Catal Lett (2009) 128:171–176
DOI 10.1007/s10562-008-9722-z

Fischer–Tropsch Synthesis over Ru Catalysts by Using Syngas Derived from Woody Biomass

**Kiyomi Okabe · Kazuhisa Murata ·
Masakazu Nakanishi · Tomoko Ogi ·
Mohammad Nurunnabi · Yangyong Liu**

Received: 14 July 2008 / Accepted: 4 October 2008 / Published online: 11 November 2008
© Springer Science+Business Media, LLC 2008

Abstract Synthesis gas of $H_2/CO = 2/1$ was obtained from Japanese cedar chips at a gasification efficiency of 93%, by using steam as a gasification agent at a gasification temperature (T_g) of 1,173 K. Carbon dioxide inevitably contained in biomass-derived synthesis gas did not affect the Fischer–Tropsch synthesis (FTS) reaction. In contrast, trace amount of sulfur impurity in the gas gave rise to fatal deactivation of Ru-based FTS catalysts under the reaction conditions of $T = 503$ K, $P = 1$ MPa, and $W/F = 2$–10 g-catal. h/mol, indicating that complete desulfurization of the gas to <1 ppm was prerequisite in order to obtain stable FTS activity. With increasing impurity levels of H_2S, selectivity for higher hydrocarbons decreased.

Keywords Biomass gasification · Fischer–Tropsch synthesis · Ru/SiO_2 catalyst · Sol–gel method

1 Introduction

Biomass is so-called “carbon neutral”, and is paid attention as one of the most promising renewable energies in the “post fossil energy society”. Recent steep hikes in crude oil prices are ready to promote the utilization of biomass that is indigenous and widely dispersed in the world, in contrast to fossil energy of which production is localized. However, most of biomass has been left unused, because of the inconvenient handling. Efficient utilization of biomass is of great importance from the standpoint of mitigation in CO_2 emission. Woody biomass is the most promising among various biomasses, since it has relatively higher content of carbon with lower contents of moisture and ash than the other biomasses, such as herbaceous biomass, cattle manure, and municipal wastes [1].

Recent progress in the gas-to-liquid (GTL) process has proven the feasibility, by using combination technologies of reforming from natural gas to synthesis gas (H_2/CO mixture) and the Fischer–Tropsch synthesis (FTS) to produce liquid hydrocarbons, which are environmentally benign with low sulfur, no aromatics, and low particulate matter (PM) emission, when they are used as transportation fuels [2].

The GTL process can be applicable to biomass-to-liquid (BTL) technology via gasification of biomass. However, the detailed basic data on the BTL technology has not been well disclosed, and most of the studies on BTL are not based on the data by using real biomass gas, but model gas [3]. Thus, the FTS reaction was conducted over stable Ru-based catalysts [4, 5] to produce clean transportation fuels via gasification of Japanese cedar wood.

2 Experimental

2.1 Gasification of Japanese Cedar Wood

Chips of Japanese cedar wood (3–7 mm) were gasified in an entrained flow reactor (50 mm∅ × 1,900 mm) at a

---

The work was presented during the conference ‘Catalysis for Society’, Krakow, May 11–15, 2008.

K. Okabe (✉) · K. Murata · M. Nakanishi · T. Ogi ·
M. Nurunnabi · Y. Liu
National Institute of Advanced Industrial Science
and Technology, Tsukuba Central #5, Higashi,
Tsukuba, Ibaraki 305-8565, Japan
e-mail: kiyo-okabe@aist.go.jp

gasification temperature $T_g = 1{,}173$ K under ambient pressure by introducing steam and O_2 without catalysts. Figure 1 shows schematic diagram of the gasifier [6]. Pressurized water was introduced into an evaporator at a rate of 1–10 g/min. If necessary, O_2 was added in the range of 0–500 cm^3/min. The steam thus obtained was blown from bottom of the entrained flow reactor, while Japanese cedar chips were fed from top of the reactor through sealing valves at a rate of 1–1.2 g/min. Char and tar in the gas obtained from the top of the reactor were removed by a filter and a drain respectively, and the composition of the gas was determined by a gas analyzer. All the system, including flowmeters, feed valves and a gas analyzer, was computer-controlled. The detailed procedure was reported previously [6]. After gas cleaning and compression, the synthesis gas obtained from Japanese cedar was used for the FTS reaction.

2.2 Catalyst Preparation

The FTS catalysts of 5 wt%Ru/γ-Al_2O_3 and 10 wt%Ru/SiO_2 were prepared by the incipient wetness impregnation method and the sol–gel method, respectively. The required amount of $RuCl_3$ (Kanto Chemicals) was dissolved in distilled water, and γ-Al_2O_3 powder (NKHD, $V_p = 0.4$ cm^3/g) was impregnated with the solution at room temperature for 15 h. After drying at 383 K, the Ru/γ-Al_2O_3 catalyst was calcined in air at 673 K for 4 h.

The detailed procedure of the sol–gel method has been described previously [7]. The required amounts of $RuCl_3$ (Kanto Chemicals) or $Ru(NO_3)_3(NO)$ (Soekawa Chemicals) were dissolved in 0.35 mol of ethylene glycol (EG; purchased from Nakarai Tesque). If necessary, a small amount of ethanol was added to promote dissolution, and the solution was mixed with 0.15 mol of tetraethyl orthosilicate ($Si(OEt)_4$); purchased from Nakarai Tesque) to form a homogeneous solution by heating below 343 K. At a higher temperature, $Si(OEt)_4$ may react to trace amount of moisture to form SiO_2 partially before forming Ru–EG–$Si(OEt)_4$ complex, resulting in non-uniform mixture [8–13]. Distilled water diluted with ethanol (11/11 cm^3) was added to the solution at room temperature, resulting in slow hydrolysis at 353 K for 40 h to form transparent glassy gel. The obtained gel was dried and calcined in an air flow at 823 K for 15 h to remove organic compounds, and crashed into fine powder (<100 mesh). The catalysts are named Ru(Cl)/SiO_2 and Ru(N)/SiO_2, according to the Ru precursors.

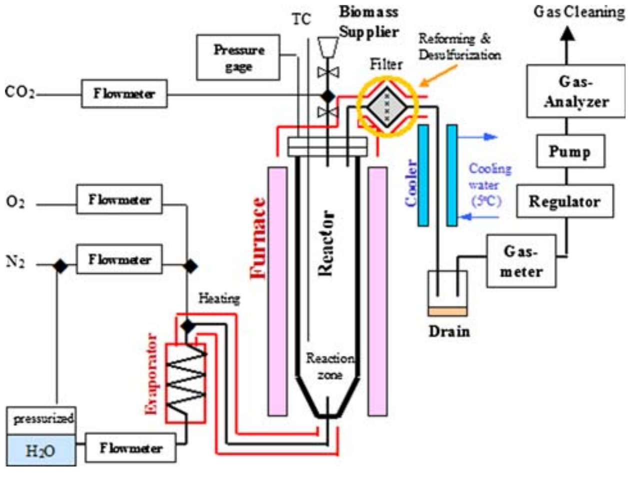

Fig. 1 Schematic diagram of entrained flow reactor for biomass gasification

2.3 Fischer–Tropsch Reaction

After reduction in a hydrogen flow (100 cm^3/min) at 573 K for 15 h, 1 g of catalyst was suspended in 50 cm^3 of hexadecane under an inert atmosphere, and used for the FTS reaction in a continuous stirring tank reactor (CSTR; V = ca. 100 cm^3) with a specially designed stirring rod to achieve complete mixing in the reactor [14]. The reaction conditions were as follows: $T = 503$ K, $P = 1$ MPa, and W/F = 2–10 g-catal. h/mol. The effluent gas was periodically analyzed with Simadzu on-line gas chromatographs (model 17A with FID detectors, and model 14B with a TCD detector), to determine the C_1–C_{10} hydrocarbons and inorganic gases, respectively. The C_{11+} hydrocarbons in the slurry were determined separately by gas chromatography after the reaction. The procedure was described in detail previously [15].

The flow rate of effluent gas was precisely determined by using the concentration changes of Ar in model gas or N_2 in biomass-derived gas as the internal standard, respectively. (i.e., If the concentration of the internal standard in the effluent gas is doubled, then the total flow rate of effluent gas is a half of the inlet gas flow rate.) Thus, the flow rates of other components in the effluent gas were precisely determined. The CO conversion was determined, as follows:

$$\text{CO conv.} = 100 \times \{\Phi_{in}(\text{CO}) - \Phi_{ex}(\text{CO})\}/\Phi_{in}(\text{CO}),$$

where Φ_{in}(CO) and Φ_{ex}(CO) are the flow rates of CO in the inlet gas and the effluent gas, respectively. The selectivity for C_n hydrocarbon was determined on carbon basis, as follows:

$$\text{C}_n \text{ selec.} = 100 \times n \times \Phi_{ex}(\text{C}_n)/\{\Phi_{in}(\text{CO}) - \Phi_{ex}(\text{CO})\},$$

where n is the carbon number of C_n hydrocarbon, and $\Phi_{ex}(C_n)$ is the flow rate of C_n hydrocarbon in the effluent gas. Thus, C_{5+} selectivity is

$$C_{5+}\ \text{selec.} = 100 - \{C_1\ \text{selec.} + C_2\ \text{selec.} + C_3\ \text{selec.} + C_4\ \text{selec.}\} - CO_2\ \text{selec.}$$

The calculation in detail was reported previously [16].

2.4 Catalyst Characterization

X-Ray powder diffraction (XRD) patterns were recorded using a Mac Science MPX-18 diffractometer with Cu-Kα irradiation (40 kV, 100 mA). X-Ray photoelectron spectroscopy (XPS) measurements were conducted with Shimadzu ESCA-850 with Mg-Kα irradiation (8 kV, 30 mA). The binding energies of XPS were referred to Au evaporated on the surface of the sample as the internal standard with Au $4f_{7/2}$ level at 83.8 eV. The metallic surface area of the catalysts was determined by H_2 adsorption at 308 K, using an automatic gas adsorption apparatus (ASAP-2000).

3 Results and Discussion

3.1 Gasification of Japanese Cedar Wood

Chemical composition of Japanese cedar was determined by elemental analysis as: C = 48.6 wt%, H = 6.1 wt%, O = 45.1 wt%, ash = 0.3 wt%, N = 0.0 wt%, and S was below the detection limit.

The effects of gasification agents are illustrated in Fig. 2. Under the condition of $[O_2]/[C] = 0$, where [C] is mol-C of cedar wood fed, H_2 concentration in the effluent gas increased, and CO concentration decreased with increasing $[H_2O]/[C]$ fed. On the other hand, under the condition of $[H_2O]/[C] = 2.5$, H_2 concentration in the effluent gas decreased and CO_2 concentration increased with increasing $[O_2]/[C]$ fed. As a consequence, synthesis gas of $H_2/CO = 2/1$ was obtained with gasification efficiency of 93% on carbon basis (the yield of tar and char was less than 7%), under the gasification conditions of $[H_2O]/[C] = 1.5$, $[O_2]/[C] = 0$, and $T_g = 1173$ K. The composition of the obtained gas is as follows on dry basis: CO = 24.8%, H_2 = 50.0%, CH_4 = 8.1%, CO_2 = 15.2%, C_2 = 0.1%, and N_2 = 1.8%.

Besides the main components of the gas, various impurities were detected. The SO_x and H_2S amounts were greatly diminished by simply bubbling the gas into water, as listed in Table 1. Concentration of COS slightly decreased after cleaning, and further desulfurization was needed.

3.2 Fischer–Tropsch Reaction by Using Model Gas

Since biomass-derived synthesis gas contains inevitably substantial amount of CO_2, the effect of CO_2 on the FTS reaction was at first investigated over 10 wt%Ru(Cl)/SiO_2 catalyst by using model gas (H_2/CO/Ar = 60:30:10). As is previously reported, the catalysts prepared by the sol–gel method generally show stable FTS activity, probably because of the ultra uniform structure [7]. Since the sol–gel method proceeds in homogeneous solution in each preparation step until the final gelation, metallic particles of an identical size are uniformly dispersed in the support of

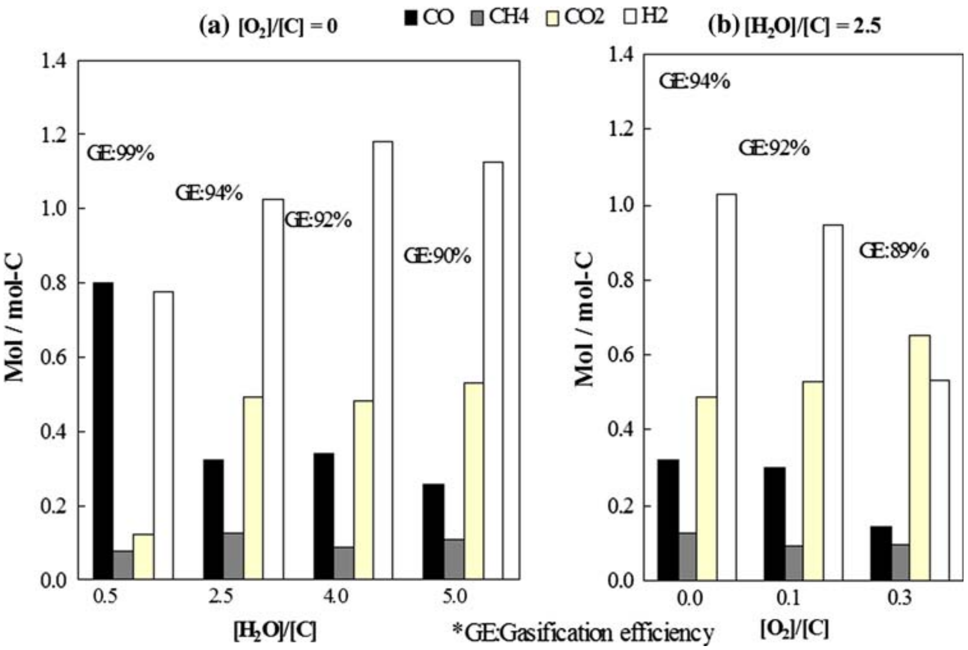

Fig. 2 Effects of gasification agents on composition of synthesis gas derived from Japanese cedar wood under the conditions of **a** $[O_2]/[C] = 0$, and **b** $[H_2O]/[C] = 2.5$

Table 1 Effect of gas cleaning with water

	COS (ppm)	SO_x (ppm)	H_2S (ppm)	NO_x (ppm)	Cl_2 (ppm)	Cl^- (ppm)	NH_3 (ppm)
Before cleaning	1.6	1.3	74	<0.1	<0.2	0.2	<0.6
After cleaning	1.2	<0.2	5	<0.1	<0.2	0.2	<06

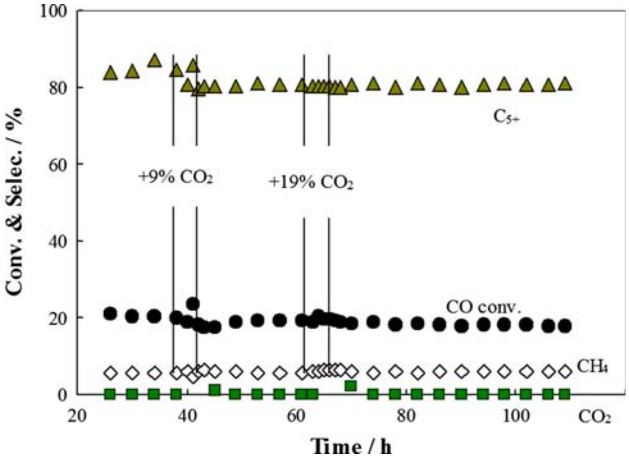

Fig. 3 Influence of CO_2 on FTS reaction over 10 wt%Ru(Cl)/SiO_2 catalyst by using model gas. Reaction conditions: $T = 503$ K, $P = 1$ MPa, $W/F = 5$ g-catal. h/mol

which pore size distribution is extremely sharp [17]. Thus, the metallic particles are stabilized during the FTS reaction for long period of time. When CO_2 was added to syngas in the range of 0–19%, CO conversion and selectivity were not varied so much, as shown in Fig. 3. It indicates that CO_2 in the biomass-derived gas does not affect the FTS reaction.

On the other hand, 10 wt% Ru(N)/SiO_2 catalysts were deactivated by adding trace amounts of H_2S to syngas, as shown in Fig. 4. Although addition of 1 ppm H_2S to syngas did not lead to remarkable deactivation, CO conversion decreased rapidly with H_2S addition in the range of 2–5 ppm. It indicates that complete desulfurization of synthesis gas below 1 ppm is prerequisite in order to obtain stable FTS activity.

The influence of H_2S on the FTS reaction selectivity is depicted in Fig. 5. With increasing H_2S concentration in syngas, selectivity for higher hydrocarbons decreased. It is reported that certain particle size of catalyst is required for higher hydrocarbon selectivity and higher catalytic activity. “Since the FTS reaction comprises of a large number of elementary steps, such as dissociation, hydrogenation, and insertion, it can be expected that a variety of sites may be needed. On small particles, the domains that combine these different active sites are not stable or they contain a non-optimum ratio of the different sites [18].”

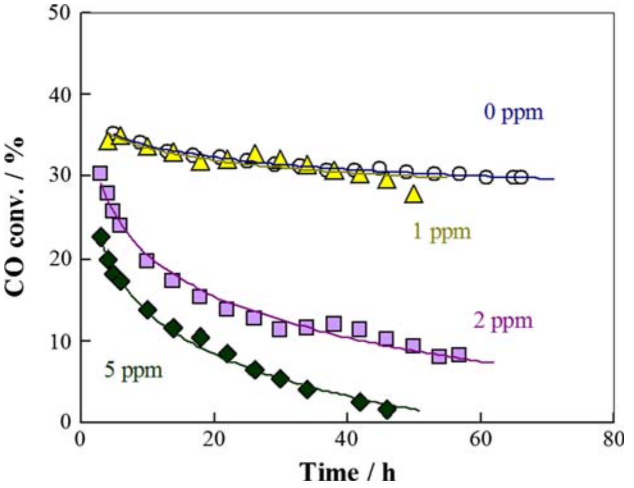

Fig. 4 Influence of H_2S on deactivation of 10 wt%Ru(N)/SiO_2 catalysts by using model gas. Reaction conditions: $T = 503$ K, $P = 1$ MPa, $W/F = 10$ g-catal. h/mol

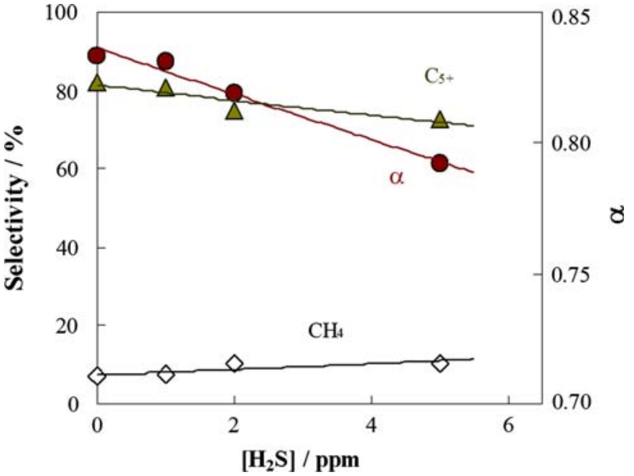

Fig. 5 Effect of H_2S on FTS reaction selectivity over 10 wt%Ru(N)/SiO_2 catalysts by using model gas. Reaction conditions: $T = 503$ K, $P = 1$ MPa, $W/F = 10$ g-catal. h/mol

However, no appreciable differences in crystallite sizes or particle sizes of Ru were observed on the spent catalysts used under various H_2S concentrations, as shown in Table 2. These results suggest that the number of active sites evaluated by H_2 adsorption is not varied so much, but the ensemble size may be decreased by H_2S poisoning.

3.3 The Fischer–Tropsh Reaction by Using Real Biomass Gas

The time courses of the FTS reaction over 5 wt%Ru(Cl)/γ-Al_2O_3 catalysts using real gas derived from biomass were depicted in Fig. 6. With decreasing W/F, the catalytic activity decreased more rapidly, probably because of the surface poisoning effect by S impurities in the gas. It was

Table 2 Effects of H_2S added on Ru crystallite size and amount of H_2 adsorbed

H_2S added	Ru crystallite size[a] (nm)	H_2 volume adsorbed (cm^3/g STP)	Ru particle size[b] (nm)
0 ppm	10	1.1	14
1 ppm	10	0.8	19
2 ppm	10	0.7	20
5 ppm	10	0.7	21

[a] Evaluated by XRD line broadening after the FTS reaction

[b] Estimated from H_2 adsorption amount

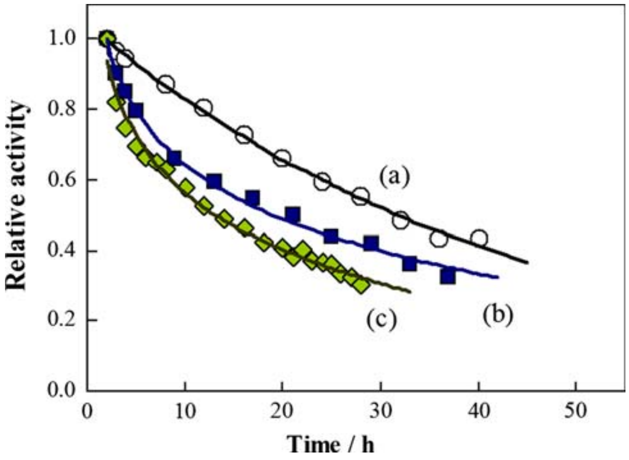

Fig. 6 Influence of *W/F* on FTS reaction over 5 wt%Ru(Cl)/g-Al_2O_3 catalysts by using real biomass gas. **a** *W/F* = 10 g-catal. h/mol, **b** *W/F* = 5 g-catal. h/mol, and **c** *W/F* = 2 g-catal. h/mol

Table 3 XPS analysis of fresh and used Ru/γ-Al_2O_3 catalysts

	O/Al	Ru/Al	C/Al[a]	Cl/Al	S/Al	$E_b(Ru3p_{3/2})$[b] (eV)
Nominal	1.5	0.03	–	–	–	–
Fresh	1.6	0.03	0.9	0.006	–	461.6
Used[c]	1.7	0.02	1.8	0.006	0.003	461.5

[a] Including contamination carbon

[b] XPS binding energy of Ru $3p_{3/2}$ level

[c] After FTS with biomass-derived synthesis gas under the reaction conditions of T = 503 K, P = 1 MPa, and *W/F* = 10 g-catal. h/mol for 40 h

supported by the fact that small amount of S was detected on the spent catalyst surface by XPS analysis, as summarized in Table 3. No appreciable difference was observed in the binding energy of Ru $3p_{3/2}$ level between fresh and spent catalysts, suggesting that S impurities do not change the electronic states of the surface Ru on the catalysts considerably.

Table 4 Effects of *W/F* on FTS reaction[a] using biomass-derived synthesis gas

W/F (g-catal. h/mol)	CO conv. (%)	CH_4 selec. (%)	CO_2 selec. (%)	C_{5+} selec. (%)	α
2	7.8	5.2	−0.1	82.5	0.77
5	12.1	5.4	−1.4	83.3	0.78
10	40.1	5.4	−1.6	85.8	0.82

[a] Average values during 40 h of the FTS reaction

Table 4 shows the effects of *W/F* on the FTS reaction selectivity, of which values are the average during the reaction. With decreasing *W/F*, the surface exposure to the gas increased, and selectivity for higher hydrocarbons decreased, that was in good accordance with the results obtained in the reaction by using model gas. While slight difference in CH_4 selectivity was obtained among the results, small but negative CO_2 selectivity was observed, suggesting incorporation of CO_2 into the FTS reaction via water gas shift reaction.

From the practical point of view, the CO conversion of the present catalysts was still not high enough. In order to increase the activity, development for a new preparation method of catalysts with higher dispersion will be important.

4 Conclusions

(1) Synthesis gas of $H_2/CO = 2/1$ was obtained from Japanese cedar chips at a gasification efficiency of 93% by using steam as a gasification agent at 1,173 K in a small scale entrained flow reactor without catalyst.

(2) Trace amounts of S impurities in the synthesis gas were greatly diminished by simply bubbling the gas into water.

(3) Substantial amount of CO_2 inevitably contained in biomass-derived synthesis gas did not affect the FTS reaction.

(4) In contrast, trace amount of S impurities in the gas gave rise to fatal deactivation of FTS catalysts, indicating that complete desulfurization of biomass-derived synthesis gas to <1 ppm was prerequisite in order to obtain stable FTS activity.

(5) With increasing impurity levels of H_2S, selectivity for higher hydrocarbons decreased.

References

1. Klass DL (1998) In: Biomass for renewable energy, fuels and chemicals. Academic Press, San Diego, p 651

2. Wu M, Wu Y, Wang M (2006) Biotechnol Prog 22:1012
3. Jun KW, Roh HS, Kim KS, Ryu JS, Lee KW (2004) Appl Catal A 259:221
4. Okabe K, Murata K, Nurunnabi M, Liu Y, Takahara I, Inaba M (2007) J Jpn Petrol Inst 50:349
5. Nurunnabi M, Murata K, Okabe K, Inaba M, Takahara I (2007) Catal Comm 8:1531
6. Nakanishi M, Ogi T, Inoue S (2005) Kankyo Gijutsu 34:522
7. Okabe K, Li X, Wei M, Arakawa H (2004) Catal Today 89:431
8. Ueno A, Suzuki H, Kotera Y (1983) J Chem Soc Faraday Trans 75:127
9. Tohji K, Udagawa Y, Tanabe S, Ueno A (1984) J Am Chem Soc 106:612
10. Niwa S, Mizukami F, Isoyama S, Tsuchiya T, Shimizu K, Imamura J (1986) J Chem Tech Biotechnol 36:236
11. Tamagawa H, Oyama K, Yamaguchi T, Tanaka H, Tsuiki H, Ueno A (1987) J Chem Soc Faraday Trans 1(83):3189
12. Sodesawa T, Morioka M, Sato T, Nozaki F (1990) Nippon Kagaku Kaishi 551
13. Sodesawa T (1990) Shokubai 32:311
14. Okabe K, Wei M, Arakawa H (2003) Energy Fuels 17:822
15. Okabe K, Li X, Matsuzaki T, Arakawa H, Fujimoto K (1999) Sekiyu Gakkaishi 42:377
16. Okabe K, Sano T, Saitoh K, Hagiwara H, Araki M, Shimomura K, Ogawa K, Hosoya T, Takaya H, Bandoh K (1985) Sekiyu Gakkaishi 28:148
17. Okabe K, Li X, Matsuzaki T, Arakawa H, Fujimoto K (2000) J Sol-gel Sci Tech 19:519
18. Bezemer GL, Bitter JH, Kuipers HPCE, Oosterbeek H, Holewijn JE, Xu X, Kapteijn F, van Dillen AJ, de Jong KP (2006) J Am Chem Soc 128:3956