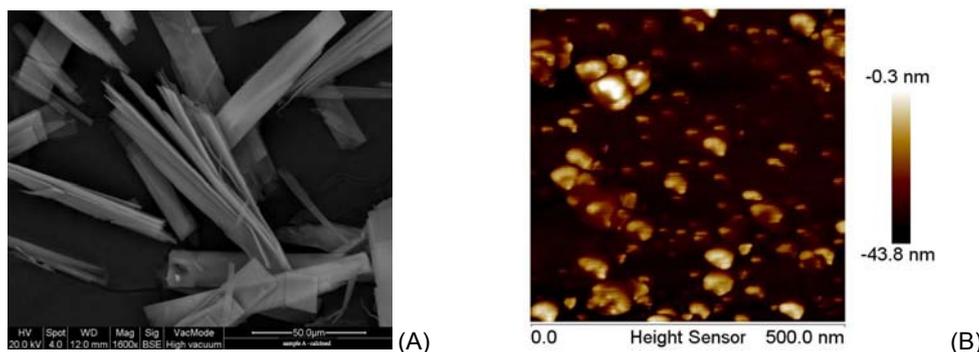


Figure 1: (A) SEM image of calcined FER support; (B) AFM images of fresh Ni-FER catalyst

The catalytic performance of these two catalysts containing cesium shows the highest CO₂ conversion and the lowest carbon deposition. Ni-Cs-FER, has been investigated in a long time test: the coke amount detected on the catalyst after 30h on stream has been lower than 0.45 wt%. This very high performance can be explained considering simultaneously two important aspects: (i) the increased basicity of the support by cesium addition that, leading to an enhanced adsorption of CO₂, favours the carbon gasification by formed water through reverse water gas shift reaction, and (ii) the lamellar structure of the support that favors the dispersion of nickel nanoparticles, thus preserving it from sintering and reducing coke deposition.

3.2 CO₂ methanation experiments discussion

The CO₂ methanation experiments have been carried out under atmospheric pressure, using a continuous fixed-bed microreactor. The catalytic experiments have been conducted at 400 °C and with a 30,000 h⁻¹ gas hourly space velocity (GHSV). Effluent gases from the reactor have been analyzed, previous removing of water through condensation in a silica gel trap, by two chromatographs equipped by TCD detectors. Monometallic nickel/gadolinia-doped ceria (Ni/GDC) and bimetallic nickel/iron gadolinia-doped ceria (Ni-Fe/GDC) catalysts have been prepared and tested. It is well known that the activity and the selectivity of metal catalysts are function not only of metal loading but also of the oxidation state of metal atoms. Very recent results on the role of iron on the dispersion of NiO nanoparticles have been reported by Lu et al. 2016 and Pandey et al. 2016. Lu et al. found that small amounts of La, Ce, Co or Fe promoters favor the best dispersion of NiO nanoparticles, increasing the quantity of reduced and active nickel species. Doped nickel catalysts have been tested on both CO and CO₂ methanation. They found that iron addition has effect in the CO₂ methanation with respect to other elements: Ni-Fe/ZrO₂ catalyst (Ni/Fe ratio equal to 5) exhibits excellent stability in the reaction. Pandey et al have studied the effect of different supports on Ni-Fe catalyst. They tested Al₂O₃, ZrO₂, TiO₂ and SiO₂ type supports. Due to the better ability of Al₂O₃ material to adsorb CO₂ with respect to the other supports, the authors claimed that Ni-Fe/Al₂O₃ catalyst (Ni/Fe ratio equal to 3) shows the best performance in the CO₂ methanation.

Table 2: CO₂ conversion and CH₄ selectivity values for monometallic and bimetallic catalysts.

Catalytic results [%]	Lu et al., 2016		Pandey et al., 2016		Frontera et al., present work	
	Ni/ZrO ₂	Ni-Fe/ZrO ₂ Ni/Fe = 5	Ni/Al ₂ O ₃	Ni-Fe/Al ₂ O ₃ Ni/Fe = 3	Ni/GDC	Ni-Fe/GDC Ni/Fe = 3
CO ₂ conversion	83	70	11	22	92	81
CH ₄ selectivity	86	96	n.d.	n.d.	100*	100*

Temperature reaction of methanation was of 400°C for Lu et al. and our tests, 250°C for Pandey et al. tests.

*Results calculated on dry-basis.

Table 2 summarizes the performance of the best catalysts studied in these two recent works with the performance of our monometallic (Ni/GDC) and bimetallic (Ni-Fe/GDC, with Ni/Fe ratio equal to 3) catalysts. Table 2 summarizes the catalytic performance of compared monometallic and bimetallic catalysts. The performances of Ni/GDC and Ni-Fe/GDC are superior to the other catalysts. Pandey et al. carried out their catalytic experiments at 250 °C and they highlighted that the iron addition in Ni/Al₂O₃ catalyst, with Ni/Al=3, has a positive effect on the CO₂ conversion. Increasing the iron amount in the catalyst, however, the CO₂ conversion strongly decreases (from 22.1% for 7.5Ni2.5Fe/Al₂O₃ catalyst to 1.9% for 2.5Ni7.5Fe/Al₂O₃

catalyst). Comparing the results obtained at higher temperature, at 400 °C, it is possible to observe that the CO₂ conversion reached by Ni/GDC catalyst is higher than that of Ni/ZrO₂.

Moreover, the CO₂ conversion obtained by iron doped Ni/ZrO₂ results to be lower than that obtained by Ni-Fe/GDC catalyst. With respect to ZrO₂ and Al₂O₃, gadolinia doped ceria support strongly promotes the CO₂ conversion over both Ni and Ni-Fe catalysts with the highest CH₄ selectivity can be obtained.

In Figure 2 the TPR profiles of Ni/GDC, Fe/GDC and Ni-Fe/GDC are reported. According to the results reported also by Lu et al., the presence of a second metal modifies the reduction profile of the monometallic catalyst. Ni/GDC reduction pattern shows two peaks centered at about 396 °C and 426 °C attributable, respectively, to the reduction of nickel oxides in the bulk and to the NiO species more strongly bonded to the support. H₂-TPR profile of Fe/GDC shows three broad peaks at about 407 °C, 604 °C and 754 °C, ascribable to the progressive reduction of Fe₂O₃ species. The Ni-Fe/GDC TPR profile shows a well defined peak at about 420 °C, related to the reduction of NiO species. This suggested that the Ni and Fe species are alloyed on the final catalyst. This evidence is in accordance with XRD results in which the (111) reflection of the cubic structure of Ni is shifted to lower Bragg angles (results not shown). The micrograph of fresh Ni/GDC catalyst shows nickel nanoparticles, in the range of 3-8 nm, homogeneously dispersed on the support (Figure 3A). In the sample, after reaction, no relevant sintering of Ni particles has been detected and no carbon is visible both for monometallic and bimetallic catalyst (Figure 3B for Ni-Fe/GDC spent catalyst, as representative sample). Anyway, the possible presence of carbon on spent catalysts has been analyzed by CHNS technique. Only the 0.43 %wt of carbon has been detected on Ni-Fe/GDC catalyst. Gadolinia doped ceria support plays a decisive role in this respect catalyst. The ability of ceria to generate oxygen vacancies is well investigated and known (Pan et al., 2014, Palma et al., 2016) as well as the ability of rare earth oxides to enhance the surface basicity of pure CeO₂ (Bernal et al., 2006). By analyzing these results, it is possible to ascribe to GDC support a dual effect: to promote the reduction of CO₂ molecules by the presence of surface oxygen vacancies that weaken the carbon-oxygen bond of CO₂ and to favour the dispersion of Ni nanoparticles. Therefore, with respect to conventional supports (ZrO₂, Al₂O₃, SiO₂, etc.), GDC is able to improve the performance of bi-metallic Ni-Fe catalysts.

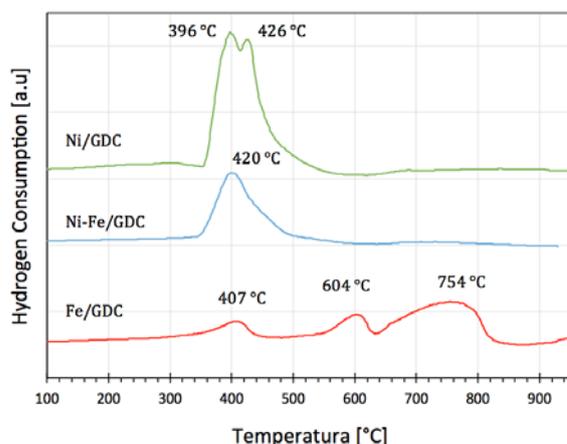


Figure 2. H₂-TPR of fresh catalysts: Ni/GDC, Ni-Fe/GDC and Fe/GDC.

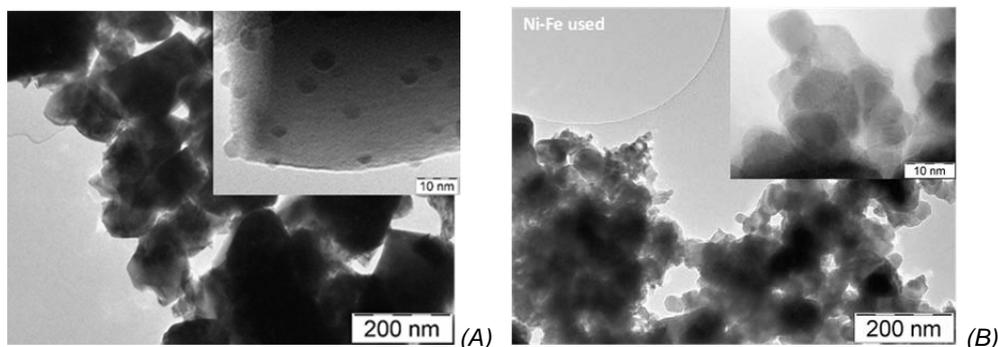


Figure 3. TEM images of (A) fresh Ni/GDC and (B) spent Ni-Fe/GDC catalysts.

4. Conclusions

CO₂ conversion by dry-reforming and by methanation represents, today, a potential solution to greenhouse gases emissions control. Both reactions can be catalysed by supported nickel nanoparticles.

The type of support plays a pivotal role in the catalytic performance of metal, both for dry-reforming and CO₂ methanation.

High metal dispersion, small metal particles dimension and presence of promoters species are characteristics in common for active and stable catalysts, in both catalytic processes.

Particularly, highly defective supports or lamellar structure, such as ITQ-6 and FER zeolite respectively, favour nickel particles dispersion, producing active species that are preserved from sintering effects and coke deactivation. Cesium addition improves the catalytic performance due to the increasing basicity of the support that leads to an enhanced adsorption of CO₂.

CO₂ methanation performance of mono-metallic nickel and of bi-metallic Ni-Fe catalyst are improved by the gadolinia doped ceria support. This material is able to combine two positive effects for CO₂ hydrogenation reaction: to produce active and stable nickel nanoparticles and to generate surface oxygen vacancies that increase the CO₂ dissociation, resulting in a superior activity and selectivity to CH₄ with respect to other supports most commonly used (ZrO₂, Al₂O₃, SiO₂).

Reference

- Bernal S., Blanco G., El Amarti A., Fitian L., Galtayries A., Martin J., Pintado J.M., 2006, Surface basicity of ceria-supported lanthana. Influence of the calcination temperature, *Surf. Interface Anal.*, 38, 229-233.
- Candamano S., Frontera P., Macario A., Crea F., Nagy J.B., Antonucci P.L., 2015, Preparation and characterization of active Ni-supported catalyst for syngas production, *Chem. Eng. Res. Des.*, 96, 78-86.
- Corma A., Chica A., Diaz U., Fornes V., World Patent WO200007722-A (2000).
- de Caprariis B., De Filippis P., Petrullo A., Scarsella M., 2015, Methane dry reforming over nickel perovskite catalysts, *Chem. Eng. Trans.*, 43, 991-996, DOI:10.3303/CET1543166.
- Frontera P., Aloise A., Macario A., Crea F., Antonucci P.L., Giordano G., Nagy J.B., 2011, Zeolite-supported Ni catalysts for methane reforming with carbon dioxide, *Res. Chem. Int.*, 37(2-5), 267-279.
- Frontera P., Macario A., Aloise A., Antonucci P.L., Giordano G., Nagy J.B., 2013, Effect of support surface on methane dry-reforming catalyst preparation, *Catal. Tod.*, 218-219, 18-29
- Frontera P., Macario A., Ferraro M., Antonucci P.L., 2017, Supported catalysts for CO₂ methanation: a review, *Catalysts*, 7(2), 59-87.
- Juan-Juan J., Roman-Martinez M.C., Illan-Gomez M.J., 2004, Catalytic activity and characterization of Ni/Al₂O₃ and NiK/Al₂O₃ catalysts for CO₂ methane reforming, *Appl. Catal. A*, 264, 169-174.
- Kang S.H., Ryu J.H., Kim J.H., Seo S.J., Yoo Y.D., Sai Prasad P.S., Lim H.J., Byun C.D., 2011, Co-methanation of CO and CO₂ on the Ni_x-Fe_{1-x}/Al₂O₃ catalysts: effect of Fe contents, *Korean J. Chem. Eng.*, 28(12) 2282-2286.
- Lu H., Yang X., Gao G., Wang J., Han C., Liang X., Li C., Li Y., Zhang W., Chen X., 2016, Metal (Fe, Co, Ce or La) doped nickel catalyst supported on ZrO₂ modified mesoporous clays for CO and CO₂ methanation, *Fuel*, 183, 335-344.
- Meylan F.D., Morean V., Elkaman S., 2016, Material constraints related to storage of future European renewable electricity surpluses with CO₂ methanation, *Appl. Catal. B: Env.*, 113-114, 2-10.
- Miao B., Ma S.S.K., Wang X., Su H., Chan S.H., 2016, Catalysis mechanisms of CO₂ and CO methanation, *Catal. Sci. Technol.*, 2, 4048-4058.
- Palma V., Ruocco C., Meloni E., Ricca A., 2016, Activity and stability of novel silica-based catalysts for hydrogen production via oxidative steam reforming of ethanol, *Chem. Eng. Trans.*, 52, 67-72 DOI:10.3303/CET1652012.
- Pan Q., Peng J., Sun T., Gao D., Wang S., 2014, CO₂ methanation on Ni/Ce_{0.5}Zr_{0.5}O₂ catalysts for the production of synthetic natural gas, *Fuel Process. Techn.*, 123, 166-171.
- Pandey D., Deo G., 2016, Effect of support on the catalytic of supported Ni-Fe catalysts for CO₂ methanation reaction, *J. Ind. Eng. Chem.*, 33, 99-107.
- Rajaram B., Ankur B., 2014, *Fuel Production with Heterogeneous Catalysis*, CRC Press, pp. 123-146.
- Rostrupnielsen J.R., Hansen J.H.B., 1993, CO₂-Reforming of methane over transition metals, *J. Catal.*, 144(1), 38-49.
- Sabatier P., Senderens J.B., 1903, Direct hydrogenation of oxides of carbon in presence of various finely divided metals, *Compt. Rend.*, 134, 689-691.