

14TH ASIAN CHEMICAL CONGRESS 2011

CONTEMPORARY CHEMISTRY FOR SUSTAINABILITY AND ECONOMIC SUFFICIENCY

5-8 SEPTEMBER 2011
BANGKOK, THAILAND

www.14acc.org



HOSTED BY CO-HOSTED BY



THE AUSPICES OF



SUPPORTED BY



14ACC International Advisory Committee

Prof. Jung-II Jin

Past-President, IUPAC, Korea University, Korea

Prof. David StC. Black

Secretary General, IUPAC, University of New South Wales, Australia

Prof. Chunli Bai

President, FACS, Key Laboratory of Molecular Nanostructure and Nanotechnology, Institute of Chemistry, the Chinese Academy of Sciences, China

Prof. Datuk Ting-Kueh Soon

Immediate Past-President, FACS, Vice President, Institute Kimia Malaysia, Malaysia

Prof. Long Lu

Secretary General, FACS, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, China

Prof. San H. Thang

Treasurer, FACS; Senior Principal Research Scientist, CSIRO Molecular and Health Technologies, Australia

Prof. Tahsin J. Chow

Coordinator of Projects, FACS, Institute of Chemistry, Academia Sinica, Chemical Society located in Taipei

Prof. Kyung Byung Yoon

Director of Scientific Affairs, FACS, Sogang University, Korea

Prof. Noriyuki Suzuki

Editor of Publication, FACS, Japan

Prof. Guoqiang Lin

Shanghai Institute of Organic Chemistry, CAS, China

Prof. Minoru Isobe

National Tsing Hua University, Taiwan

Prof. Thomas H. Lane

Past-President, ACS, USA

Prof. Nancy B. Jackson

President, ACS, USA

Prof. Timothy Deming

Professor, Department of Bioengineering University of California, Los Angeles, USA

Prof. Yongyuth Yuthavong

NSTDA, Thailand

Prof. M.R. Jisnuson Svasti

President, the Science Society of Thailand

Prof. Somsak Rujirawatana

Chulabhorn Research Institute, CRI, Thailand

Prof. Apichart Suksamran

Ramkhamhang University, Thailand

14ACC Local Organizing Committee

Supawan Tantayanon	<i>Chairperson</i>	<i>Chulalongkorn University</i>
Supa Hannongbua	<i>Secretary – General</i>	<i>Kasetsart University</i>
Warinthorn Chavasiri		<i>Chulalongkorn University</i>
Jintana Siripitayananon		<i>Chiangmai University</i>
Somkiat Srijaranai		<i>Khonkaen University</i>
Pranee Phinyocheep		<i>Mahidol University</i>
Walailak Puetpaiboon		<i>Prince of Songkla University</i>
Nittaya Ngawatana		<i>Rajamangala University of Technology Thanyaburi</i>
Surin Laosooksathit		<i>King Mongkut's University of Technology North Bangkok</i>
Thanattkhun Mongkolaussavarat		<i>Chulabhorn Graduate Institute</i>
Kitti Amornraksa		<i>Thammasat University</i>
Thongdee Leksophee		<i>Thammasat University</i>
Chanpen Chaitheerapapkul		<i>Department of Science Service, Ministry of Science and Technology</i>
Ladda Meesuk		<i>Kasetsart University</i>
Vudhichai Parasuk		<i>Chulalongkorn University</i>
Mongkol Sukwattanasinitt		<i>Chulalongkorn University</i>
Waraporn Parasuk		<i>Kasetsart University</i>
Patchanita Thamyongkit		<i>Chulalongkorn University</i>
Apinya Chaivisuthangkura		<i>Srinakharinwirot University</i>
Voravee Hoven		<i>Chulalongkorn University</i>
Churairat Duangduen		<i>Rajamangala University of Technology Thanyaburi</i>
Somma Pivsa-Art		<i>Rajamangala University of Technology Thanyaburi</i>
Chutarad Saridara		<i>Rajamangala University of Technology Thanyaburi</i>
Pornpan Pungpo		<i>Ubonratchathani University</i>
Paweena Kreurnil		<i>Department of Science Service, Ministry of Science and Technology</i>
Supavadee Kiatisevi		<i>Mahidol University</i>
Supakorn Boonyuen		<i>Thammasat University</i>
Wanchai Pluempanupat		<i>Kasetsart University</i>
Duangruthai Sridaeng		<i>Rangsit University</i>
Piyada Jittangprasert		<i>Srinakharinwirot University</i>
Thitinat Sukonket		<i>Suan Dusit Rajabhat University</i>
Charnsak Thongsornkleeb		<i>Chulabhorn Research Institute</i>
Rachada Hemapattawee		<i>Department of Science Service, Ministry of Science and Technology</i>
Jinda Yeyongchaiwat		<i>Bansomdejchaopraya Rajabhat University</i>
Winai Oungpipat		<i>Rajamangala University of Technology Krungthep</i>

The Program is Overseen by International Scientific Committee

Supa Hannongbua	<i>Chairperson</i>	<i>Kasetsart University, Thailand</i>
Waraporn Parasuk	<i>Co-chairperson</i>	<i>Kasetsart University, Thailand</i>
Bhinyo Panijpan		<i>Mahidol University, Thailand</i>
David StC. Black		<i>University of New South Wales, Australia</i>
David Evans		<i>Elsevier Properties SA, Neuchâtel, Switzerland</i>
David Winker		<i>CSIRO Molecular and Health Technologies, Australia</i>
Ekasith Somsuk		<i>Mahidol University, Thailand</i>
Kate Grudpan		<i>Chiangmai University, Thailand</i>
Kyung Byung Yoon		<i>Sogang University, Korea</i>
Margaret E. Kerr		<i>Worcester State University, USA</i>
Minoru Isobe		<i>National Tsing Hua University, Taiwan</i>
Mohamed Eisa		<i>UNIDO, Austria</i>
Mohammed Mosihuzzaman		<i>University of Dhaka, Bangladesh</i>
Nancy B. Jackson		<i>Sandia National Laboratories, USA</i>
Proespichaya Kanatharana		<i>Prince of Songkla University, Thailand</i>
Ornanong Arquero		<i>Chiangmai University, Thailand</i>
Somdej Kanokmedhakul		<i>Khonkaen University, Thailand</i>
Supawan Tantayanon		<i>Chulalongkorn University, Thailand</i>
Tahsin J. Chow		<i>Academia Sinica, Taiwan</i>
Thawatchai Tuntulani		<i>Chulalongkorn University, Thailand</i>
Ting-Kueh Soon		<i>Institute Kimia Malaysia, Malaysia</i>
Warinthorn Chavasiri		<i>Chulalongkorn University, Thailand</i>
Xiaoxia Li		<i>Institute of Process Engineering, CAS, China</i>
Yasushi Nishihara		<i>Okayama University, Japan</i>
Zuriati Zakaria		<i>Institute Kimia Malaysia, Malaysia</i>

List of Sponsors

The International Union of Pure and Applied Chemistry
Elsevier Properties SA
The Kavli Foundation
Royal Society of Chemistry
IRPC Public Company Limited
Bangkok Bank Public Company Limited
The Siam Cement Group
Mettler-Toledo (Thailand) Limited
L'OREAL (Thailand) Limited

Code	Title	Page
PO-G2-12	Parabens Determination by Ultra-Performance Liquid Chromatography Coupled with Electrochemical Detection	106
PO-G2-23	Preparation of Sewage Sludge-Based Adsorbent for Ammonia Gas Removal	112
PO-G2-39	Liquid Chromatographic Determination of Scopolamine in Hair with Free-Swimming Single Drop Liquid Phase Microextraction Technique	119
PO-G2-54	Two New Fluorescent Macrocycles Derived from a Novel Dialdehyde: A Novel Fluorescent Chemosensor for Zinc Ion	129
PO-G2-55	Greener Anodic Stripping Voltammetric Method Employing In Situ Plated Bismuth Film Electrode for Determination of Cadmium and Lead	135
PO-G2-75	Liquid Chromatography with C8-Silica Monolith in a Microchip	141
OR-G3-04	A Laboratory on Kinetics of Reaction between Iodate and Bisulfite for Secondary Students	146
OR-G4-06	Synthesis, Characterization and Emission Properties of Yttrium(III) and Lanthanide(III) Complexes of Tripodal Heptadentate Schiff-Base Ligands	152
OR-G4-19	Antimicrobial and Photocatalytic Activity of ZnO Nanostructures	158
OR-G4-20	NiFe ₂ O ₄ Catalyst: The Influence of Gas Feed Composition on CO ₂ /H ₂ Conversion into Alcohol Compounds	167
PO-G4-05	Effect of Calcination Temperature on Crystal Structure and Morphology of LaCoO ₃ Powder Prepared by Mechanochemical Method	173
PO-G4-07	Study on the Interaction between Curcumin with d ¹⁰ Metal Ion	179
PO-G4-15	RuCl ₃ .nH ₂ O: A Valuable Catalyst for One-Pot Synthesis of Hormone Steroid Derivatives	185
PO-G4-31	Synthesis and Characterization of Mesoporous CoFe ₂ O ₄	190
PO-G4-33	Hydrothermal Synthesis of Calcium Titanate Nanostructures	197
PO-G4-53	Hg(II)-Selective Fluoroionophoric Behaviors of a 2-(3-(2-Aminoethylsulfanyl) Propylsulfanyl)Ethanamine Bearing a Naphthalimide Fluorophore	203
PO-G4-84	Structural Property of Copper Phosphates Studied by X-ray Absorption Spectroscopy and Their Catalytic Property	209
PO-G4-88	Microwave Synthesis of Nano-Zeolite a From Rice Husk Ash	215

NiFe₂O₄ Catalyst : The Influence of Gas Feed Composition on CO₂/H₂ Conversion into Alcohol Compounds

Rudy Situmeang, Sukmawibowo, Mitra Septianto and Septian Tri Sulisthio

Department of Chemistry, FMIPA University of Lampung, BandarLampung 35415
E-mail address : situmeang@unila.ac.id

Abstract

Ni_xFe_{1-x}O₄ catalyst (where x = 0, 2) was prepared by using citric acid method from its precursor of nitrates. The catalyst furthermore is characterized by using X-ray diffractometer, IR spectrophotometer, and EDX-SE microscopy. To examine its activity, the catalyst was used in CO₂/H₂ conversion at different temperatures (200 – 400 °C) by varying the ratio of CO₂/H₂ (3/1 ; 4/1 ; and 5/1) in gases feed. The experiment results indicated the dependency of CO₂/H₂ conversion on both temperature and feed ratio of CO₂/H₂, with the highest alcohol formation (almost 800 ppm) was achieved at 300 °C under the ratio of CO₂/H₂ (4/1, 50 mL min⁻¹). Moreover, a more distributed product of alcohol compounds (such as methanol, ethanol and butanol) are happened, included propanol in the CO₂/H₂ ratio of 5/1. X-ray diffraction examination confirmed that the catalyst has a spinel structure as a major phase in Fe_{0.8}Ni_{0.2}O_{3±δ} crystalline. FTIR analysis indicated that both the Lewis acid sites which are located in wave numbers of 1490 and 1450 cm⁻¹ and Bronsted – Lowry acid sites which are located in wave numbers of 1645 and 1622 cm⁻¹ were involved in the catalytic conversion. Furthermore, Rietveld analysis proved that catalyst consists of NiFe₂O₄, NiO, Fe₂O₃, and Fe₃O₄ crystalline phases.

Keywords : CO₂/H₂ Conversion, CO₂/H₂ ratio, alcohols formation, Lewis and Brønsted-Lowry acid properties

1. Introduction

With regards to steadily increased energy use and the limited oil production as well as the environmental concerns, development of renewable energy sources is a crucial need around the world. In this respect, development of alternative energy sources which simultaneously help to reduce the environmental deterioration is an ideal solution, which remains a challenge to scientific society. Acknowledging the need to consider two aspects of energy mentioned above, production of alcohols, which is an important type of alternative energy resources, from CO₂ gas and syn – gas is a very promising scheme. Considering the predicted amount of CO₂ gas released to the atmosphere that reach 22 x 10⁶ tones every year, it could be seen that this gas is a very potent raw materials. At the same time, utilization of this gas will result in significant improvement of the atmosphere.

Proceedings of 14th Asian Chemical Congress (14ACC)

Moreover, alcohols are important raw materials for production of a large number of other chemicals such as dimethyl ether, olefin, gas – fuel oil, acetic acid, and aldehydes [1 – 3].

In an attempt to utilize CO₂ gas, catalytic conversion of CO₂/H₂ mixture into alcohols is currently the most intensively pursued. CO₂ gas is thermodynamically very stable molecule and the end product of many reactions needs an activation. Many efforts have been made attempted to mitigate CO₂ into such as light olefin or liquid hydrocarbon [4,5], alternative energy fulfillment needed [6], methanol [7,8], Liquid Petroleum Gas, ethylene and propylene [9]. In addition, this method can also produce CO gas which is used in Fischer-Tropsch process [10].

In general, results of CO₂ catalytic hydrogenation reaction is predominantly affected by the type of catalyst used [10 – 12]. Catalyst that can be used in this reaction has to have both activity and stability against to Reverse Water-Gas Shift, RWGS and Fischer-Tropsch reaction [8, 13 – 15]. Furthermore, reaction condition such as feed gas ratio (CO₂/H₂), temperature reaction and pressure will also affect a product distribution.

For example, if reaction goes on at low temperature (220 – 250 °C and 25 bar), the product tends to both wax and diesel fuel selectivities. Otherwise, the product will tends to olefin selectivity [16]. Then, it is observed that molar feed ratio of CO₂/H₂ has been one of the important factors affecting alcohol production, for example, H₂/CO₂ feed gas ratio of 4/1 is the better catalyst's performance [12].

Aims: Based on these informations as mentioned above, this research is focused on how CO₂/H₂ ratio affects the catalytic activity performance of NiFe₂O₄ to converse CO₂/H₂ at a range of temperature (200 – 400 °C).

2. Materials and Methods

2.1 Catalysts Preparation

Solid Fe_{0.8}Ni_{0.2}O_{3±δ} was prepared by dissolving Fe(NO₃)₃ · 9 H₂O, and Ni(NO₃)₂ · 6 H₂O in citric acid solution, respectively. Then, these solutions were mixed, heated and evaporated at 80 °C until sol – gel solution formed. Furthermore, this precursor was calcinated at 600 °C for 6 hours (increased by 2 °C min⁻¹). Solid formed was crushed into a fine grain before making a characterization.

2.2 Catalysts Characterization

X-rays power diffraction pattern of Fe_{1-x}Ni_xO_{3±δ} were recorded from 2θ = 10 to 90 ° on a Philips diffractometer Model PW 1710 using Cu K_α radiation at a step 0.02 ° per second and quantitative analysis is done by Rietveld method. Electron micrographs were obtained with Scanning Electron Microscopy in order to know its morphology. To determine Lewis and Brønsted – Lowry sites, catalysts were previously contacted over

night to pyridin saturated vapor at ambient temperature, then analyzed by using FT-IR spectrophotometer.

2.3 Catalytic Measurements

The CO_2/H_2 reaction was carried out in a vertical down flow U – tube natural quartz reactor (with inner diameter 12 mm) at atmospheric pressure and 100 – 400 °C. In a typical experiment, ca. 50 mg of sieved catalyst was placed in U-tube between two quartz wool. The reactor was placed vertically inside a programmable cylindrical furnace, which was heated electrically. Before the reaction, the catalyst was pretreated in flowing process gas (Ar/H_2 , 2 L h^{-1}) at 500 °C for 30 minutes. The product stream coming from the reactor was passed through collector tube with water as a trapper and immersed into ice cubes. Then, the product were analyzed with gas chromatography.

3. Results and Discussion

3.1 Catalyst Characterizations

In Fig. 1, it is shown that $\text{Fe}_{0.8}\text{Ni}_{0.2}\text{O}_{3\pm\delta}$ catalyst and others consist primarily of NiFe_2O_4 crystalline phase which has representative peaks appearing at 2θ : 35,96° (100%), 63,24° (35,73%), 30,78° and 57,74° (31,64%). These peaks were appropriated to JCPDS file of 10-0325. Furthermore, crystalline phases of Fe_2O_3 , NiO , and Ni_2O_3 were formed even in relative small quantity. Based on Reitveld analysis, the percentages of crystalline phases formed is 65,74% NiFe_2O_4 , 30,23% NiO , 1,02% Fe_2O_3 , and 3,01% Fe_3O_4 .

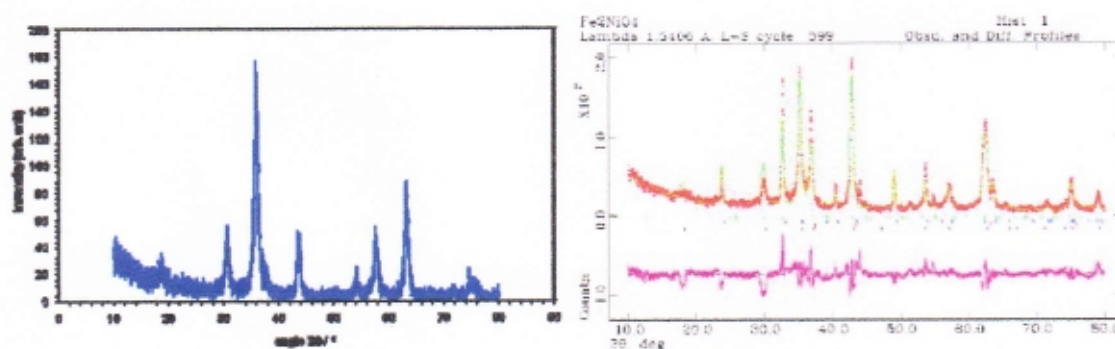


Figure 1. Diffractogram catalyst and Rietveld analysis of $\text{Fe}_{0.8}\text{Ni}_{0.2}\text{O}_{3\pm\delta}$

3.2 FTIR Analysis of Bronsted-Lowry and Lewis acid sites

Both Brønsted – Lowry and Lewis acid sites of $\text{Fe}_{1-x}\text{Ni}_x\text{O}_{3\pm\delta}$ catalysts (where $x = 0.2$) was investigated by FTIR instrument. Infra red spectrum showed that $\text{Fe}_{1-x}\text{Ni}_x\text{O}_{3\pm\delta}$ catalysts, in general, has Brønsted – Lowry acid sites at wavenumber of ± 1645 and $\pm 1622 \text{ cm}^{-1}$. Then, Lewis acid sites appeared at wavenumber of ± 1490 and $\pm 1450 \text{ cm}^{-1}$. These acid sites are believed that involved in attracting and polarizing CO_2 and H_2 molecules.

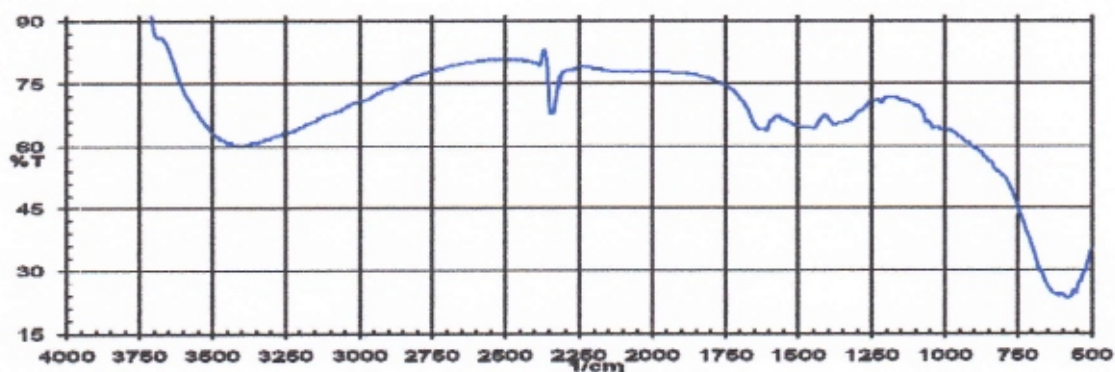


Figure 2. Infra red spectra of $\text{Fe}_{1-x}\text{Ni}_x\text{O}_{3\pm\delta}$ catalyst which had been treated by Pyridine (where $x = 0.2$).

3.3 Catalyst activity

Fig. 4 shows that $\text{Fe}_{0.8}\text{Ni}_{0.2}\text{O}_4$ catalyst is active in CO_2/H_2 reaction to produce alcohol compounds in a various H_2/CO_2 ratio and temperature. In fact, the gas feed of H_2/CO_2 ratio affects its catalytic activity such as a various compound formed and a temperature reaction.

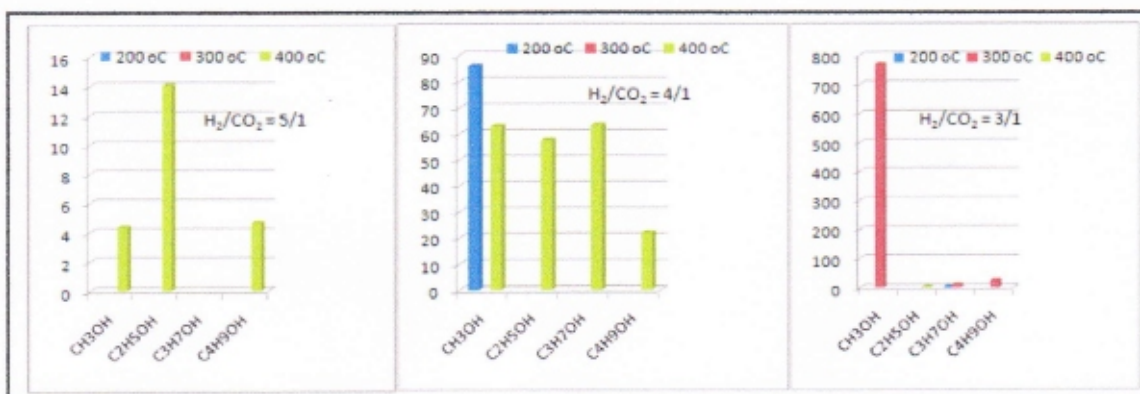


Figure 4. Alcohol formation (yields in ppm) by $\text{Fe}_{0.8}\text{Ni}_{0.2}\text{O}_4$ catalyst in different reaction temperature and H_2/CO_2 ratio.

As shown on Fig. 4, the activity of $\text{Fe}_{0.8}\text{Ni}_{0.2}\text{O}_4$ catalyst is appeared in each H_2/CO_2 ratio of gas feed. Distribution product is occurred at every reaction condition. However, the more selective product is happened in H_2/CO_2 ratio of 4/1 and 3/1 at temperature of 200 and 300 °C, respectively. At temperature of 400 °C, a varied products of alcohol is observed on H_2/CO_2 ratios of 5/1 and 4/1. This product consists of methanol, ethanol, propanol, and butanol. It can be implied that catalyst was holding intermediate products up so further reaction was possibly happened. Frankly speaking, it was enough

time to form C_2^+ , C_3^+ and C_4^+ cations in order to produce a related alcohol compounds if hydrogen gas in gas feed is exceeded.

4. Conclusions

Based on this experiment, we can conclude that the H_2/CO_2 ratio in gas feed affects the formation of alcohol compounds. In general, $Fe_{0.8}Ni_{0.2}O_4$ catalyst is active and promising to be developed on this CO_2/H_2 reaction under mild temperature conditions. Increasing hydrogen content in gas feed distributing a varied products of alcohol compounds. Furthermore, acid sites of catalyst play a role on CO_2/H_2 reaction.

5. Acknowledgments

This research project was financially supported by The National Strategic Research University of Lampung and Ministry of Indonesia Higher Education program under contract No. 287/H26/PL/2010.

6. References

- [1]. Roger, Anne-Cecile., C.A Guerrero F., Daniel N., Yvonne N'Guyen., and Claire Courson. 2008. *Methane selective oxidation to formaldehyde with Fe-catalyst on supported on silica or incorporated into the support*. Cat. Comm., vol. 9(5), p. 864 – 869.
- [2]. Spetcht, M., A. Bandi., F. Staiss., and T. Weimer. 1998. *Comparison of the renewable transportation fuel liquid hydrogen and methanol with gasoline energetic and economic Aspects*. Int. J. Hydrogen Energy 23, p. 387.
- [3]. Lunsford, Jack H., 2000. *Catalytic conversion of methane to more useful chemicals and fuels : A challenge for the 21st century*. Cat. Today , Vol. 63, p. 165 – 174.
- [4]. Indala, S. 2004. *Development and Integration of New Processes Consuming Carbon Dioxide in Multi-Plant Chemical Production Complexes*. Thesis. Department of Chemical Engineering. Andhra University. India, p. 4 – 22.
- [5]. Mamedov, A. Kh., and Krylov., O.V. 1995. *Heterogeneous catalytic reactions of carbon dioxide*. Russian Chemical Reviews 64(9), p. 877 – 900.
- [6]. Williams, R. H., E. D. Larson, H. Jin. 2006. *F-T Liquids Production from Coal and Coal + Biomass with CO₂ Capture and Alternative Storage Options: Aquifer CO₂ Storage vs CO₂-Enhanced Oil Recovery*. Princeton Environmental Institute. Princeton University. Princeton, p. 1 – 24.
- [7]. Cabrera, I. M., M. L. Granados, P. Terreros, J. L. G. Fierro. 1998. *CO₂ Hydrogenation Over Pd-Modified Methanol Synthesis Catalysts*. Catalysis Today, Vol 45, p. 251 – 256.
- [8]. Joo, O. S. 1999. *Camere Process for Carbon Dioxide Hydrogenation to Form Methanol*. Catalysis Laboratory. Korea Institute of Science and Technology. Seoul. South Korea, p. 686 – 689.
- [9]. Fujiwara, M., R. Kieffer, H. Ando, Q. Xu, Y. Souma. 1995. *Hydrogenation of Carbon Dioxide over Fe-ZnO/HY Composite Catalyst*. LERCSI, ECPM Strasbourg. France, p. 1 – 5.
- [10]. Srinivas, S., R. K. Malik, S. M. Mahajani. 2009. *Fischer-Tropsch Synthesis Using* Proceedings of 14th Asian Chemical Congress (14ACC)

- Bio-Syngas and CO₂*, Department of Chemical Engineering, Indian Institute of Technology Bombay, p. 66 – 71.
- [11]. Lapidus, A. L., N. A. Gaidai, N. V. Nekrasov, L. A. Tishkova, Yu. A. Agafonov, T. N. Myshenkova. 2006. *Mechanism of Carbon Dioxide Hydrogenation over Copper and Nickel Catalyst*. DGMK/SCI-Conference “Synthesis Gas Chemistry”. Dresden German, p. 274.
- [12]. Udron, Laurence. 1997. Mise au point de catalyseurs au cuivre pour la synthèse du méthanol à partir de CO₂ + H₂. Université de Louis Pasteur, Strasbourg France.
- [13]. Riedel, T., M. Claeys, H. Schulz, G. Schaub, S. S. Nam, K. W. Jun, M. J. Choi, G. Kishan, K. W. Lee. 1999. *Comparative Study of FTS with H₂/CO and H₂/CO₂ Syngas Using Fe and Co Catalysts*. App. Cat. A, Vol. 186, p. 201 – 213.
- [14]. Luo, M., S. Bao, T. Das, B. H. Davis. 2007. *Fischer-Tropsch Synthesis: Is a Single Site Responsible for FTS and WGS on Iron Catalysts?*. Center for Applied Energy Research, University of Kentucky, p. 1 – 2.
- [15]. Jung K.D., and O.S Joo. 2003. *Stability of ZnAl₂O₄ Catalyst for Reverse-Water-Gas-Shift Reaction (RWGS)*. Bull. Korean Chem. Soc., Vol. 24, p. 86 – 90.
- [16]. Dry, M. E. 2002. *Fischer-Tropsch Process: 1950 – 2000*. Catalysis Today, Vol. 71, pp. 227 – 241.