Available online at www.sciencedirect.com
ScienceDirect
Journal of Natural Gas Chemistry 19(2010)198–202
Journal of Natural Gas Chemistry
www.elsevier.com/locate/jngc

Fast- and ultra-fast laser pulse induced reactions between carbon dioxide and methane

F. Jaco Kotze[1], Christien A. Strydom[1*], Anton du Plessis[2], Thulani L. Dlamini[2]

1. School of Physical and Chemical Science, Faculty of Science, North West University, Private Bag X6001, Potchefstroom 2520, South Africa;
2. CSIR National Laser Centre, P O Box 395, Pretoria 0001, South Africa

[Manuscript received September 22, 2009; revised November 10, 2009]

Abstract

The direct excitation of CO_2 using fast (nanosecond) and ultrafast (femtosecond) pulsed lasers was investigated. A gas reaction cell was used to excite CO_2 in a 50 : 50 mixture of CO_2 and CH_4 using nano- and femtosecond laser systems, to induce a reaction between these two compounds. FT-IR spectra showed that CO was formed using the nanosecond and femtosecond laser systems. It was also found that hydrocarbons, containing C–C bonds were formed. For both the nanosecond and femtosecond laser, it was found that more C-C higher hydrocarbons were formed after 5 h compared to 3 h of irradiation. Irradiation at pressures of 250, 350 and 500 kPa with the femtosecond laser system showed the expected increase in the amount of CO formed with an increase in pressure. Results from this study showed that carbon dioxide and methane can be activated successfully using nanosecond laser pulses at 2000 nm and femtosecond laser pulses at 795 or 2000 nm and that these activated species react to form CO and C-C containing products.

Key words

nanosecond; femtosecond; tuneable laser systems; carbon dioxide; methane

1. Introduction

One of the greatest challenges facing mankind in this century is to find a balance between the need for energy and the responsibility towards the environment. The two main contributors to global warming are carbon dioxide (CO_2) and methane (CH_4). It is imperative to obtain a better understanding of the chemical characteristics of these molecules and to develop new technologies for use of these gasses emitted by industries [1].

Interest in the conversion of CO_2 and CH_4 to higher value compounds exists. The aim of this investigation is to use fast and ultra-fast laser pulses to excite CO_2, and thereby try to induce a reaction between carbon dioxide and methane. As these compounds do not readily react with each other, attempts at enhancing the reaction between carbon dioxide and methane had been made in the past. These attempts include using catalysts, photo-catalysts, high temperatures and high pressures [2−7].

In 1928, Fischer and Tropsch explored the catalytic reforming of CH_4 and CO_2 to produce synthesis gas, a mixture of carbon monoxide and hydrogen [8]. Their main objective was to describe a route by which they could produce synthesis gas with a ratio of $H_2/CO = 1$ [8].

Yuliati et al. [9] indicated that methane and carbon dioxide can be photo-catalytically converted to higher hydrocarbons, CO and hydrogen via mainly non-oxidative coupling of methane (NOCM) and CO_2 (dry) reforming of methane (DRM) over a Ga_2O_3 photo-catalyst. The NOCM process can proceed at room temperature, but the photo-catalytic DRM process requires both photo-energy and thermal energy.

Gondal et al. [10] used a high power laser at 355 nm to irradiate a reaction cell containing methane and carbon dioxide, without using a catalyst. They observed the production of hydrogen and higher hydrocarbons. They showed that through laser excitation, methane molecules were converted into methylene and methyl radicals, which could react to produce hydrocarbons. According to the HITRAN database, CO_2 absorbs light in the region of 2000 nm [11]. Methane absorbs radiation in the region of 1600 nm [11].

Laser chemistry includes the study of chemical reactions on extremely short timescales, approximately 10^{-15} seconds (ultra-fast) in femtochemistry and 10^{-9} seconds (fast) in nanochemistry. Laser chemistry poses the possibility to control and induce chemical reactions otherwise difficult or impossible to achieve [12].

* Corresponding author. Tel and Fax: +27 18 299 2350; E-mail: christien.strydom@nwu.ac.za

doi:10.1016/S1003-9953(09)60057-8

2. Experimental

The diagnostic method employed in this study was to detect the formation of CO and hydrocarbons containing C–C bonds within a specialized gas cell, using Fourier Transform Infrared (FT-IR) spectroscopy of the irradiated gas samples. A Vertex 40 FT-IR spectrometer was used and 30 scans were used to obtain a single spectrum. A gas cell equipped with CaF_2 windows to allow transmission of IR beams was built to use as a reaction vessel and to use for FT-IR analyses of the gas product mixtures.

2.1. Nanosecond laser system

A Powerlite 9000 Series Nd:YAG laser was used to pump the LAMBDA PHYSIK Optical Parametric Power Oscillator (OPPO) at 355 nm, which makes use of a Barium Borate (BBO) crystal. A frequency of 10 Hz was used in the Nd:YAG laser system and the maximum energy per pulse was determined as 185 mJ at 355 nm. The pulse length for this Nd:YAG laser system was measured as 3.5 nm to 3.9 nm and the pulse duration was just below 10 ns.

2.2. Femtosecond laser system

The femtosecond laser setup consists of an oscillator, regenerative amplifier, pump lasers and an optical parametric amplifier (OPA). The mode-locked Ti:Sapphire femtosecond seed laser (Mira oscillator) emits pulses of approximately 120 fs at a repetition rate of 76 MHz. This laser is optically pumped by a Verdi pump laser, a 5 W Nd:YVO_4 continuous laser.

2.3. Experimental set-up

Figure 1 illustrates the experimental setup. A gas cell was built and fitted with two CaF_2 windows to allow transmission of infrared (IR) radiation. This gas cell was manufactured to hold gas pressures up to 500 kPa. The gas cell was filled with a 50 : 50 mass ratio of CO_2 and CH_4 up to the indicated pressures. All the experiments were carried out at room temperature of approximately 20 °C. The gas mixture was obtained from AFROX South Africa and was certified as being 99.995% pure.

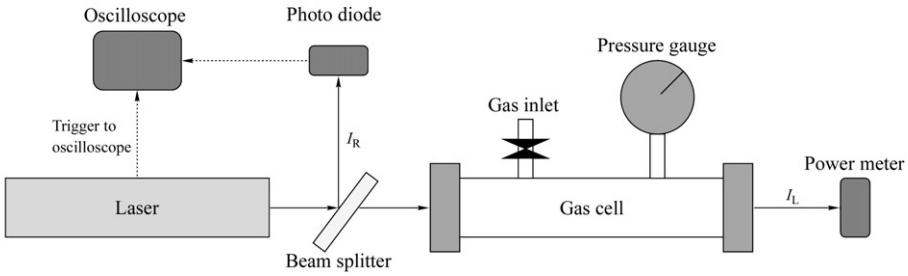

Figure 1. Experimental setup for the absorption measurements

A Quartz beam splitter was used to split off approximately 8% of the laser beam, which was used as a reference beam. The reference beam (I_R) is measured by an IR Photo diode (1.0–3.8 μm). The transmitted power (I_L) was measured by a power meter. The ratio I_L/I_R was calculated and a good linear correlation of 0.9887 was obtained over a wavelength range of 1950 to 2060 nm.

3. Results and discussion

3.1. Laser excitation of CO_2 at 150 kPa in the nanosecond laser system

FT-IR spectroscopic analysis of the CO production during the possible reaction between carbon dioxide and methane after irradiation at 2 μm by the nanosecond laser system for 3 h and 5 h are shown in Figure 2. FT-IR measurements were performed on the gas mixtures before and after irradiation in all cases and the un-irradiated FT-IR spectra were used and reported as the baseline from which product formation may be

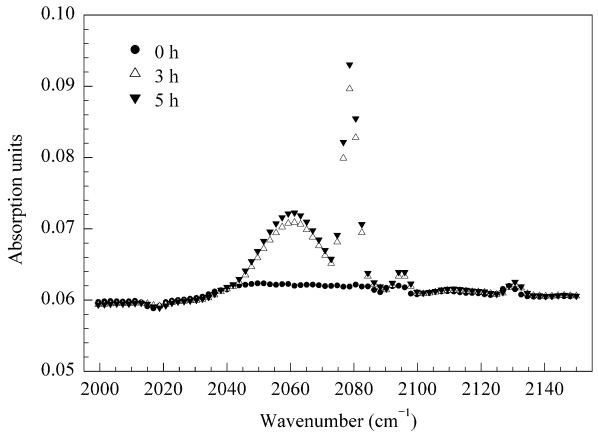

Figure 2. Infrared spectra after irradiation of a carbon dioxide and methane (50 : 50) mixture at 2 μm for 3 and 5 h with the nanosecond laser, focusing on the region of the C≡O FT-IR peak

indicated. The formation of CO is indicated by a C≡O IR vibration peak at 2080 cm^{-1} [13]. This peak is due to the stretch mode of CO while a peak at 2060 cm^{-1} is reported to be due to the stretch mode of other organic CO bonds that may have

formed [13]. Results show that CO_2 has been excited by the nanosecond laser pulse at 2 μm and that it either decomposed or reacted with CH_4.

Figures 3 and 4 show peaks in the 1600 to 1500 cm^{-1} region of the FT-IR spectrum. These peaks represent the formation of higher hydrocarbons [14]. The peaks at 1540 cm^{-1} in the un-irradiated cells are due to the C-H bending modes of CH_4 as well as C-C stretching vibrations [14]. The peak height at 1540 cm^{-1} (Figure 3) is 15% higher than the peak observed for the un-irradiated sample, which indicates that C–C bonds have formed during the irradiation process.

The 29% difference in peak heights between the un-irradiated and irradiated samples after 5 h of irradiation under similar conditions (Figure 4) is bigger than that in the case of 3 h of irradiation (Figure 3), indicating an increase in reaction products. These results showed that after nanosecond laser irradiation at 2 μm for 5 h, although the yields were still small, more higher hydrocarbons were produced than after 3 h of irradiation under similar conditions of temperature and pressure.

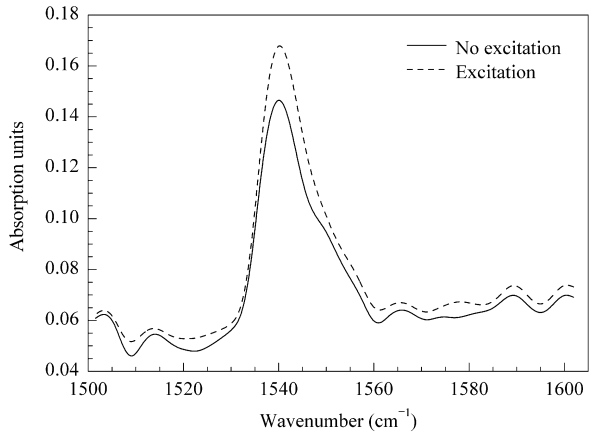

Figure 3. Infrared spectra after irradiation of a carbon dioxide and methane (50 : 50) mixture at 2 μm for 3 h with the nanosecond laser, focusing on the region of the C-C FT-IR peak of higher hydrocarbons

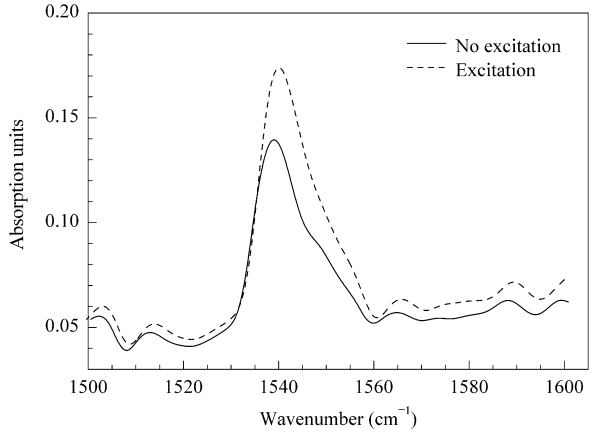

Figure 4. Infrared spectra after irradiation of a carbon dioxide and methane (50 : 50) mixture at 2 μm for 5 h with a nanosecond laser, focused on the region of the C-C FT-IR peak of higher hydrocarbons

3.2. Femtosecond laser system

3.2.1. Laser excitation of CO_2 at 150 kPa

FT-IR spectroscopic analysis of CO production after irradiation of the gas mixture at 2 μm and 150 kPa by the femtosecond laser system for 3 h and 5 h is shown in Figure 5. FT-IR measurements were performed on the gas mixtures before and after irradiation and the un-irradiated FT-IR spectrum was used and reported as the baseline from which product formation may be indicated. These result in a unique baseline for each set of data.

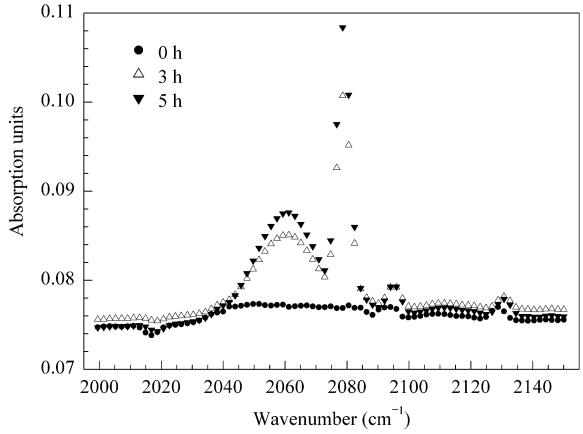

Figure 5. Infrared spectra after irradiation of a carbon dioxide and methane (50 : 50) mixture at 2 μm for 3 and 5 h with the femtosecond laser, focusing on the region of the C≡O FT-IR peak

As indicated by the C≡O peak of CO at 2080 cm^{-1} in Figure 5, it is clear that CO was produced after femtosecond irradiation at 2 μm and that the amount of CO produced increased with increasing irradiation duration.

Peaks formed for higher hydrocarbons were observed in the region of 1600 to 1500 cm^{-1} (Figures 6 and 7) [14]. As in the case of the nanosecond laser irradiation, the peaks at 1540 cm^{-1} in the un-irradiated cells are due to the C-H bending and the C-C stretching modes. The peak height at

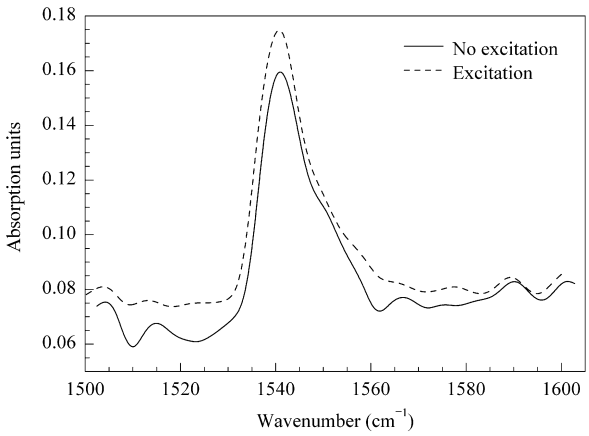

Figure 6. Infrared spectra after irradiation of a carbon dioxide and methane (50 : 50) mixture at 2 μm for 3 h with the femtosecond laser, focusing on the region of the C-C FT-IR peak of higher hydrocarbons

1540 cm^{-1} (Figure 6) is higher than the peak observed for the un-irradiated sample, which indicates that C–C bonds have formed during the irradiation process. The C-H bending mode peak and the C-C peaks in the spectra of the irradiated cell overlap, but differences in the spectra and increased peak heights indicate the formation of more C–C bonds.

The 33% difference in peak heights between the un-irradiated and irradiated samples after 5 h of exposure (Figure 7) is bigger than that in the case of 3 h of irradiation (Figure 6), indicating an increase in the amounts of reaction products. These results show that after femtosecond laser irradiation at 2 μm for 5 h, more hydrocarbons containing C–C bonds were produced than after 3 h of similar irradiation.

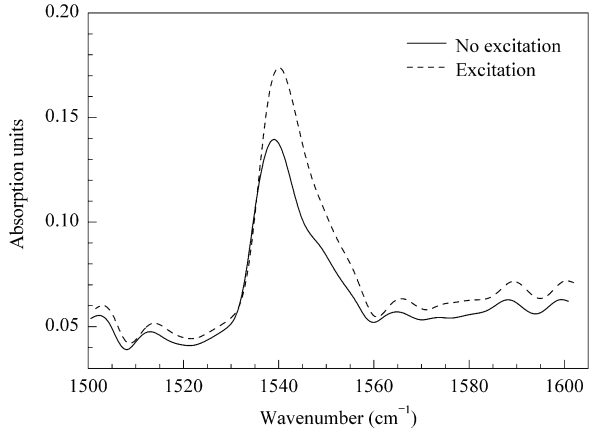

Figure 7. Infrared spectra after irradiation of a carbon dioxide and methane (50 : 50) mixture at 2 μm for 5 h with the femtosecond laser, focusing on the region of the C-C FT-IR peak of higher hydrocarbons

3.2.2. Laser excitation of CO_2 at higher pressures

The effect of the pressure in the reaction cell on the product formation was investigated. Figure 8 gives the infrared spectra of carbon dioxide and methane (50 : 50 mixtures) at 250, 350 and 500 kPa after irradiation at 2 μm for 5 h with the femtosecond laser system.

Figure 8 shows the increase in amount of CO formed with an increased pressure. Using the C≡O stretching peak height at 2080 cm^{-1} as an indication of the amount of CO formed, Figure 9 illustrates the increase in formation of CO with pressure inside the gas cell. A linear increase in amount of CO with pressure is observed between 250 and 500 kPa.

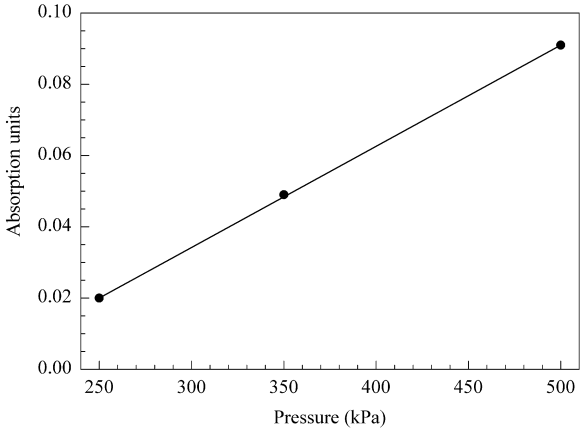

Figure 9. C≡O FT-IR peak heights (as an indication of the amount of CO formed) with increase in the pressure inside the gas cell

3.2.3. Laser excitation of CO_2 at 795 nm

To explore the possibility that the femtosecond laser system induces a reaction of carbon dioxide regardless of the wavelength at which it irradiates the femtosecond laser excitation was repeated at 795 nm. The gas cell at a pressure of 500 kPa was irradiated with 70 mW and 700 mW laser pulses at 795 nm for 5 h.

The CO peaks on the FT-IR spectra after irradiation at 795 nm and 700 mW (Figure 10) was only slightly higher than the peak obtained at 70 mW. The results after femtosecond

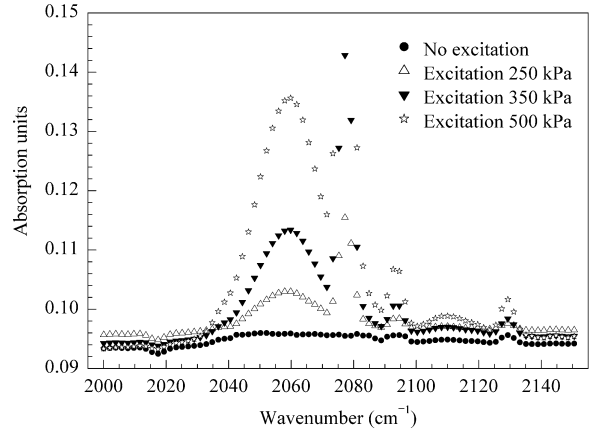

Figure 8. Infrared spectra after irradiation of a carbon dioxide and methane (50 : 50) mixture at 2 μm for 5 h with a femtosecond laser, focussed on the region of the CO FT-IR peak, at 250, 350 and 500 kPa

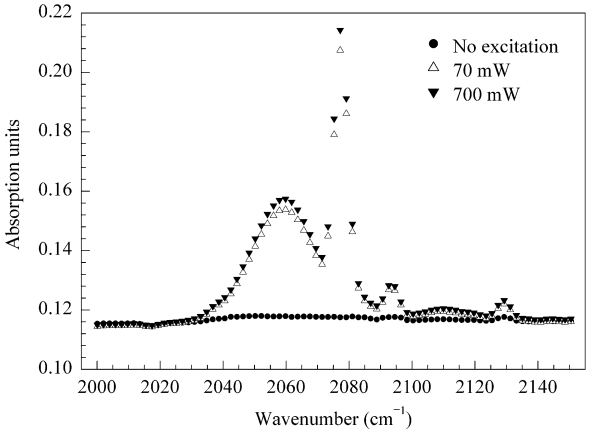

Figure 10. Infrared spectra after 70 and 700 mW irradiation of a carbon dioxide and methane (50 : 50) mixture (500 kPa) at 795 nm for 5 h with a femtosecond laser, focussing on the region of the CO FT-IR peak

laser pulse irradiation of the gas mixture at 500 kPa for 5 h at 2000 and 795 nm are similar.

4. Conclusions

CO_2 absorbs laser pulse energy at approximately 2000 nm [12]. A gas cell was filled with a 50 : 50 mixture of CO_2 and CH_4 to a pressure of 150 kPa and exposed to nanosecond laser pulses at 2000 nm for 3 and 5 h. A similar mixture in the gas cell was exposed under similar conditions to femtosecond laser pulses of 2000 nm.

FT-IR spectra showed that CO was formed using the nanosecond and femtosecond laser systems at a wavelength of 2000 nm. Some higher hydrocarbons were also formed as indicated by the C-C stretching modes at 1540 cm^{-1} on the FT-IR spectra.

The results of the laser irradiation by the nanosecond and femtosecond laser systems after 3 and 5 h indicated a slightly higher yield of CO formed. Repeating irradiation at pressures of 250 kPa, 350 kPa and 500 kPa with the femtosecond laser system showed an expected increase in the amount of CO formed as the pressure increased.

A comparison was made between irradiation at 795 nm and 2000 nm of the femtosecond laser pulses. It was found that the femtosecond laser system excited carbon dioxide, regardless of the wavelength.

Gondal et al. [10] used a high power laser at 355 nm to irradiate a reaction cell containing methane and carbon dioxide, without using a catalyst. They observed the production of hydrogen and higher hydrocarbons through their process [10]. They proposed the following mechanism for the irradiation process:

$$CH_4 + nh\nu \text{ (UV laser)} \rightarrow CH_3^{\cdot} + H^{\cdot}$$
$$H^{\cdot} + H^{\cdot} \rightarrow H_2 \text{ (Hydrogen production)}$$
$$CH_4 + nh\nu \text{ (UV laser)} \rightarrow CH_2^{\cdot} + H_2$$
$$CH_2^{\cdot} + CH_2^{\cdot} \rightarrow C_2H_4 \text{ (Ethane production)}$$
$$C_2H_4 + CH_2^{\cdot} \rightarrow C_3H_6 \text{ (Higher hydrocarbons)}$$

Through laser excitation, methane molecules are converted into methylene and methyl radicals, which could react to produce hydrocarbons. The mechanism proposed by Gondal et al. [10] contributes to the explanation of the presence of C-C peaks on the FT-IR spectra that were obtained after nanosecond and femtosecond laser pulse irradiation at 2000 nm.

Kroll et al. [2] reported that CO_2 would dissociate into gaseous CO and adsorbed O on a catalytic surface. Similarly, a reaction mechanism for the formation of CO is proposed. Upon irradiation the CO_2 may dissociate into gaseous CO and $O^{\cdot}$. The oxygen radical may further react with gases in the cell.

$$CO_2 + nh\nu \rightarrow O^{\cdot} + CO$$

Results from this study show that carbon dioxide may be excited successfully using nanosecond laser pulses at 2000 nm and femtosecond laser pulses at 795 or 2000 nm. The excited carbon dioxide and methane then decompose and/or react to produce CO and hydrocarbon products containing C–C bonds.

References

[1] Solomon S, Qin D, Manning M, Alley M B, Berntsen T, Bindoff N L, Chen Z, Chidthaisong A, Gregory J M, Hegerl G C, Heimann M, Hewitson B, Hoskins B J, Joos F, Jouzel J, Kattsov V, Lohmann U, Matsuno T, Molina M, Nicholls N, Overpeck J, Raga G, Ramaswamy V, Ren J, Rusticucci M, Somerville R, Stocker T F, Whetton P, Wood R A, Wratt D. In: Climate Change 2007: The Physical Science Basis. Contribution of Working Group I to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change. Cambridge: Cambridge University Press, 2007
[2] Kroll V C H, Swaan H M, Lacombe S, Mirodatos C. *J Catal*, 1996, 164: 387
[3] Wang S, Lu G Q M. *Appl Catal B*, 1998, 16: 269
[4] Seok S, Han S H, Lee J S. *Appl Catal A*, 2001, 215: 31
[5] Wang L, Murata K, Inaba M. *Catal Commun*, 2003, 4: 147
[6] Mattos L V, Rodino E, Resasco D E, Passos F B, Noronha F B. *Fuel Process Technol*, 2003, 83: 147
[7] Teramura K, Tsuneoka H, Shishido T, Tanaka T. *Chem Phys Lett*, 2008, 467: 191
[8] Fischer F, Tropsch H. *Brenstoff Chem*, 1928, 3: 39
[9] Yuliati L, Itoh H, Yoshida H. *Chem Phys Lett*, 2008, 452: 178
[10] Gondal M A, Yamani Z H, Dastgeer A, Ali M A, Arfaj A. *Spectrosc Lett*, 2003, 36: 313
[11] Rothman L S, Gamache R R, Goldman A, Brown L R, Toth R A, Pickett H M, Poynter R L, Flaud J M, Camy-Peyret C, Barbe A, Husson N, Rinsland C P, Smith M A H. *Appl Opt*, 1987, 26: 4058
[12] Zewail A H. *J Phys Chem A*, 2000, 104: 5660
[13] http://webbook.nist.gov/chemistry:NIST Standard Reference Database Number 69. Accessed November 2008
[14] Silverstein R M, Webster F X, Kiemle D J. Spectrometric identification of organic compounds. New York: John Wiley & Sons, 2005. 120