INTERNATIONAL SEMINAR
ON SUSTAINABLE BIOMASS PRODUCTION AND UTILIZATION: CHALLENGES AND OPPORTUNITIES

The University of Lampung, Indonesia, August 3rd- 4th, 2009

PROCEEDING

ISBN 978-979-18755-7-8

University of Lampung
Yokohama National University
Goverment of Lampung Province
Ministry of Research and Technology
Directorate General of Higher Educations

Main Menu

Preface

Environmental issues and uncertainly in the future of fossil based energy sources have stimulated global interest in the development of alternative and renewable fuels. In this context, biomass has been identified as a promising resource because of it is abundantly available and convertible into different forms of bio-energy which suits various needs. In addition, bio-energy is acknowledged as environmental friendly because it produces less CO2. There is also a high potential benefits from C-sink for carbon trade in line with Kyoto protocol. However, during the past few years, several controversies have complicated bio-energy development. It has been implicated for exacerbating climate change rather than mitigating and also been cited as a major factor in rising food prices. Such different views reflect that in addition to technical issues, socio-economic issues should be taken into account in pursuing of bio-energy development.

Recognizing the important roles of biomass, The University of Lampung placed biomass development as one of the priorities. In line with this commitment, currently The University of Lampung has established The Biomass Laboratory, under the management of Research Institution. This particular laboratory is devoted to biomass development in a board sense related to biomass utilization, including development of alternative energies. Further development is projected to up-grade this laboratory into A Centre of Excellent on Biomass Research in the next few years. As a part of development plan toward establishment of the centre, Lampung University and Yokohama National University are planning to collaboratively host international seminar on biomass utilization and management, in order to gain more insight on biomass utilization impacts on Green House Gas Emission (GHGE).

The seminar is planned to be carried out to pursue the following three main goals (1) to improve knowledge and understanding of Indonesian scientists (participants) on the ongoing development of science and technology in the field of biomass, (2) to enhance the capacity of the participants in carrying out research on various aspects of biomass, and (3) to enhance understanding on the impacts of biomass utilizations and related issues of C-sink issues for carbon trade in line with Kyoto Protocol and Green House Effects due to CO2 emission.

In this opportunity, on behalf of the Organizing Committee and The University of Lampung, I would like to thank all the participants for their presentation. I would like to extent our sincere thanks and highest appreciation to Yokohama National University for invaluable supports, including financial support for the seminar. Our appreciation also extent to the Government of the Province of Lampung, PT Gunung Madu Plantation, BNI 46, Directorate General of Higher Education Department of National Education, and many others for their supports.

Seminar Organization

Organizing Committee:

- Chairman : Dr. Eng. Admi Syarif
- Vice Chairman : Ir. Zainal Abidin, M.Sc.
- Secretary : Wasinton Simanjuntak, Ph.D.
- Vice Secretary : Dr. Suripto Dwi Yuwono
- Treasurer : Dr. Irwan Ginting Suka, M.Sc.

Scientific committee:

- Prof. Dr. Ir. Muhajir Utomo (Indonesia)
- Prof. Dr. Koichi Fujie (Japan)
- Prof. Dr. Nobuhiro Kaneko (Japan)
- Prof. Dr. Ryohei Kada (Japan)
- Prof. Dr. Michel Ritz (USA)*
- Prof. Dr. Ir. Jamalam Lumban Raja (Indonesia)
- Prof. Dr. Bustanul Arifin (Indonesia)
- Dr. John Hendri (Indonesia)
- Dr. Udin Hasanuddin (Indonesia)

Seminar Committee:

- Dr. F.X. Susilo (Coordinator)
- Dr. Ainin Niswati
- Dr. Bartoven Vivit Nurdin

Secretariat Committee:

- Yasir Wijaya, S.Si (Coordinator)
- Frensi Riastuti S.Sos
- Adiguna Setiawan

PROCEEDING

International Seminar

ON SUSTAINABLE BIOMASS PRODUCTION AND UTILIZATION: CHALLENGES AND OPPORTUNITIES

Editor:

Prof. Muhajir Utomo (Indonesia)

Prof. Jamalam Lumban Raja (Indonesia)

Prof. Nobuhiro Kaneko (Japan)

Prof. Ryohei Kada (Japan)

Prof. Koichi Fujie (Japan)

Prof. John Hendri (Indonesia)

Dr. Udin Hasanuddin (Indonesia)

Dr. Irwan Ginting Suka, M.Sc (Indonesia)

Wasinton Simanjuntak, Ph.D (Indonesia)

Dr. Darwin Pangaribuan (Indonesia)

Dr. Suripto Dwi Yuwono (Indonesia)

Ir. Zainal Abidin, M.Sc (Indonesia)

Dr. Eng. Admi Syarif (Indonesia)

Dr. F.X. Susilo (Indonesia)

Organizing Editor:
Yasir Wijaya, S.Si

Proceeding of International Seminar :
August 2009 / Editor,
John Hendri … [et al.].—Bandar
Lampung : Lembaga Penelitian
Universitas Lampung, 2009.
viii +437 pg. ; 21 x 29,7 cm
ISBN 978-979-18755-7-8

Published by :
LEMBAGA PENELITIAN UNIVERSITAS LAMPUNG
Jl. Prof. Dr. Sumantri Brojonegoro no. 1 Gedungmeneng
Bandarlampung 35145
Telp. (0721) 705173, 701609 ext. 136, 138,
Fax. 773798,

Content:

Horisawa, S., Sunagawa, M., Tamai, Y., Matsuoka, Y., Miura, T., Terazawa, M., 1999. Biodegradation of nonlignocellulosic substances II: physical and chemical properties of sawdust before and after use as artificial soil. Journal of Wood Science 45 (6), 492-497.

Houghton, J.I., Burgess, J.E., Stephenson, T., 2002. Off-line particle size analysis of digested sludge. Water Resources 36, 4643-4647.

Hwang, S.I., Lee, K.P., Lee, D.S., Powers, S.E., 2002. Models for estimating soil particle-size distributions. Soil Science Society of America Journal 66 (4), 1143-1150.

Kitsui, T., Terazawa, M., 1999. Bio-Toilet environmentally-friendly toilets for the 21 century (dry closet using sawdust as an artificial soil matrix). In: Proceedings of international symposium of bio-recycling/composting. 6-8 september, Sapporo, Japan.

Paulrud, S., Mattsson, J.E., Nillson, C., 2002. Particle and handling characteristics of wood fuel powder: effects of different mills. Fuel Processing Technology 76, 23-39.

Rühlmann, J., Körschens, M., Graefe, J., 2006. A new approach to calculate the particle density of soils considering properties of the soil organic matter and the mineral matrix. Geoderma 130, 272-283.

Terazawa, M., Horisawa, S., Tamai, Y., Yamashita, K., 1999. Biodegradation of Lignocellulosic substance I: System for complete degradation of garbage using sawdust and aerobic soil bacteria. Journal of Wood Science 45 (4), 354-358.

Terazawa, M., 2003. Sawdust Saves Globe—Bioconversion of biomass wastes into multifunctional recyclates using sawdust as an artificial soil matrix—. In: Proceedings of the 1st International Symposium on Sustainable Sanitation, Nanjing, China (1), 9-12.

The Ministry of Forestry Republic of Indonesia., 2007. Forestry Statistics of Indonesia year 2006. Jakarta, Indonesia. http://www.dephut.go.id/INFORMASI/STATISTIK/2006/IV24_06.pdf>.

Zavala, M.A.L., Funamizu, N., Takakuwa, T., 2004. Modeling of aerobic biodegradation of feces using sawdust as a matrix. Water Resources 38 (5), 1327-1339

$NiO/LaCrO_3$ Catalyst for converting methane to Methanol

Rudy Situmeang, R. Supryanto, Wasinton Simanjuntak, and Joko Susilo
Department of Chemistry, FMIPA University of Lampung, BandarLampung 35415
situmeangr@unila.ac.id

Abstract

$NiO/LaCrO_3$ catalyst was prepared using citric acid method from its' precursor of nitrates. The preparation steps consist of wet impregnation of varied percentages (b/b) NiO into $LaCrO_3$, evaporation and calcination. To examine its activity, the catalyst was used in CH_4 conversion experiment at different temperatures. The experimental results indicated the dependency of CH_4 conversion on temperature, with the highest methanol formation (176.05 µL) was achieved at 100 ^oC under Ar/CH_4 (40/10, 50 mL min^{-1}) as a feed. Adding O_2 gas into feed increasing the methanol formation and the increment achieved 68%. X-ray diffraction examination proved that its crystalline phases consist of NiO cubic structure in a bulk crystalline of $LaCrO_3$ perovskite structure. Furthermore, increasing Ni content enlarging unit cell volume of catalyst. FTIR analysis appeared to indicate that both the Lewis and Brønsted-Lowry acid sites were involved in the catalytic conversion of CH_4.

Keywords : *CH_4 Conversion, $NiO/LaCrO_3$ activity, CH_3OH formation, Lewis and Brønsted-Lowry acid properties*

1. Introduction

Now days, air emission regulation has been applied a broadly across the nations, especially on activities resulting pollutant gases such as NO_x, SO_x, and CO_x. In addition, source of fuel energy is limited for 20 – 30 years. Therefore, finding out the energy resource dealt with environment is really interesting and challenging (Bell et al., 2004, AtlanticBiomass@aol.com, www.acrion.com, and www.methanol.org).

One of alternative energy resources is biomass with its marvelous abundance. Biomass can be change simply to biogas by catalytic pyrolyse or microbial process. The main product of these processes is methane gas. Furthermore, methane gas is processed to methanol by these methods, first forming synthesis gas and then methanol or direct methane oxidation to oxygenates excluding the synthesis gas generating step. In the first method, including synthesis gas forming, unfortunately is a highly endothermic process, thus also expensive.

In case of direct methane oxidation to oxygenates, many researchers are involved in over the world. For instances, HZSM-5 supported Fe and Na were considered to be active to methanol production both in intermediate and high temperatures (Michalkiewicz, 2004). In other research, one group reported that methane can be transformed into higher hydrocarbons or alcohol by using first row transitional metal oxides – containing ZSM-5 catalyst . The reaction is happened via C_5^+ ion formation (Han et al., 1994). Another group

of research used water as a feed due to increase the methanol formation (Alptekin, et al., 2000).

In this moment, we study the conversion of methane into methanol using $LaCrO_3$ doped NiO. Here, we emphasize our study on how increasing Ni content into $LaCrO_3$ can give a synergic effect in directly partial oxidation of methane to methanol at low reaction temperature.

2. Experimental

2.1. Catalysts Characterization

X-rays power diffraction pattern of $NiO/LaCrO_3$ were recorded from $2\theta = 10$ to 90^o on a Philips diffractometer Model PW 1710 using Cu K_α radiation at a step 0.02^o . Electron micrographs were obtained with Scanning Electron Microscope . To determine Lewis and BrØnsted – Lowry sites, catalysts were previously contacted to ammonia saturated vapor at ambient temperature, using FT-IR spectrophotometer.

2.2. Catalysts Preparation

Solid $LaCrO_3$ was prepared by dissolving $Cr(NO_3)_3 . 9\ H_2O$, and $La(NO_3)_3 . 6\ H_2O$ in citric solution. Then, these solutions (1:1) was mixed and evaporated until sol – gel solution formed. Furthermore, this precursor was calcinated at 600 ^oC for 6 hours (increased by 2 $^oC\ min^{-1}$). Solid formed was crushed into a fine grain. Catalyst $LaCrO_3$ supported NiO were prepared by dissolving nickel nitrate solid in citric solution and then adding $LaCrO_3$ solid with ratio 5 to 7% (NiO : $LaCrO_3$). After solvent evaporated, sol – gel form was dried and calcinated as before. Solid NiO was also prepared as follow as mentioned above.

2.3. Catalytic Measurements

The reaction was carried out in the U – tube reactor containing catalyst. A schematic diagram of the experiment is shown in Fig. 1. Methane (1), oxygen (2), hydrogen (3), and Argon (4) were supplied from the gas cylinders equipped by micrometric valves (5). The

ISBN : 978-979-18755-7-8

mixing reagents were passed by valve (6) to the quartz reactor (7) of an inside diameter 12 mm. The catalyst bed was placed on quartz grains. The reactor was heated by furnace. The measurement and control of temperature was ensured by thermocouple and temperature regulator with a digital meter. The gas products are passed to dichloromethane solution as a trapper. The reaction was held at 100 – 250^{o}C. The contact time was carried out for 30 minutes. The composition of mixture products was analyzed chromatographically using a Varian apparatus equipped with mass spectrometer detector with argon as a carrier gas.

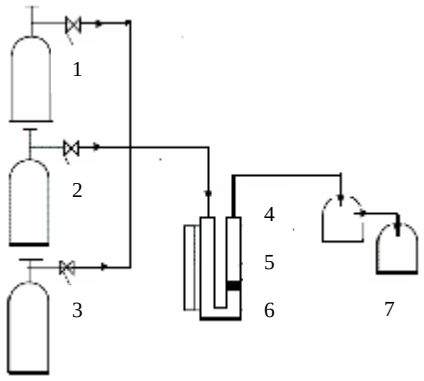

Figure 1. A schematic diagram of the experimental set up : Methane (1), oxygen or hydrogen (2), and Argon (3) were supplied from the gas cylinders equipped by micrometric valves. The mixing reagents were passed by valve to the quartz reactor (4) and catalyst is located on (5), furnace with temperature program (6). The gas products was collected on trapper containing dichloromethane (7) and gas plastic bag before analyzing.

3. Results and Discussion

3.1. Catalyst Characterizations

In Figs. 2 and 3 XRD powder patterns of the prepared $LaCrO_3$, NiO and 6% NiO/$LaCrO_3$ catalysts are presented. All the patterns of prepared solids exhibit the typical lines for $LaCrO_3$, NiO and 6% NiO/$LaCrO_3$ solids respectively.

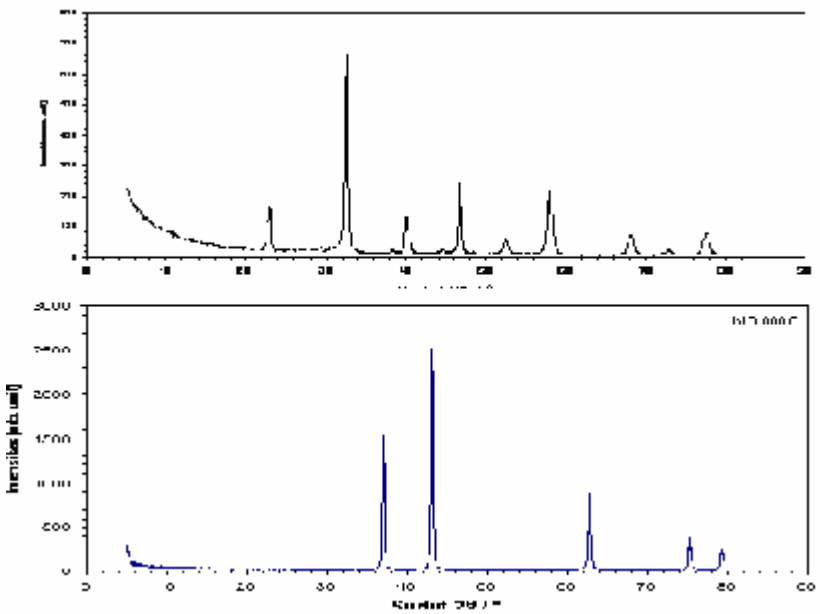

Figure 2. Diffractogram $LaCrO_3$ and NiO calinated at 600^oC and reduced by H_2 gas

In case of NiO/$LaCrO_3$ solid, there are two lines at 2θ = 44.5 and 62^o which are the strong lines of Cubic NiO, JCPDF 47 – 1049. No evidence of any other phase besides $LaCrO_3$ and NiO was found in all samples. For catalyst impregnated various NiO, the obtained line intensities and patterns are not depending on NiO content.

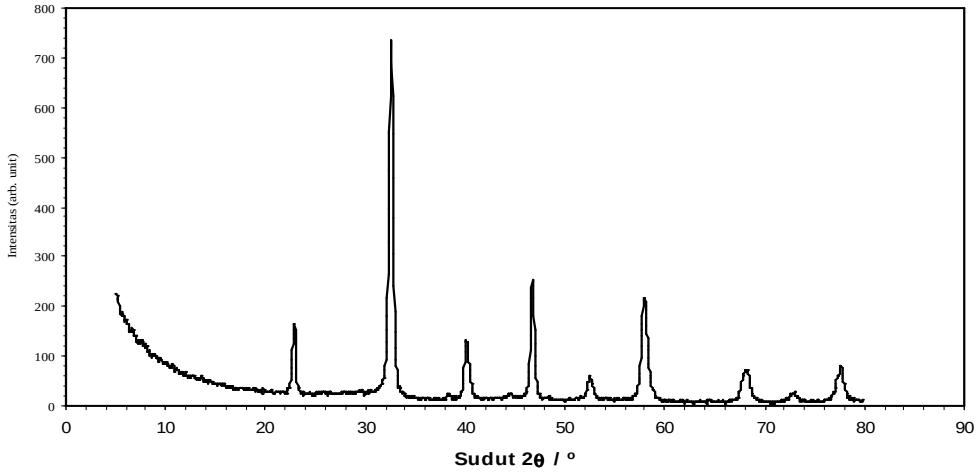

Figure 3. Diffractogram 6% NiO/$LaCrO_3$ calinated at 600^oC and reduced by H_2 gas

Further investigation using Rietveld program to 6%NiO/$LaCrO_3$ solid, proved that its unit cell change such as parameter a = 5,536Å , b=5,4794Å, dan c = 7,7941Å (goodness of fitting, χ^2 = 1,306 and unit cell - volume = 236,426Å^3) as shown on Figure 5 and Table 1 below. Increasing NiO content in $LaCrO_3$ enlarging unit cell volume of NiO/$LaCrO_3$ catalyst.

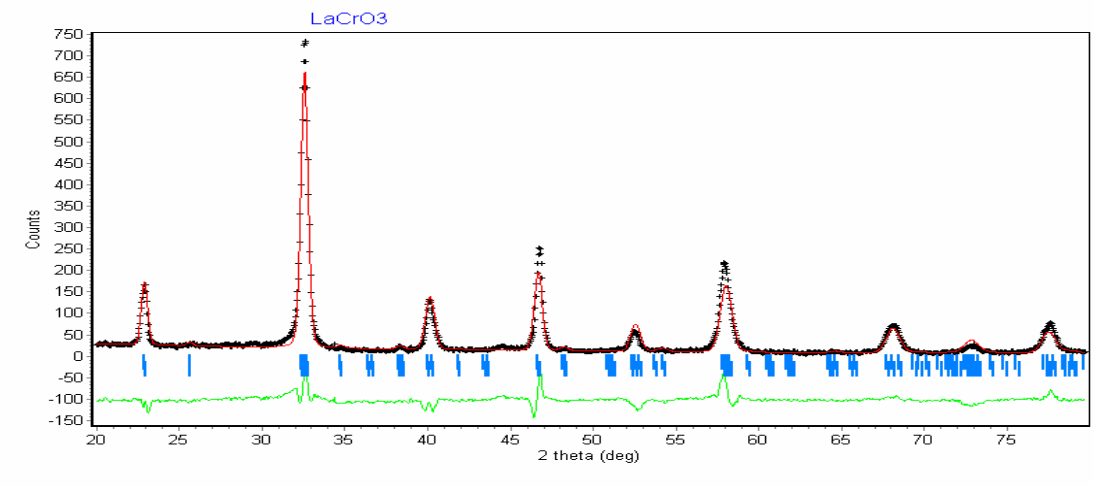

Figure 5. XRD diffractogram 6% NiO/$LaCrO_3$ calculated by Rietveld method

Table 1. Unit cell Parameter of 5 – 7% NiO/$LaCrO_3$ obtained by Rietveld method

NiO/$LaCrO_3$	**a (Å)**	**b (Å)**	**c (Å)**	**Volum (Å^3)**
5%	5,5300	5,4867	7,7850	236,208
6%	5,5360	5,4794	7,7941	236,426
7%	5,5390	5,4800	7,7950	236,607

Note: calculated cell volume, V = a x b x c because simple *orthorhombic* structure

Fig. 6 shows the typical scanning electron microscopy (SEM) picture. The background homogeneity of $LaCrO_3$ phase was covered partially distribution of NiO. Analysis of EDAX ZAF result showed that 6% NiO/$LaCrO_3$ consists of 34.53% La atom, 34.05% Cr atom, and 6,38% Ni atom. It implies that the solid of LaCrO3 doped 6% NiO has formed in an apropriate ratio.

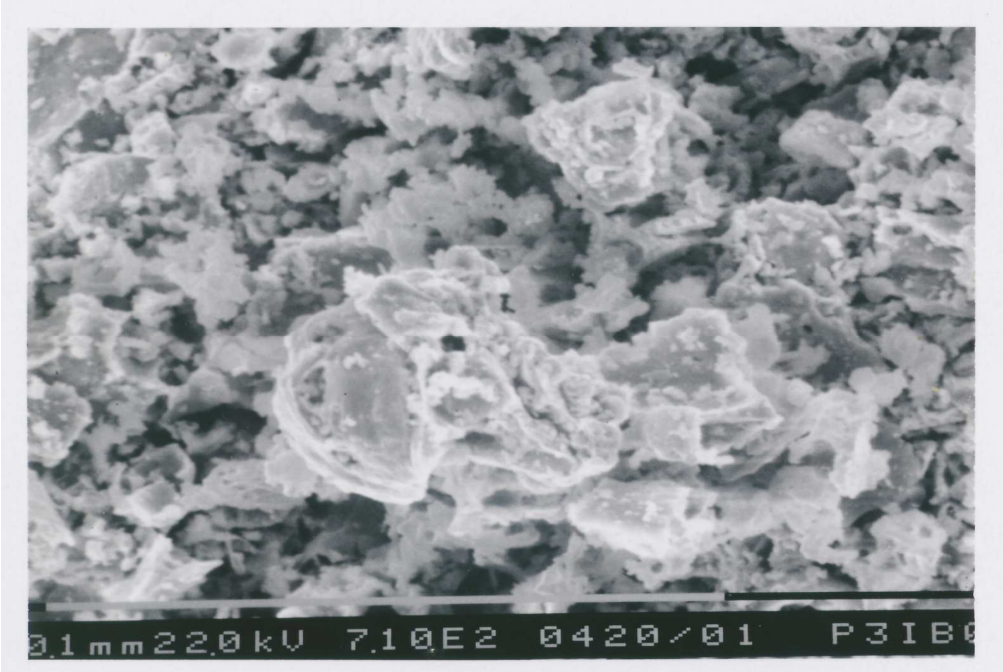

Figure 6. Electron micrograph 6% $NiO/LaCrO_3$

Gravimetric acidity of $NiO/LaCrO_3$ increases if it is compared to *those* of both NiO and $LaCrO_3$ as shown on Figure 7 below. Quantitatively, acidity increment caused of NiO addition to $LaCrO_3$ is about 24%. Acidity distribution of brønsted-Lowry and Lewis sites respectively is further discussed.

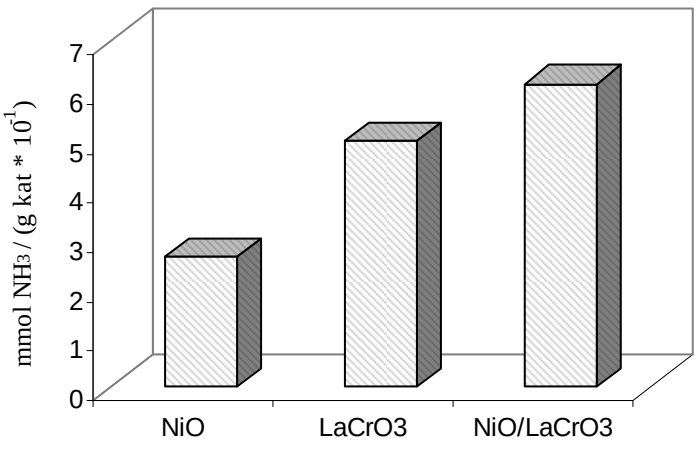

Figure 7. Gravimetric acidity of NiO, $LaCrO_3$, and 6% $NiO/LaCrO_3$ respectively

Infra red spectra analysis of 6% $NiO/LaCrO_3$ absorbed ammonia have done in order to knowing acid distribution on both brønsted-Lowry and Lewis sites . Vibration of $–NH_3$ and $–NH_4^+$ forms is referred BrØnsted-Lowry and Lewis acid sites respectively. This spectra is showed on Figure 8, scanned on the range 450 – 4000 cm^{-1}. Wave number range of 3100 – 3700 cm^{-1} refers to stretching vibration and below 2500 cm^{-1} is indicated to bending and rocking vibrations.

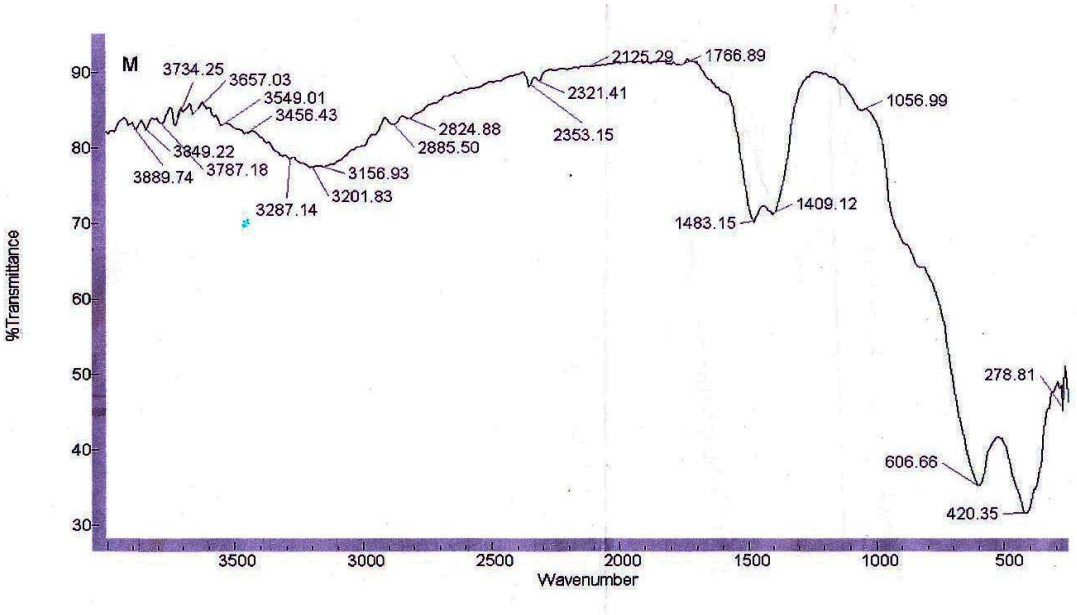

Figure 8. FTIR spectra of 6% $NiO/LaCrO_3$ treated ammonia for 24 hours

Formation ammonium ion, $–NH_4^+$ (BrØnsted-Lowry acid) is showed on wave number of 1483,15 and 1409,12 cm^{-1}, whereas coordinated species is referred to Lewis acid site and is showed on wave number of 1600 cm^{-1}. Peak appeared at 606,66 dan 420,35 cm^{-1} is referred respectively to O-Cr-O deformation and Cr-O stretching vibration (Zheng et al., 1999). However, peaks appeared on wave number 498; 488; dan 510 cm^{-1} as a characteristic adsorption of NiO is not exist .

3.2. Methane oxidation

In this experiment, the gas composition as a feed is Ar/CH_4 (40/10) and temperature reactions are 100, 150, 200, and 250^oC, respectively . As shown on Figure 9 below, the tendency of methanol formation is decreased as temperature increase. Since there was no oxygen supply from outside, the transformation is only occured by oxygen bulk involved.

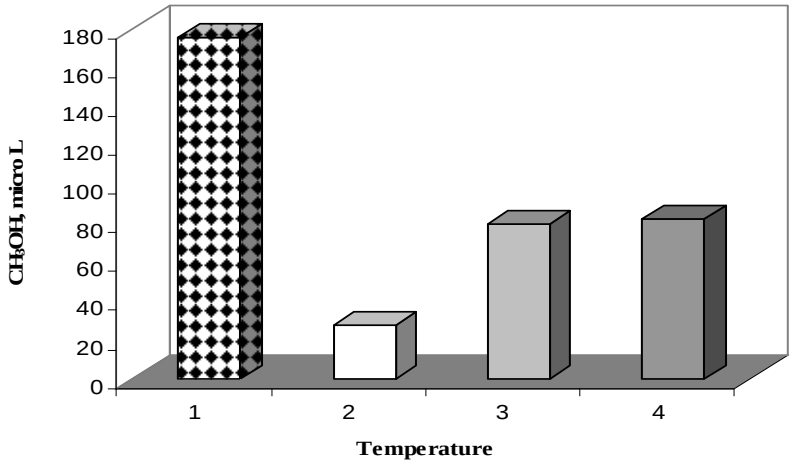

Figure 9. Methanol formation in various temperature reaction on 6% $NiO/LaCrO_3$
(Label 1 = 100°C, 2= 150°C, 3= 200°C, 4= 250°C)

The same pattern of tendency is also happened on $LaCrO_3$ doped by 7% NiO as shown on Figure 10. However, the tendency on $LaCrO_3$ doped by 5% NiO is the methanol formation increases as temperature reaction increases even though its quantity is lesser than that of 6% $NiO/LaCrO_3$ catalyst.

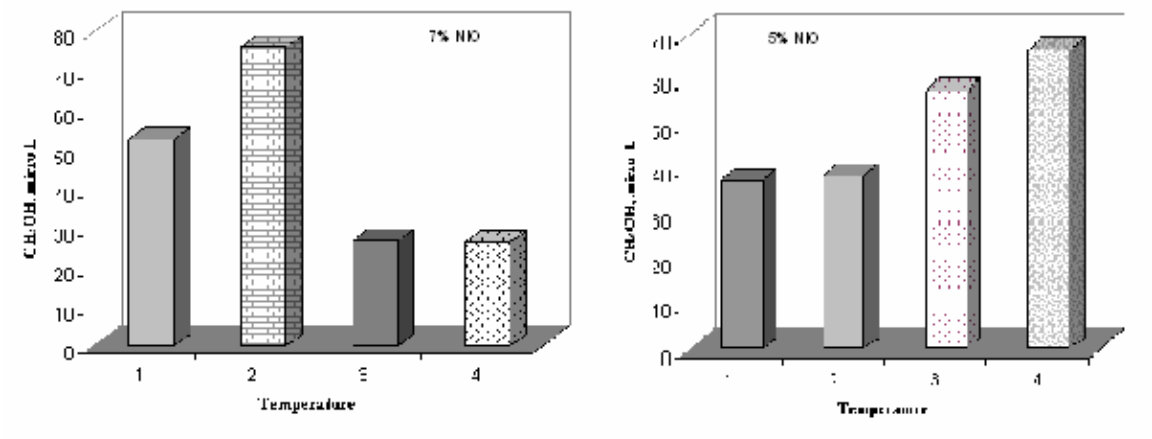

Figure 10. Methanol formation in various temperature reaction on 5 and 7% $NiO/LaCrO_3$
(Label 1 = 100°C, 2= 150°C, 3= 200°C, 4= 250°C)

Furthermore, by adding O_2 gas in the feed as $Ar/CH_4/O_2$ (35/10/5), the methanol formation on the lowest reaction temperature, 100°C is increased as shown in Figure 11 below.

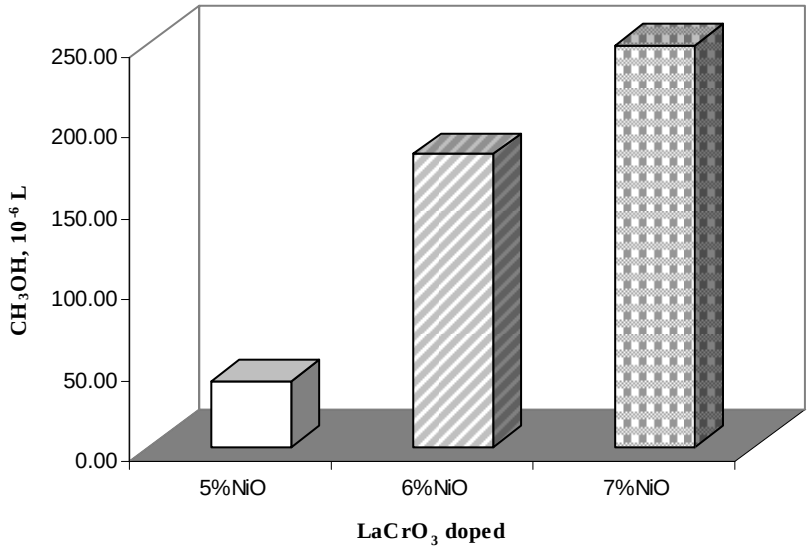

Figure 11. Methanol formation under the feed of $Ar/CH_4/O_2$ (35/10/5) at 100^oC

In general, by adding O_2 gas on the feed, the methanol formation is increased. In addition, as NiO quantity as dopant increases the methanol formation also increases. The biggest increment is happened on 7% $NiO/LaCrO_3$ catalyst. The increment is almost achieved 68%. It means that oxygenous supply on transform CH_4 gas into CH_3OH is working.

Conclusions

Based on this experiment, we can conclude that the temperature reaction affect the formation of methanol from methane gas. In general, all catalyst of $LaCrO_3$ doped NiO is active on this reaction. In the reaction under Ar/CH_4 as a feed, the bulk oxygen of catalyst played a role on transforming methane gas into methanol. Increasing the Ni content in $LaCrO_3$ catalyst giving a negative effect to methane conversion. Furthermore, adding O_2 gas on the feed increasing methanol formation.

Acknowledgements

This research project was financially supported by The National Fundamental Research and Technology of Indonesia program under contract No. 030/RD/Intensif/PTK/II/2008. I

would like to thank Andi Setiawan Ph.D for chromatography – mass spectroscopy data discussion.

References

1.Alexis T. Bell, Benjamin R. Wood, Jeffrey A. Reimer, Michael T. Janicke and Kevin C. Ott. 2004. Methanol formation on Fe/Al-MFI via the oxidation of methane by nitrous oxide. J. Catal Vol. 225, issue 2, 2004, p. 300 – 3006.

2.Alptekin, Gokhan O., Andrew M. Herring, D.L. Williamson, Tim R. Ohno and Robert L. McCormick. 2000. Methane partial oxidation by unsupported and silica supported iron phosphate catalysts : Influence of reaction conditions and co-feeding of water on activity and selectivity. J. Catal. Vol. 181, issue 1, p. 104 – 112.

3.AtlanticBiomass@aol.com

4.Han S. , Martenak D.J., Palermo R.E., Pearson J.A. and Walsh D.E. 1994. The Direct partial oxidation of methane over ZSM-5 catalyst : Metals effects on Higher Hydrocarbon Formation . J. Catal Vol. 148, issue 1, p. 134-137.

5.Han S. , Martenak D.J., Palermo R.E., Pearson J.A. and Walsh D.E. 1992. The Direct partial oxidation of methane to liquid hydrocarbons over ZSM-5 catalyst. J. Catal Vol. 136, issue 2, p. 578-583.

6.Michalkiewicz Beata. 2004. Partial oxidation of methane to formaldehyde and methanol using molecular oxygen over FeZSM-5. Appl. Catal. A : General, Vol. 277, issues 1 – 2, p. 147 – 153.

7. www.acrion.com

8. www.methanol.org

9. Zheng Wenjun., Wenqin Pang., GuangYao Meng and Dingkun Peng 1999. Hydrothermal synthesis and Characterization of $LaCrO_3$. J. Mater. Chem., 9, 2833 – 2836.