Effect of silica coating on performance of copper-zinc oxide based catalyst for methanol synthesis

Tetsuo Umegaki[1*], Yoshiyuki Kojima[1], Kohji Omata[2]

[1]*Department of Materials and Applied Chemistry, College of Science and Technology, Nihon University, Tokyo 101-8308, Japan*

[2]*Department of Materials Science, Interdisciplinary Faculty of Science and Engineering, Shimane University, 1060, Nishikawatsu-Chou, Matsue, Shimane 690-8504, Japan*

[*]Corresponding author. Tel: (+81) 33-2590810; E-mail: umegaki.tetsuo@nihon-u.ac.jp

ABSTRACT

The present study investigated the effect of silica coating on catalytic activity of copper-zinc oxide based catalyst for methanol synthesis. Silica coated catalysts prepared using ammonia and L(+)-lysine as promoters of silica coating shows almost same specific surface area and pore size distribution compared with pristine commercial copper-zinc oxide based catalyst, while silica coated catalyst prepared using L(+)-arginine shows significantly lower specific surface area than the pristine catalyst and its mesopores and macropores disappear. Silica coated using ammonia and L(+)-lysine weakly bonds to the commercial catalyst without loading into pores of the catalyst, while silica using L(+)-arginine strongly bonds to the catalyst with loading into the pores of the catalyst. Reduction temperature of fine copper species of the silica coated catalysts shifts to the higher temperature than that of the pristine catalyst, and shift temperatures of the silica coated samples prepared using ammonia and L(+)-lysine are lower than that of the sample prepared using L(+)-arginine, indicating that strongly bonding silica prevents reduction of fine copper species in the commercial catalyst. Among the silica coated catalysts, the coated catalyst prepared with ammonia shows highest CO_x conversion, and the catalytic activity increase with the decrease of weight ratios of silica to catalyst. Copyright © 2015 VBRI Press.

Keywords: Copper-zinc oxide based catalyst; methanol synthesis; silica coated; kinds of promoters; weight ratio of silica to catalyst.

Introduction

Special attention has been paid to sequestration of carbon dioxide by conversion to liquid compounds as a means of mitigating its environmental impact. In this context, a viable alternative is the efficient conversion to methanol, via selective hydrogenation of carbon dioxide liberated from point emission sources, such as power station, cement and steel industries, or natural gas field related processes, among others. On industrial scale, the production of methanol is generally achieved using $Cu/ZnO/Al_2O_3$ catalysts from synthesis gas, which is obtained via the steam reforming of natural gas and mainly contains carbon monoxide and hydrogen along with a small amount of carbon dioxide **[1-4]**. The reactions that this gas mixture undergoes, when there is no appreciable production of dimethyl ether, are: the synthesis of methanol from carbon dioxide (1), the reverse water gas shift reaction, RWGS (2), and the 'dry' methanol synthesis reaction from carbon monoxide (3) **[5]**:

$$CO_2 + 3H_2 \leftrightarrow CH_3OH + H_2O \quad \Delta H^0_{298K} = -49.58 \text{ kJ mol}^{-1} \quad (1)$$

$$CO_2 + H_2 \leftrightarrow H_2O + CO \quad \Delta H^0_{298K} = 41.12 \text{ kJ mol}^{-1} \quad (2)$$

$$CO + 2H_2 \leftrightarrow CH_3OH \quad \Delta H^0_{298K} = -90.55 \text{ kJ mol}^{-1} \quad (3)$$
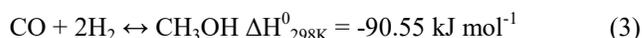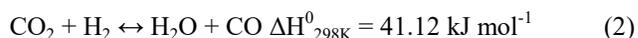
Stability of the copper based catalysts is affected by the feed containing CO_2/CO molar ratio more than unity. Furthermore, water is produced during methanol synthesis via carbon dioxide hydrogenation (reaction (1)) and water gas shift reaction (reaction (2)) accelerates oxidation and deactivation of active sites, which is the influence of water by-product produced via carbon dioxide hydrogenation **[6-10]**. The number of active sites decreases with forming inactive copper compounds such as copper oxide, sintered active copper species, strongly adsorbed by water molecule, and so on. Generally, mixing or coating the catalyst with inorganic materials such as silica is a promising technique to reduce the negative effect of water vapor **[11-13]**.

In the present study, we investigated the effect of silica coating on commercial copper-zinc based catalyst for

methanol synthesis from synthesis gas including small amount of carbon dioxide.

Experimental

Catalyst preparation

Silica was coated on commercial copper-zinc oxide based catalyst (Süd-Chemie; MDC-3) by sol-gel based method. Aqueous solution of ammonia (Kanto Chemical Co., 28 wt % solution, > 99.0 %), L(+)-lysine (Kanto Chemical Co., > 99.0 wt %), or L(+)-arginine (Wako Chemical Co., > 99.0 %) were mixed with 0.5 g of MDC-3 in ethyl alcohol, then tetraethoxysilane (TEOS, Wako Pure Chem. Co., > 99.0 %) was added into the solution followed by stirring at 323 K for 3 h and centrifuging at a rotating speed of 6000 rpm for 5 min.

Characterization

The specific surface area and porosity of silica coated MDC-3 were measured by N_2 adsorption-desorption isotherms at 77 K using a Micromeritics Model ASAP 2010MC analyzer. The morphology of the silica coated MDC-3 was observed using a Hitachi FE2000 transmission electron microscope (TEM) operating at an acceleration voltage of 200 kV. The TPR–TGA (temperature-programmed reduction–thermogravimetric analysis) investigations were performed on a Rigaku TG8120 instrument. TPR profiles were recorded by passing a 10 vol % H_2 in Ar (260 mL min^{-1}) through the sample ($\approx$ 2 mg) heated at a constant rate of 5 K min^{-1} up to 1173 K. The valence state of the surface Cu species was determined by X-ray photoelectron spectroscopy (XPS) using a Kratos ESCA-3400 spectrometer.

Catalytic activity

The catalysts were evaluated in a tubular stainless steel, fixed-bed reactor (1/2" i.d) equipped with a temperature-programmed control unit and a K-type thermocouple. Each sample was loaded between two layers of quartz wool in the reactor. Before experiment, the catalyst was firstly pre-reduced at 553 K and atmospheric pressure in a hydrogen stream (1 vol % H_2 in Ar) and then cooled to desired temperature. Subsequently the synthesis gas ($H_2/CO/CO_2/Ar = 60/30/5/5$ (molar ratio)) controlled by a mass flow controllers (Brookhaven) was introduced at W/F = 5 g h^{-1} mol^{-1} with the pressure being raised to 3.0 MPa. After leaving the reactor, the effluent gases were analyzed by two GC-TCD (Shimadzu GC-8A, Shincarbon ST column and Shimadzu GC-8A, Flusin T column). Conversion and selectivity were calculated by internal standard and mass-balance methods. The XRD radiation was CuKα of 0.154 nm wavelength. Scanning was performed from 20 to 60 2θ degrees at a scan rate of 0.2° min^{-1}. The UV-vis scan was between wavelengths of 400 nm and 900 nm.

Results and discussion

The specific surface area and pore volume of the as-prepared samples were determined by BET and BJH method (**Table 1**). The pore size distribution and pore volume were calculated by using the adsorption branch of the isotherm. The BET surface area and pore volume of samples depend on the promoters for coating silica on MDC-3. The specific surface area and pore volume of silica coated catalyst prepared using ammonia and L(+)-lysine are the same level as those of pristine MDC-3, while the surface area and the pore volume of silica coated catalyst prepared using L(+)-arginine were much smaller than those of pristine MDC-3.

Table 1. Physicochemical properties of pristine copper-zinc oxide based catalyst and silica coated catalysts.

	S_{BET} [m^{2}g^{-1}]	Average Pore Size [nm][a]	Pore Volume [cm3g-1][b]
MDC-3	25.1	21.8	0.118
SiO$_2$ coat (NH$_3$)	29.4	12.2	0.124
SiO$_2$ coat(L-lysine)	24.3	18.0	0.142
SiO$_2$ coat(L-arginine)	3.1	10.4	0.016

[a], [b]Calculated from the adsorption branches of their nitrogen adsorption-desorption isotherms.
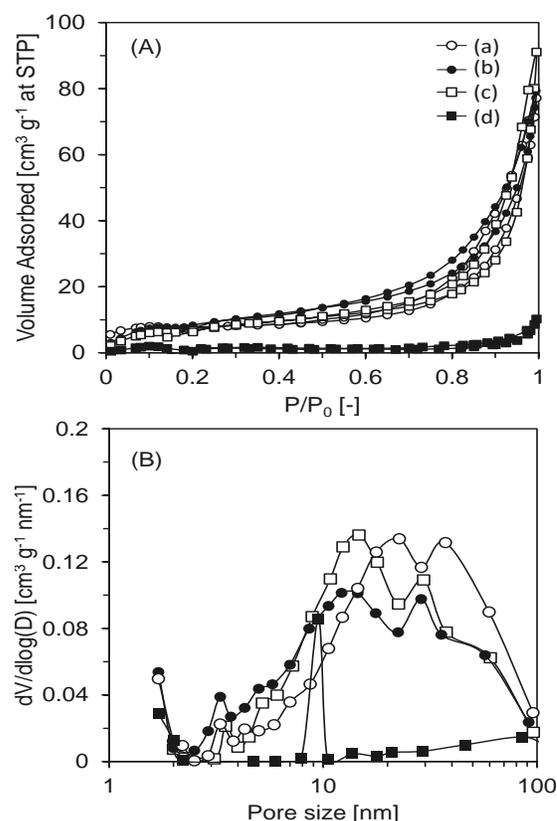
Fig. 1. Nitrogen sorption isotherms (A) and pore size distributions (B) of pristine MDC-3(a), silica coated MDC-3 catalyst prepared with ammonia (b), L(+)-lysine (c), and L(+)-arginine (d).

Fig. 1 shows the N_2 adsorption-desorption isotherm and pore size distribution of the silica coated catalysts prepared using ammonia, L(+)-lysine, and L(+)-arginine. The N_2 sorption amount, surface area, and pore volume for the silica-coated catalysts prepared using ammonia or L(+)-lysine were identical to those of the pristine catalyst; however, these values were drastically reduced for the coated catalyst prepared using L(+)-arginine. This is reflected in the pore size distribution of the hollow spheres (**Fig. 1(b)**). Almost all the pores in the hollow spheres prepared using L(+)-arginine are micropores and

mesopores, and a narrower pore size distribution is observed for the hollow spheres prepared using L(+)-arginine than in the hollow spheres prepared using ammonia.

The valence state of the copper species in the samples prepared using various promoters was investigated. **Fig. 2** shows the XPS spectra in the Cu 2p region of silica coated MDC-3. The figure shows that the peaks assigned to copper species in the samples is around 933.5 eV, indicating that this sample mainly includes Cu^{2+} (932-935 eV) **[14-16]** species. While, the binding energy of the peaks assigned to copper species depends on the samples, and the binding energy in the pristine MDC-3 and the silica coated catalysts prepared with ammonia, L(+)-lysine, and L(+)-arginine is 935.2, 934.3, 933.0, and 932.0 eV. The results indicate that copper species in the silica coated catalysts prepared with ammonia and L(+)-lysine weakly bonded with the silica, while copper species in the silica coated catalyst prepared with L(+)-arginine strongly bonded with the silica with MDC-3.
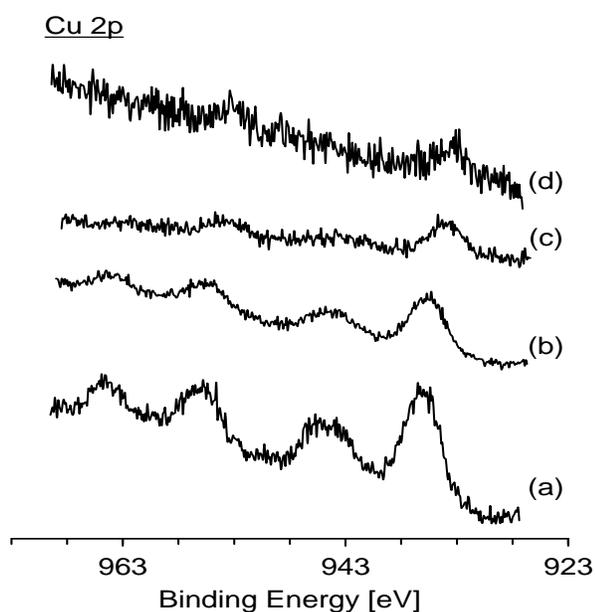
Fig. 2. Cu 2p XP spectra obtained from pristine MDC-3(a), silica coated MDC-3 catalyst prepared with ammonia (b), L(+)-lysine (c), and L(+)-arginine (d).

From the TEM images (not shown in this paper), the pristine MDC-3 consists of finely dispersed particles with the diameters of approximately 20 nm, while the silica coated catalysts prepared with ammonia and L(+)-lysine consist of the MDC-3 particles covered with irregular shape of silica with low contrast. The results indicate that the MDC-3 weakly bonded with the silica coating with ammonia and L(+)-lysine. On the other hand, the silica coated catalyst prepared with L(+)-arginine consists of the particles with silica covering along with MDC-3. The results indicate that the MDC-3 strongly bonded with the silica coating with L(+)-arginine.

In order to obtain information about reducibility of active copper species, the temperature programmed reduction (TPR) profiles observed upon treatment of the as-prepared samples in H_2 are obtained by TGA. **Fig. 3** shows the DTG curves of the as-prepared samples. The curves

involved two main domains that point to the presence of different kinds of copper species with diverse reducibility: one reduced at the lower temperature (T_{max} at about 443 K) and another reduced at higher temperatures (T_{max} over about 523 K). The peak in the profile of silica-coated catalysts prepared with L(+)-lysine and L(+)-arginine around 503 K is assigned as the peak of decomposition of L(+)-lysine and L(+)-arginine. From the reduction profile of pristine MDC-3 (**Fig. 3(a)**), the clearly defined peaks at around 443 and 523 K appear in the DTG curve. Those peaks are assigned to finely dispersed copper species and bulk copper species [**17-20**]. Compared with the result of the pristine MDC-3, both the peak temperatures are higher than those of pristine MDC-3, and the temperatures depends on the samples from the reduction profiles of the silica coated catalysts (**Fig. 3(b-d)**). The low temperature peaks of the silica coated catalysts prepared with ammonia, L(+)-lysine, and L(+)-arginine are 441.8, 444.7, and 445.3 K, respectively. The results indicate that the temperatures are related with bond strength between copper species and silica, and that the copper species in the silica coated catalyst weakly bonded with the silica coating with ammonia and L(+)-lysine, while the copper species in the silica coated catalyst strongly bonded with the silica coating with L(+)-arginine the MDC-3 strongly bonded with the silica coating with L(+)-arginine.
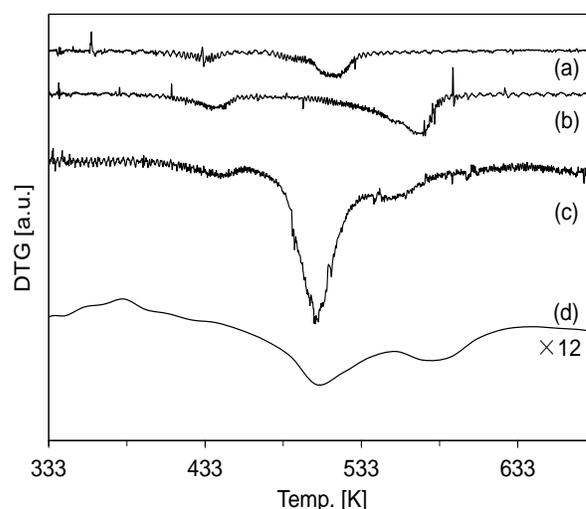
Fig. 3. DTG curve registered upon H_2-TPR of pristine MDC-3 (a), silica coated MDC-3 catalyst prepared with ammonia (b), L(+)-lysine (c), and L(+)-arginine (d).

Methanol synthesis from CO_x (x = 1, 2) hydrogenation was tested over the silica coated catalysts after pre-reduction procedures. **Fig. 4** shows temperature dependence of CO_x conversion over the silica coated catalysts. The conversion profiles of the silica coated catalysts (**Fig. 4(b-d)**). The low temperature peaks of the silica coated catalysts prepared with ammonia, L(+)-lysine, and L(+)-arginine are 441.8, 444.7, and 445.3 K, respectively. The results indicate that the temperatures are related with bond strength between copper species and silica, and that the copper species in the silica coated catalyst weakly bonded with the silica coating with ammonia and L(+)-lysine, while the copper species in the silica coated catalyst strongly bonded with the silica coating

with L(+)-arginine the MDC-3 strongly bonded with the silica coating with L(+)-arginine.

From the results of temperature programmed reduction (TPR) profiles of silica coated catalysts with various weight ratios of silica to catalyst, the lower temperature peak are same level as all the samples, while the higher temperature peak depends on the samples, indicating that the reduction temperatures decrease as weight ratio of silica to catalyst decreases, and reducibility of bulk copper species in the silica coated catalysts decrease with the ratios.
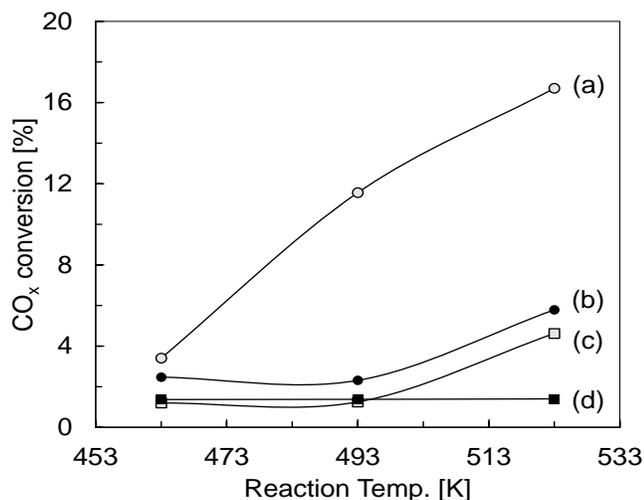
Fig. 4. Catalytic activity over pristine MDC-3(a), silica coated MDC-3 catalyst prepared with ammonia (b), L(+)-lysine (c), and L(+)-arginine (d). Reaction conditions: 3 MPa, W/F = 5 g h^{-1} mol^{-1}, H$_2$/CO/CO$_2$/Ar = 60/30/5/5 (molar ratio).

Dependence of CO$_x$ conversion on weight ratios of silica to catalyst was examined. **Fig. 5** shows temperature dependence of CO$_x$ conversion over the silica coated catalysts with various weight ratios of silica to catalyst. In this figure, the conversion was normalized by weight of MDC-3. In addition, the conversion over pristine MDC-3 is also shown in **Fig. 5**. With the weight ratio of silica to MDC-3 over 0.58, the conversion over the catalyst at 463 and 493 K is much lower than that over pristine MDC-3, while the conversion over the catalyst except for the catalyst the weight ratio of silica to MDC-3 below 0.58 at 523 K is higher than that over pristine MDC-3. The result indicates that coating of certain amount of silica improves the activity, especially at high temperature, probably because of the prevention of sintering of active copper species.

In order to confirm durability of the silica coated catalyst, the silica coated catalyst with maximum activity was tested for longer reaction time. **Fig. 6** shows CO$_x$ conversion over the silica coated catalyst prepared using ammonia with the weight ratio of silica to MDC-3 = 0.15. For comparison, CO$_x$ conversion over pristine MDC-3 catalyst is also shown in this figure. From the result, the conversion over the silica coated catalyst does not significantly change for the reaction time, while the conversions over pristine MDC-3 catalyst gradually decrease with reaction time. Methanol was produced as only product for the reaction time. The result indicates that

the silica coated catalyst shows suitable activity for the reaction time. Compared with the activity over pristine MDC-3, certain silica coatings prevent metal sintering and delay catalyst degradation without significantly reducing catalytic activity compared to pristine MDC-3.
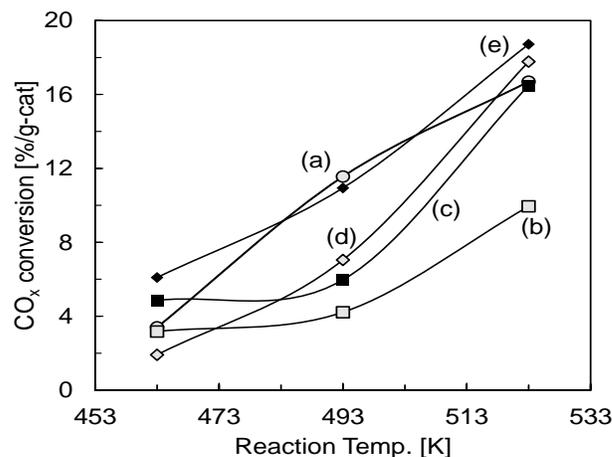
Fig. 5. Catalytic activity per weight of MDC-3 over pristine MDC-3(a), silica coated MDC-3 catalyst with weight ratio of silica to MDC-3 = 1.17 (b), 0.58 (c), 0.29 (d), and 0.15 (e). Reaction conditions: 3 MPa, W/F = 5 g h^{-1} mol^{-1}, H$_2$/CO/CO$_2$/Ar = 60/30/5/5 (molar ratio).
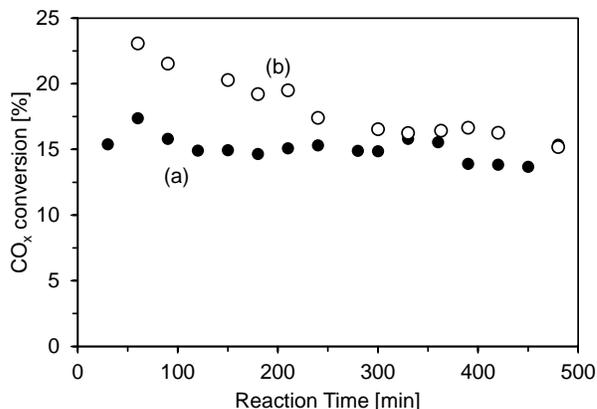
Fig. 6. Catalytic activity with reaction time over silica coated MDC-3 catalyst (a) and pristine MDC-3 and (b) weight ratio of silica to MDC-3 = 0.15. Reaction conditions: 3 MPa, W/F = 5 g h^{-1} mol^{-1}, H$_2$/CO/CO$_2$/Ar = 60/30/5/5 (molar ratio).

Conclusion

The present study investigated effect of silica coating on activity of copper-zinc based catalyst for methanol synthesis. Commercial copper-zinc oxide based catalyst was coated with silica by sol-gel based method. In the present study, we investigated influence of preparation conditions such as kinds of promoters (ammonia, L(+)-lysine, L(+)-arginine) of sol-gel reaction, weight ratios of silica to catalyst for methanol synthesis, and so on. From the result of nitrogen adsorption/desorption measurement, silica coated catalysts prepared using ammonia and L(+)-lysine shows almost same BET surface area and pore size distribution compared with original commercial copper-zinc oxide based catalyst, while silica coated catalyst prepared using L(+)-arginine shows significantly lower BET surface area and narrower pore size distribution

than original commercial copper based catalyst. In addition to peak shift of XP spectra in Cu 2p region, the results indicate that silica weakly bonds to the commercial catalyst without loading into pores of the commercial catalyst using ammonia or L(+)-lysine, while silica strongly bonds to the catalyst with loading into the pores. On the other hand, from the result of TPR-TG analysis, two reduction peaks assigned as fine copper species and bulk copper species existed in all the profiles. While lower reduction peak of the samples prepared using ammonia and L(+)-lysine shift to the lower temperature compared with the peak of the sample prepared using pristine commercial catalyst. From the results of activity tests, certain silica coating prevents metal sintering and delay catalyst degradation without significantly reducing catalytic activity compared to pristine commercial catalyst.

Reference

1. Kiler, K.; *Adv. Catal.* **1983**, *31*, 243.
2. Waugh, K.C.; *Catal. Today*, **1992**, *15*, 51.
   DOI: 10.1016/0920-5861(92)80122-4
3. Wender, I.; *Fuel Proc. Tech.,* **1996**, *48*, 189.
   DOI: 10.1016/S0378-3820(96)01048-X
4. Wu, J.; Saito, M.; Takeuchi, M.; Watanabe, T.; *Appl. Catal. A: Gen.* **2001**, *218*, 235.
   DOI: 10.1016/S0926-860X(01)00650-0
5. Marschner, F.; Moeller, F.W.; *Appl. Ind. Catal.*, Leach, B.E., Ed.; Academic Press: New York, NY, USA, **1983**, 2, 215.
6. Arena, F.; Mezzatesta, G.; Zafarana, G.; Trufio, G.; Frusteri, F.; Spadaro, L.; *Catal. Today*, **2013**, *210*, 39.
   DOI: 10.1016/j.cattod.2013.02.016
7. Arena, F.; Mezzatesta, G.; Zafarana, G.; Trunfio, G.; Frusteri, F.; Spadaro, L.; *J. Catal.*, **2013**, *300*, 141.
   DOI: 10.1016/j.jcat.2012.12.019
8. Saito, M.; Fujitani, T.; Takeuchi, M.; Watanabe, T.; *Appl. Catal. A: Gen.* **1996**, *138*, 311.
   DOI: 10.1016/0926-860X(95)00305-3
9. Arena, F.; Barbera, K.; Italiano, G.; Bonura, G.; Spadaro, L.; Frusteri, F.; *J. Catal.* **2007**, *249*, 185.
   DOI: 10.1016/j.jcat.2007.04.003
10. Bartholomew C.H.; *Appl. Catal. A: Gen.*, **2001**, *212*, 17.
    DOI: 10.1016/S0926-860X(00)00843-7
11. Wu, J.; Luo, S.; Toyir, J.; Saito, M.; Takeuchi, M.; Watanabe, T.; *Catal. Today*, **1998**, *45*, 215.
    DOI: 10.1016/S0920-5861(98)00218-1
12. Wu, J.; Saito, M.; Mabuse, H.; *Catal. Lett.*, **2000**, *68*, 55.
    DOI: 10.1023/A:1019010831562
13. Zha, F.; Ding, J.; Chang, Y.; Ding, J.; Wang, J.; Ma, J.; *Ind. Eng. Chem. Res.*, **2012**, *51*, 345.
    DOI: 10.1021/ie202090f
14. Mosser, C.; *Clays Clay Miner.*, **1992**, *40*, 593.
    DOI: 10.1346/CCMN.1992.0400514
15. Wang, Z.; Wang, W.; Lu, G.; *Int. J. Hydrogen Ener.*, **2003**, *28*, 151.
    DOI: 10.1016/S0360-3199(02)00043-5
16. Subasri, R.; Malathi, R.; Jyothirmayi, A.; Hebalkar, N.Y.; *Ceram. Int.* **2012**, *38*, 5731.
    DOI: 10.1016/j.ceramint.2012.04.018
17. Chary, K.V.R.; Sagar, G.V.; Srikanth, C.S.; Rao, V.V.; *J. Phys.Chem. B*, **2007**, *111*, 543.
    DOI: 10.1021/jp063335x
18. Kurr, P.; Kasatkin, I.; Girgsdies, F.; Trunschke, A.; Schlögl, R.; Ressler, T.; *Appl. Catal. A: Gen.*, **2008**, *348*, 153.
    DOI: 10.1016/j.apcata.2008.06.020
19. Guo, X.; Mao, D.; Lu, G.; Wang, S.; Wu, G.; *J. Mol. Catal. A: Chem.*, **2011**, *345*, 60.
    DOI: 10.1016/j.molcata.2011.05.019
20. Jeong, H.; Cho, C.H.; Kim, T.H.; *React. Kinet. Mech. Catal.*, **2012**, *106*, 435.
    DOI: 10.1007/s11144-012-0441-5