

Hydrogen production by steam reforming of dimethyl ether in single use of copper alumina-silica catalysts prepared by using sol-gel methods

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Abstract— Several copper alumina-silica catalysts prepared by using sol-gel methods were examined to produce hydrogen from dimethyl ether (DME) by DME steam reforming. In order to obtain hydrogen by DME steam reforming, the mixed catalysts with DME hydrolysis catalysts, and methanol steam reforming catalysts are used, based on the reaction mechanism of DME steam reforming. However, each catalyst prepared by the sol-gel method is used for DME steam reforming individually without mixing of DME hydrolysis catalysts. Acidity for DME hydrolysis is important, and then copper catalysts were prepared by using sol-gel methods for alumina and silica. Mixture of alumina and silica has high acidity including Brønsted acid. However, the most hydrogen produced catalyst was copper alumina catalyst, not with silica. We concluded that Lewis acid is more important for DME hydrolysis to produce methanol than Brønsted acid, and hydrogen will be more produced on Cu/Al₂O₃ catalysts that have much amount of Lewis acid sites than on Cu/Al₂O₃-SiO₂ catalysts that have much amount of Brønsted acid sites and less amount of Lewis acid sites.

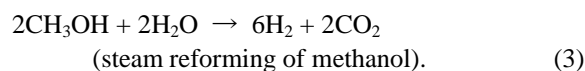
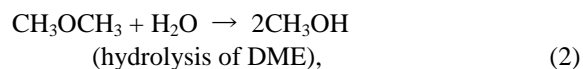
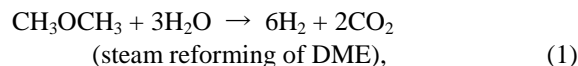
Keywords— Dimethyl ether (DME), steam reforming catalyst, alumina, Lewis acid.

I. INTRODUCTION

It is expected that fuel cell is one of the methods for restraint of global warming because of the excellent energy efficiency. Steam reforming of fossil fuels is actively researched and developed as hydrogen supply methods for the fuel cells. Dimethyl ether (DME) is expected as one of clean fuels and energy of 21st century [1, 2], because DME burns with emission of no particulate matter (PM), no SO_x, and less NO_x. The cetane number of DME is 55-60, and DME is attractive as a clean fuel for diesel engines. Physical properties are similar to those of liquefied petroleum gas (LPG). DME is easily liquefied at -25 °C under atmospheric pressure, and under 0.6 MPa at ambient temperature. DME is easily handled like LPG. DME will be produced from coal, natural gas from small and medium-size gas field, biomass, and so forth. In China, there are many DME plants with more than 10,000 tons/year capacity. The produced DME is mixed with LPG, and the mixed DME/LPG is used for cooking and heating as domestic fuel. DME has also recently become a potential fuel

for hydrogen production to be used in fuel cells. There is possibility that DME infrastructures will be settled more rapidly than those of hydrogen, because LPG infrastructures existing are able to use for DME.

We have been studying on steam reforming of DME for the hydrogen production. The new types of catalysts prepared by a sol-gel method have been developed [3-5]. Hydrogen production by steam reforming of DME (SRDME) consists of two steps: the first is DME hydrolysis, and the second is steam reforming of methanol (SRM). The chemical equation of SRDME (Eq. (1)) is separated for that of DME hydrolysis (Eq. (2)) and that of SRM (Eq. (3)), as follows:



Almost all researchers [6-22] have reported about mixed catalysts with DME-hydrolysis catalysts and SRM catalysts, because of the above mentioned reaction system. However, we focused on single-use-type catalysts prepared by the sol-gel method in terms of catalyst life and for ease of industrial processing that eliminate the mechanical mixing procedure. The copper alumina catalysts prepared by the sol-gel method in the single use produce more hydrogen than mixed catalysts by commercial catalysts of DME hydrolysis and SRM. The mixed catalysts with γ -Al₂O₃ prepared by the sol-gel method and copper silica catalysts prepared by the sol-gel also produce less hydrogen than the single type copper alumina catalysts prepared by the sol-gel method [3-5]. We speculate that the Lewis acid sites on γ -Al₂O₃ for DME hydrolysis and active sites for SRM such as copper are coexistent and well dispersed on the surfaces of the catalysts. In this paper, catalysts that have much amount of acid sites were prepared by mixing of Al₂O₃ and SiO₂ by using sol-gel methods. Hydrolysis of DME (2) is a step-determining reaction and very important for hydrogen production. Mixture of Al₂O₃ and SiO₂ has much more acidity than Al₂O₃. Therefore, we prepared several Cu/Al₂O₃-SiO₂ catalysts and tested for hydrogen production by DME steam

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reforming in order to get more active catalysts for DME steam reforming than alumina catalysts.

II. EXPERIMENTAL

A. Catalyst preparation

All catalysts used for this research were prepared by sol-gel methods. For example, Cu/Al₂O₃ was obtained by hydrolysis of mixed solution with aluminium isopropoxide (AIP), Cu(NO₃)₂, water, and small amount of ethylene glycol (EG). Amount of Cu(NO₃)₂ for the catalyst preparation depended on the loading metal amount of the needed catalysts. From the previous results [4], 30 wt.% Cu in each catalyst was used for the metal loading percent and amount in this research. Zn was not added to copper catalysts in order to not affect acidity of SiO₂-Al₂O₃. AIP (purity: 95%), EG, and Cu(NO₃)₂·3H₂O (purity: 99%) were manufactured by Wako Pure Chemical Industries, Ltd. (Wako). AIP (10.0 g) was crushed using a mortar, and then dissolved in hot water (~70 °C), and a mixed aqueous solution of Cu(NO₃)₂·3H₂O (3.90 g) was added into the mixed hot water. A small amount of EG (e.g. ~5% of the all solution amount) was also added as a sort of a surfactant into the mixed hot water. This mixture was stirred and heated at ~70 °C for ~30 min. Then, diluted HNO₃ (Wako) aqueous solution was added every 15 min in several times, and pH of the mixture was lowered with the several addition until the pH decreased to 1-2. Usually all this process took ~5 h. In the way of the HNO₃ addition, a clear-sol of boehmite was formed. Water in this sol was evaporated and taken out under reduced pressure using a rotary evaporator, and the gel was obtained. The obtained gel was dried at 170 °C for a night. The dried gels were ground using an agate mortar until the diameter of each grain of powder was less than 150 μm. The powder was calcined at 500 °C for 5 h, and usually ~3.4-g copper alumina catalysts were obtained. Before steam reforming of DME, the catalysts were reduced by flowing H₂ (99.99%, 10ml min⁻¹) at 450 °C for 10 h, and were evacuated at 300 °C for 1 h, respectively. These treatments may be sever condition for copper catalysts, and sinter the metals of the catalysts and the catalysts themselves, and lead to a deterioration of activity. However, we consider that the sintering before steam reforming is smaller trouble for a comparison of catalyst activity than sintering while steam reforming. Instead of duration test of the catalysts, the catalysts after this sever pretreatment were compared on the activity, selectivity, and so forth.

SiO₂-Al₂O₃ was also examined as a catalyst support. Several Cu(30 wt.%)/SiO₂-Al₂O₃ catalysts were prepared by the sol-gel method, and the ratios of SiO₂-Al₂O₃ were 0 wt.%-100 wt.%, 25 wt.%-75 wt.%, 35 wt.%-65 wt.%, 50 wt.%-50 wt.%, 60 wt.%-40 wt.%, 70 wt.%-30 wt.%, and 100 wt.%-0 wt.%. Each Cu(30 wt.%)/SiO₂-Al₂O₃ catalysts were prepared by hydrolysis of the mixed ethanol solution that consist from optimum amounts of tetraethyl orthosilicate (TEOS) (Purity: 95%, Wako), AIP, EG, Cu(NO₃)₂, and ethanol. TEOS is more easily hydrolyzed by a small amount of water than AIP, and changes to the sol faster than AIP. Therefore, ethanol was used for

solvent of TEOS and AIP. This ethanol mixture was stirred and heated at ~65 °C for ~30 min. Then, diluted HNO₃ (Wako) aqueous solution was added every 15 min in several times, and pH of the mixture was lowered with the several addition until the pH decreased to 1-2. Usually all this process took ~5 h. In the way of the HNO₃ addition, a clear-sol was formed. Water in this sol was evaporated under reduced pressure, and the gel was obtained. The obtained gel was dried at 170 °C for a night. The dried gels were ground using an agate mortar until the diameter of each grain of powder was less than 150 μm. The powder was calcined at 500 °C for 5 h. Before reaction, the catalysts were reduced by flowing H₂ (99.99%, 10 ml min⁻¹) at 450 °C for 10 h, and were evacuated at 300 °C for 1 h, respectively.

B. Apparatus and steam reforming of DME

DME steam reforming was performed in a flow reactor (7.6 mm i.d. Pyrex glass tube) using 0.10 g of catalyst in the temperature range from 200 to 400 °C at atmospheric pressure. The reaction gas, a mixture of DME (2 mmol g_{cat}⁻¹ h⁻¹) and water (6 mmol g_{cat}⁻¹ h⁻¹), was supplied to the catalyst layer. Reactant flow with Ar carrier gas was adjusted using two mass flow controllers (Brooks 580E). The reactor was part of a closed circulation system. After the above-mentioned reduction and evacuation, and before the reaction, the BET specific surface area of the catalyst in the reactor without the exposure to the air was measured using N₂ gas at -196 °C.

For the analysis of reactant and products, two gas chromatographs (GCs) were used. One was a Shimadzu GC-6AM equipped with a thermal conductivity detector (TCD), a methanizer (for CO analysis), and a flame ionization detector (FID). The GC had an MS-5A stainless column (80-100 mesh, 5 m long, i.d. 3mm) and its carrier gas was nitrogen. H₂, Ar (as internal standard for GC analysis), CH₄, and CO were quantitatively analyzed. The other was a Shimadzu GC-4C with TCD and FID, and equipped with a Porapak Q stainless column (80-100 mesh, 1m long, i.d. 3 mm) and a Porapak R stainless column (80-100 mesh, 0.5 m long, i.d. 3 mm) in series. Its carrier gas was helium. CH₄, CO₂, H₂O, DME, methanol, and some hydrocarbons were quantitatively analyzed.

III. RESULTS AND DISCUSSION

Acidity which include Brönsted acid and Lewis acid in SiO₂-Al₂O₃ composition, especially in SiO₂-Al₂O₃ (30-70 wt.%) composition, is more than that of Al₂O₃ [23]. Loading amount of Cu in the catalysts was settled in 30 wt.%, based on the previous results. Several Cu(30 wt.%)/SiO₂-Al₂O₃ catalysts were prepared by the sol-gel method changing the ratio of SiO₂/(SiO₂-Al₂O₃). These catalysts were examined on BET surface area and DME steam reforming. The result on the specific surface area is shown in Figure 1. The surface area increased with an increase of the SiO₂-percentage of SiO₂/(SiO₂-Al₂O₃). Relationship between the ratio of SiO₂/(SiO₂-Al₂O₃) and DME conversion of SRDME at 275 °C and 300 °C is shown in Figure 2. The results of H₂ production rate and produced CO concentration are shown in Figure 3.

Activity of SRDME was not much related to the surface area in

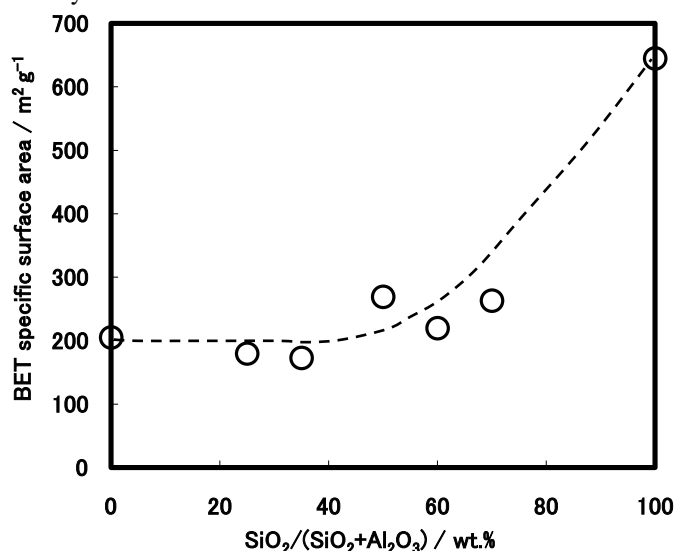


Fig. 1. BET specific surface area of some Cu(30 wt.)/SiO₂-Al₂O₃ catalysts prepared by the sol-gel method.

this case. SRDME does not occur over Cu(30 wt.)/SiO₂ catalyst which the ratio of SiO₂/(SiO₂-Al₂O₃) was 100 wt.%. DME conversion and H₂ production rate increased with an increase of Al₂O₃ percentage in Cu(30 wt.)/SiO₂-Al₂O₃ catalysts. The maximum both values of DME conversion and H₂ production rate were obtained when Al₂O₃ was 100 wt.% in the support (SiO₂-Al₂O₃). Moreover, the DME conversion and H₂ production rate showed the each curve very resembled. This suggests that all methanol was reformed if methanol was produced by DME hydrolysis, so DME hydrolysis is the rate

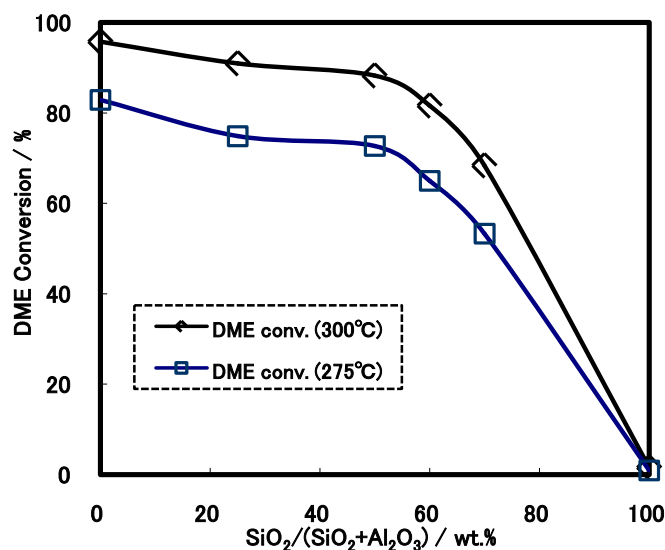


Fig. 2. DME conversion of DME steam reforming over some Cu(30 wt.)/SiO₂-Al₂O₃ catalysts prepared by using the sol-gel method. (Reaction temperature: 275 °C and 300 °C; catalyst weight: 0.1g; DME-water = 2-6 mmol g_{cat}⁻¹ h⁻¹.)

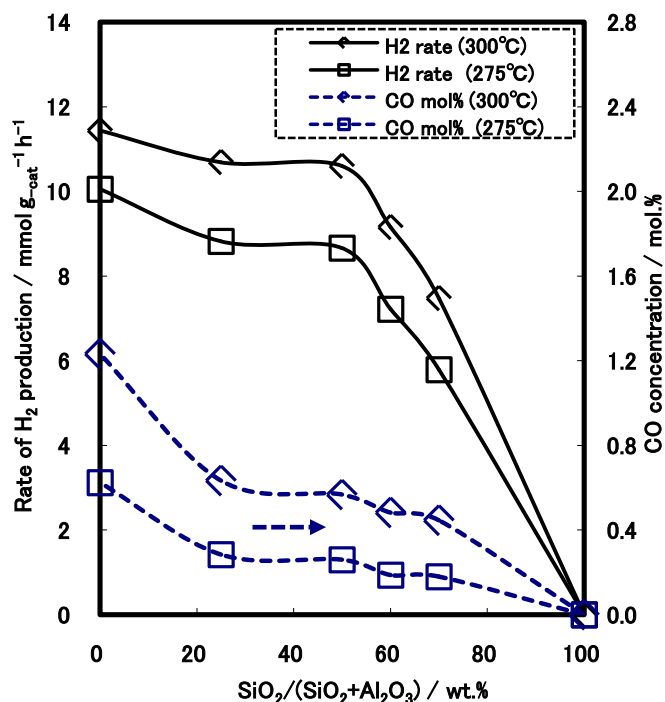


Fig. 3. Rate of H₂ production and CO concentration of DME steam reforming over some Cu(30 wt.)/SiO₂-Al₂O₃ catalysts prepared by the sol-gel method.

(Reaction temperature: 275 °C and 300 °C; catalyst weight: 0.1g; DME-water = 2-6 mmol g_{cat}⁻¹ h⁻¹.)

determining step in SRDME. The CO concentration increased with an increase of Al₂O₃ percentage of Cu(30 wt.)/SiO₂-Al₂O₃ catalysts. When the rate of H₂ production increased, the CO concentration also increased. It is suggested that CO is formed by the reverse-water-gas-shift reaction of H₂ and CO₂ produced by SRDME.

Shiba et al. [23] reported on acidity of SiO₂-Al₂O₃, and Figure 4 is the relationship between acidity and SiO₂ percentage of SiO₂-Al₂O₃ composition. Total acidity ($H_0 \leq 1.5$) (curve a) was obtained by the amine titration method, Lewis acidity (curve b) was gotten by Leftin-Hall method [24], and Brönsted acidity (curve c) was obtained by the calculation of "[Total acidity (curve a)] - [Lewis acidity (curve b)]." The curve d was obtained by the ion-exchange method [25]. There is a disagreement between curve a and curve d obtained by two methods, and the existence of water and the different acidity areas of the measurements might be the reasons [23, 26, 27]. Figure 4 shows that SiO₂-Al₂O₃ composition consisting of SiO₂:Al₂O₃ = 60:40 ~ 80:20 (wt.%) has maximum amount of Brönsted acid and also has maximum amount of the total acid (Brönsted acid and Lewis acid). Al₂O₃ alone (0 wt.% of SiO₂) has maximum amount of the Lewis acid, and SiO₂ alone (100 wt.% of SiO₂) has no Lewis acidity. The amount of Lewis acid straightly increases with an increase in the ratio of Al₂O₃ in the SiO₂-Al₂O₃ composition.

Comparing between Figure 2, 3 and Figure 4, the shapes of the curve on the DME conversion and the rate of H₂ production are similar to the shape of curve b of Lewis acidity. The Cu(30

wt.)/SiO₂ catalyst (100 wt.% of SiO₂ in the SiO₂-Al₂O₃ support) did not convert DME and did not produce H₂. The Cu(30 wt.)/SiO₂-Al₂O₃ catalyst (70 wt.% of SiO₂ in the SiO₂-Al₂O₃ support) has the biggest amount of Brönsted acid and the biggest amount of the total acid (Brönsted acid and Lewis acid), and converts 68 wt.% of DME at 300 °C and produces H₂ at the value of 7.5 mmol g-cat h⁻¹ at 300 °C, not with the biggest values. However, the Cu(30 wt.)/Al₂O₃ catalyst (0 wt.% of SiO₂ in the SiO₂-Al₂O₃ support) converts almost of DME (96 wt.%) at 300 °C and produces H₂ with the biggest value (e.g. 11.4 mmol g-cat h⁻¹ at 300 °C) among all the Cu(30 wt.)/SiO₂-Al₂O₃ catalysts. The Cu(30 wt.)/Al₂O₃ catalyst (0 wt.% of SiO₂ in the SiO₂-Al₂O₃ support) has smaller amount of the total acid than other Cu/SiO₂-Al₂O₃ catalysts, and has smaller BET specific surface area than other Cu/SiO₂-Al₂O₃ catalysts. However, the Cu(30 wt.)/Al₂O₃ catalyst has the biggest amount of Lewis acid among all Cu/SiO₂-Al₂O₃ catalysts. Therefore, it is considered that Lewis acid works for DME hydrolysis and Brönsted acid does not work for DME hydrolysis. It is speculated that Al^{δ+} of the Lewis acid site will connect with the lone electron-pair of O atom of CH₃OCH₃ and the lone electron-pair of O atom of H₂O, and these connections will work for DME hydrolysis [28, 29, 30]. DME hydrolysis is a rate determining step of SRDME, and produced methanol by DME hydrolysis easy to be reformed to H₂ over Cu sites coexisting with Lewis acid sites on the catalysts surface. Curves of Figure 2 and Figure 3 are very similar. This is also the reason of the above-mentioned reaction system. Therefore, the Cu(30 wt.)/Al₂O₃ catalyst that has the biggest amount of Lewis acid among all Cu/SiO₂-Al₂O₃ catalysts produces H₂ with the biggest value among all Cu/SiO₂-Al₂O₃ catalysts and is the best catalyst for DME steam reforming in the Cu/Al₂O₃, Cu/SiO₂, and Cu/SiO₂-Al₂O₃ catalysts.

IV. CONCLUSIONS

Lewis acid is very important for DME hydrolysis, and Cu/Al₂O₃ catalyst is more effective for SRDME than Cu/SiO₂-Al₂O₃ catalysts which have more amount of acidity of Brönsted acid and Lewis acid than Cu/Al₂O₃ catalyst. The 70 wt.% Al₂O₃-composition has the most comfortable Al₂O₃-surface percent of Cu/Al₂O₃ for hydrolysis of DME, and 30 wt.% Cu-loading amount is the most suitable Cu-surface percent of Cu/Al₂O₃ for SRM, among all Cu/SiO₂-Al₂O₃, Cu/Al₂O₃, and Cu/SiO₂ catalysts.

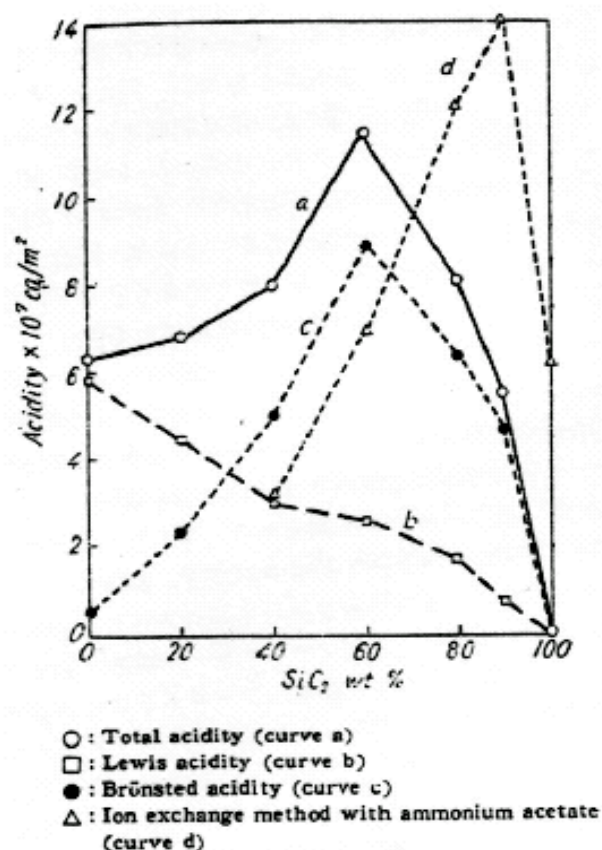


Fig. 4. Acidity of some SiO₂-Al₂O₃ compositions [23].

REFERENCES

- [1] T.H. Fleisch, A. Basu, M.J. Gradassi, J.G. Masin, *Studies in Surface Science and Catalysis*, **107** (2000) 117-125.
- [2] K. Takeishi, *Biofuels*, **1**, (2010) 217-226.
- [3] K. Takeishi, H. Suzuki, *Applied Catalysis A: General* **260** (2004) 111-117.
- [4] K. Takeishi, Y. Akaike, *Applied Catalysis A: General* **510** (2016) 20–26.
- [5] K. Takeishi, H. Suzuki, Y. Yamamoto, N. Konagai, F. Kimata, Japan. Kokai Tokkyo Koho (2002), JP 2002263504; Japan Patent No. 4106645 (2008).
- [6] V.V. Galvita, G.L. Semin, V.D. Belyaev, T.M. Yurieva, V.A. Sobyenin, *Applied Catalysis A: General* **216** (2001) 85-90.
- [7] T. Matsumoto, T. Nishiguchi, H. Kania, K. Utani, Y. Matsumura, S. Imamura, *Applied Catalysis A: General* **276** (2004) 267-273.
- [8] Y. Tanaka, R. Kikuchi, T. Takeguchi, K. Eguchi, *Applied Catalysis B: Environmental* **57** (2005) 211-222.
- [9] T. Mathew, Y. Yamada, A. Ueda, H. Shioyama, T. Kobayashi, *Applied Catalysis A: General* **286** (2005) 11-22.
- [10] T.A. Semelsberger, K.C. Ott, R.L. Borup, H.L. Greene, *Applied Catalysis B: Environmental* **65** (2006) 291-300.
- [11] T. Kawabata, H. Matsuoka, T. Shishido, D. Li, Y. Tian, T. Sano, K. Takehira, *Applied Catalysis A: General* **308** (2006) 82-90.
- [12] T.A. Semelsberger, K.C. Ott, R.L. Borup, H.L. Greene, *Applied Catalysis A: General* **309** (2006) 210-223.
- [13] K. Faungnawakij, Y. Tanaka, N. Shimoda, T. Fukunaga, R. Kikuchi, K. Eguchi, *Applied Catalysis B: Environmental* **74** (2007) 144-151.
- [14] S.D. Badmaev, G.G. Volkova, V.D. Belyaev, V.A. Sobyenin, *Reaction Kinetics and Catalysis Letters* **90** (2007) 205-211.
- [15] K. Faungnawakij, T. Fukunaga, R. Kikuchi, K. Eguchi, *Journal of Catalysis* **256** (2008) 37-44.
- [16] T. Fukunaga, N. Ryumon, S. Shimazu, *Applied Catalysis A: General* **348** (2008) 193-200.
- [17] N. Shimoda, K. Faungnawakij, R. Kikuchi, T. Fukunaga, K. Eguchi, *Applied Catalysis A: General* **365** (2009) 71-78.

- [18] N. Shimoda, K. Faungnawakij, R. Kikuchi, K. Eguchi, *Applied Catalysis A: General* **378** (2010) 234-242.
- [19] X. Wang, X. Pan, R. Lin, S. Kou, W. Zou, J.-X. Ma, *International Journal of Hydrogen Energy* **35** (2010) 4060-4068.
- [20] X. Long, Q. Zhang, Z.-T. Liu, P. Qi, J. Lu, Z.-W. Liu, *Applied Catalysis B: Environmental* **134-135** (2013) 381-388.
- [21] G. Volkova, S. Badmaev, V. Belyaev, L. Plyasova, A. Budneva, E. Paukshtis, V. Zaikovskiy, V. Sobyenin, *Studies in Surface Science and Catalysis* **167** (2007) 445-450.
- [22] P.V. Snytnikov, S.D. Badmaev, G.G. Volkova, D.I. Potemkin, M.M. Zyryanova, V.D. Belyaev, V.A. Sobyenin, *International Journal of Hydrogen Energy* **37** (2012) 16388-16396.
- [23] T. Shiba, M. Satoh, H. Hattori, K. Yoshida, *Shokubai*, **6** (1964) 80-87.
- [24] H.P. Leftin, W.K. Hall, "Actes du Deuxieme Congress International de Catalyse" (1961) No. 65.
- [25] V.C.F. Holm, G.C. Bailey, A. Clark, *Journal of Physical Chemistry*, **63** (1959) 129-133.
- [26] T. Seiyama, "Kinzoikusankabutsu To Sono Shokubaisayou," Koudansha Scientific (1978) pp. 212-218.
- [27] T. Keii ed., "Shokubaikagaku," Tokyo Kagakudohjin (1981) pp. 272-277.
- [28] H. Pines and W.O. Haag, *Journal of American Chemical Society*, **82** (1960), 2471-2483.
- [29] J.B. Peri, *Journal of Physical Chemistry*, **69** (1965) 211-239.
- [30] K. Takeishi, H. Suzuki, N. Yasui, A. Ueno, *90th CATSTJ Meeting, Abstracts A*, (2002) 7-7.