Catal Lett (2009) 130:198–203
DOI 10.1007/s10562-009-9862-9

Controlled Nanocrystal Deposition for Higher Degree of Reduction in Co/Al_2O_3 Catalyst

Yun-Jo Lee · Jo-Yong Park · Ki-Won Jun ·
Jong Wook Bae · P. S. Sai Prasad

Received: 10 October 2008 / Accepted: 7 January 2009 / Published online: 22 January 2009

Abstract Alumina supported 5% Co catalyst was prepared, by the controlled nanocrystal deposition method using oleic acid as a capping agent, and tested for its activity and selectivity in Fischer–Tropsch synthesis. The catalyst exhibited facile reducibility of the cobalt species. The CO conversion and C_{5+} selectivity obtained on this size-controlled catalyst were higher than those observed on the catalysts prepared by impregnation and precipitation techniques. Decrease in the mobility of the nanoparticle towards the tetrahedral sites of alumina could be the reason for high reducibility, as the formation of cobalt aluminate was found to be considerably reduced during temperature programmed reduction.

Keywords Co/Al_2O_3 · Fischer–Tropsch Synthesis · Cobalt oxide nano crystal · Reduction degree

1 Introduction

Fischer–Tropsch synthesis (FTS) has been recognized as an economic and environmentally viable technology for the production of hydrocarbons by the hydrogenation of CO. Cobalt-based catalysts are very competitive systems for the FTS due to their high activity and selectivity for linear hydrocarbons [1, 2]. Alumina, silica and titania are frequently used as supports for the dispersion of cobalt. The activity of cobalt catalysts in FTS depends on the number of active sites on the surface, which in turn is determined by the cobalt particle size (dispersion), loading amount, degree of reduction and cobalt-support interaction [3–5]. Small metal particles on the support are highly prone to metal-support interaction leading to the formation of difficultly reducible cobalt species. This is particularly so in the case of interacting supports like alumina. In many practical applications, cobalt-based catalysts with high metal loadings are often produced via incipient wetness technique through reduction of metal precursors [6]. Such catalysts often show a non-uniform size distribution of metal particles and hence it is difficult to achieve high degree of reduction of cobalt oxide. Bezemer et al. [7] have utilized non-interacting carbon nanofiber as the support and obtained very promising FTS catalysts in terms of relatively high activity and selectivity. But the carbon supported catalysts rapidly deactivate during time on stream [8]. There is also enough possibility for the gasification of carbon during the reaction. Hence, new approaches are needed to synthesize the size-controlled nano cobalt particles to be deposited on supports like alumina in order to decrease Co-support interaction and to design catalysts with high degree of reduction that show better CO hydrogenation activity and C_{5+} selectivity in the FTS, apart from remaining stable under reaction conditions. Martinez and Prieto [9] have adopted ex-carrier synthesis of cobalt nanoparticles in the core of reverse micelles and their subsequent deposition on a surface-protected delaminated all-silica zeolite. In their case, as the particle diameter obtained was about 4 nm the turnover frequency showed a lower value than the impregnated catalysts. The present investigation is a new step forward in

---

Y.-J. Lee · J.-Y. Park · K.-W. Jun (✉) · J. W. Bae ·
P. S. Sai Prasad
Alternative Chemicals/Fuel Research Center,
Korea Research Institute of Chemical Technology,
P.O. Box 107, Yusong, Daejon 305-600, South Korea
e-mail: kwjun@krict.re.kr

Y.-J. Lee
e-mail: yjlee@krict.re.kr

this direction. We report on the methodology adopted for the controlled synthesis of nano crystals with uniformity in size and shape. The superiority of the catalyst obtained after deposition of these nanocrystals on γ-Al_2O_3 in terms of degree of reduction, and CO conversion activity and C_{5+} selectivity during FTS, is demonstrated by comparing its performance with that of two other catalysts prepared by incipient wetness and precipitation techniques.

2 Experimental

2.1 Catalyst Preparation

Unsupported cobalt oxide nanocrystals were first prepared according to the procedure described in detail elsewhere [10]. 8.7 g of $Co(NO_3)_2 \cdot 6H_2O$ (Samchun, 97%) was dissolved in 100 mL of deionized water. 4.8 g of ammonia solution (Junsei, 28–30%) was diluted with 100 mL of deionized water, and added to the $Co(NO_3)_2$ solution under stirring to make a precipitation of cobalt hydroxide. 2.0 g of oleic acid (Sigma–Aldrich, 90%) and 200 mL of kerosene was subsequently added to above the cobalt hydroxide slurry under stirring. The mixture was heated to 90 °C and kept for 30 min to obtain cobalt-oleate precursor slurry separated by clear water solution. The cobalt-oleate precursor was mixed with deionized water to remove remaining ammonium nitrate salt in the oil layer. The separated oil layer was heated in 100 °C for 1 h to remove water impurity, and transferred to Teflon-lined autoclave and crystallized at 230 °C for 5 h under stirring. After cooling it to room temperature, the resulting oil solution containing Co oxide nanocrystals was mixed with acetone to precipitate the Co oxide nanocrystals from kerosene solution, and then the collected nanocrystals were dispersed in hexane. After repeated washing with acetone, the sample was air-dried and finally re-dispersed in hexane to obtain Co_3O_4 colloidal solution. The bulk cobalt sample is designated as nano-Co. The support, a high surface area ($\sim$350 m^2/g) γ-Al_2O_3, was prepared by a method reported previously [11]. 5 wt% Co/Al_2O_3 catalyst was prepared by impregnation of the support with the required quantity of the above colloidal solution. The impregnated catalyst was dried at 60 °C for 12 h and then calcined at 500 °C for 5 h in static air. The prepared sample is designated as nano-CoAl. Two more 5 wt% Co/Al_2O_3 samples were also prepared for the sake of comparison; one by impregnating γ-Al_2O_3 support with cobalt (II) nitrate solution and the other by the precipitation of the cobalt nitrate on the support in presence of NH_3 solution. The drying and calcination procedures were similar to that of nano-CoAl. These samples are denoted as i-5CoAl and p-5CoAl, respectively.

2.2 Catalyst Characterization

The morphologies and structures of bulk Co oxide nanocrystal (nano-Co), nano-5CoAl, i-5CoAl and p-5CoAl were examined using X-ray diffraction (XRD, Rigaku D/MAX-2200 V) and transmission electron microscopy (TEM, FEI Tecnai 20). BET specific surface areas of the catalysts were determined by nitrogen adsorption at −195 °C using a Micromeritics ASAP-2420 system. Temperature programmed reduction (TPR) was performed using a Micromeritics TPR equipped with a thermal conductivity detector (TCD) where the samples were first pretreated in a helium flow at 200 °C and kept for 2 h to remove the adsorbed water and then cooled to 100 °C. A reducing gas containing 5% H_2/Ar mixture was passed over the samples at a flow rate of 30 mL/min, then heated from 100 to 800 °C with a heating rate of 10 °C/min and kept at final temperature for 30 min. Hydrogen chemisorption experiment was carried out by using Micromeritics ASAP 2020C. The sample (0.5 g) was first reduced in situ at 450 °C for 12 h under H_2 flow of 50 mL/min. The adsorption of H_2 was carried out at 100 °C. After the hydrogen chemisorption, the sample was reoxidized at 450 °C by 10% O_2 in helium to determine the extent of reduction.

2.3 Catalytic Measurements

For the FTS test, typically, 0.5 g of pelletized and sized (0.85–1.18 mm particles) of the Al_2O_3 supported Co catalyst was reduced in situ in flowing 5% H_2/Ar (200 cm^3) at 450 °C for 12 h in a fixed bed reactor and FTS reactions were performed under the following reaction conditions; reaction temperature = 220–240 °C; pressure = 10 bar and SV ($L/kg_{cat}/h$) = 6,000 with feed compositions (H_2/CO/Ar; mol% = 63.2/31.3/5.5).

3 Results and Discussion

Figure 1a represents the TEM images of the bulk nano-Co and the alumina supported catalysts. The cobalt crystals of nano-Co are fairly uniform and cubic in shape. The average size of the crystals, as determined by the TEM image, corresponds to 10.3 nm. The cubic morphology is retained after supporting the nano crystals on alumina (Fig. 1b). The nano crystals are found well dispersed in the needle-type alumina support without any significant agglomeration or sintering to bigger particles. The average particle size of nano-5CoAl is about 13.0 nm. The Co/Al_2O_3 catalysts prepared by the impregnation and precipitation routes (i-5CoAl and p-5CoAl) have irregular shaped particles, with smaller size than those prepared by the oleate route.

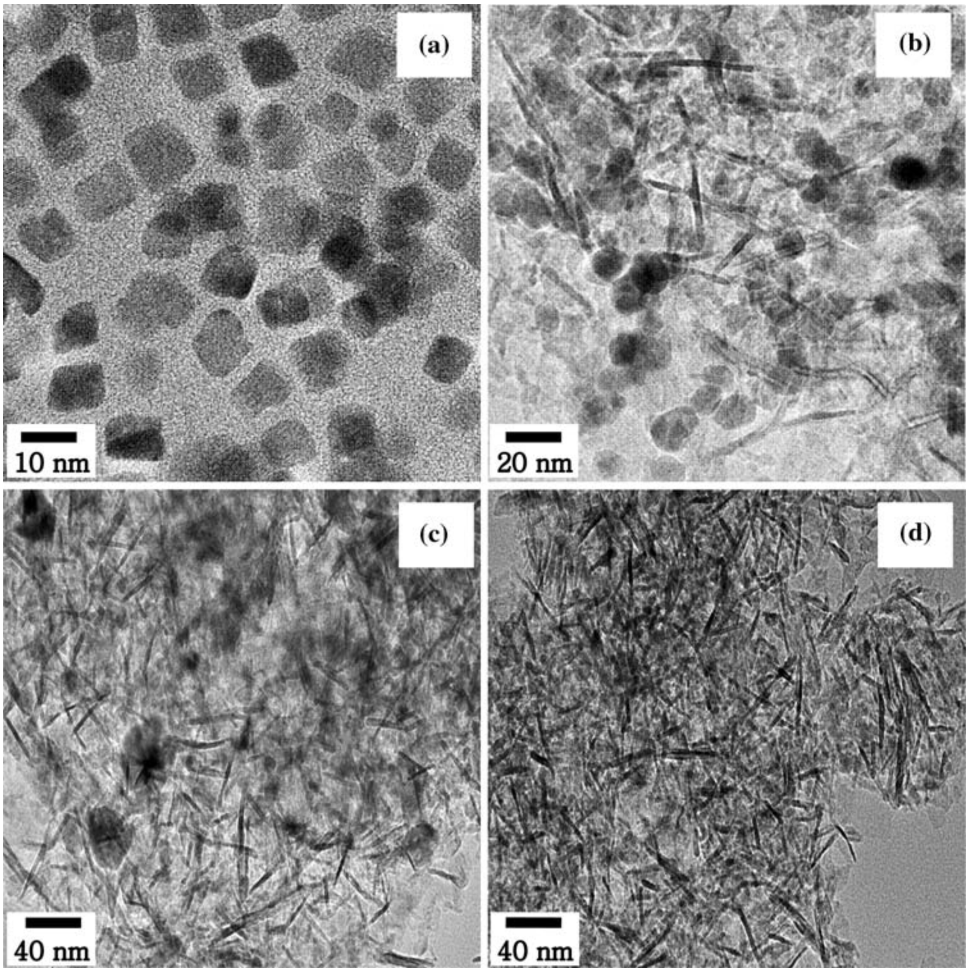

Fig. 1 TEM images of cobalt nanocrystal and Co/Al_2O_3 catalysts: **a** nano-Co, **b** nano-5CoAl, **c** i-5CoAl, **d** p-5CoAl

The XRD pattern of nano-5CoAl catalyst (Fig. 2a) shows peaks at $2\theta = 19, 32, 36$ and 60° coinciding well with that of Co_3O_4. The peaks coexist with the broad peaks of γ-alumina at around $2\theta = 37, 45$ and 66°. The XRD peaks of i-5CoAl and p-5CoAl catalysts prepared by both impregnation and precipitation methods are very broad as shown in Fig. 2b and c, indicating that the crystal size is very small, supporting the information obtained from the TEM.

The values of hydrogen and oxygen uptakes, as calculated from hydrogen chemisorption and oxidation experiments are presented in Table 1. Nano-5CoAl shows a superior uptake value. Normally small particles are expected to give higher values of chemisorption. The smaller values, in the present case indicate a possible interaction with the support forming a difficultly reducible cobalt aluminate species. The reduction degree of the supported catalysts is also summarized in Table 1. The reduction degree of the nanocrystal-loaded catalyst is considerably higher (71.7%) compared to those of the conventionally prepared ones. This is an important observation. Very low values of 18.4 and

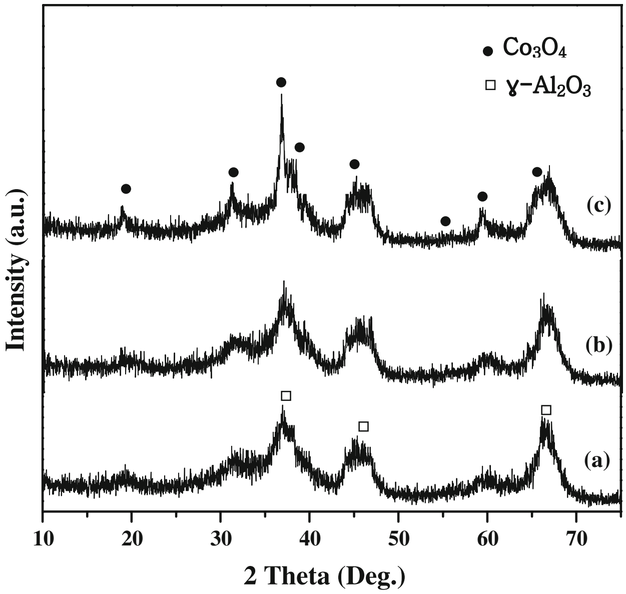

Fig. 2 XRD patterns of Co/Al_2O_3 catalysts: **a** i-5CoAl, **b** p-5CoAl, **c** nano-5CoAl

Table 1 Physico-chemical properties of the catalysts

Catalyst	Surface area (m^2/g)	H_2 uptake (μmol/g)	O_2 uptake (μmol/g)	Reduction (%)[a]	*d* (nm)[b]
i-5CoAl	279	12.5	97.5	18.4	5.6
p-5CoAl	276	12	106.4	20.1	6.3
nano-5CoAl	264	18.6	379.8	71.7	14.6

[a] Calculated from O_2 uptake data

[b] Cobalt oxide crystallite size calculated by the chemisorption data

20.1% are recorded for i-CoAl and p-CoAl catalysts, respectively. This also supports the assumption that a considerable amount of surface cobalt is lost in the formation of the metal complex with the alumina surface, in the case of the conventionally prepared catalysts. The cobalt oxide crystallite size for the three catalysts, as calculated by the chemisorption data and corrected by taking the degree of reduction into consideration, indicates smaller size crystallite formation for the conventionally prepared catalysts. A value of 14.6 nm calculated for the nano-5CoAl closely agrees well with that of the TEM data. Thus, the advantage of the nano crystal cobalt catalyst rests on providing larger particles with higher degree of reducibility due to reduced salt-support interaction.

Alumina is the most commonly investigated support for cobalt used in slurry phase FTS reaction. However, the main disadvantage of the support is the well established interaction between Co and the support, particularly at lower loadings. Under normal activation conditions, a not so easily reducible cobalt-aluminate spinel is formed covering most of the surface and allowing only lower degree of reduction. The activity of the catalyst in FTS largely depends on the degree of reduction of the metal precursor. The shape and size of the metal particles, which control the number of active sites is also important [12]. A considerable amount of discussion has gone into establishing the existence of structure sensitivity or not in supported Co catalysts during the FTS. Bezemer et al. [7], using carbon nanofibre as support for Co, indicated that the TOF is constant for Co particles larger than 6–8 nm. Iglesia et al. [2] have shown that for large cobalt particles the reaction rate is proportional to the number of cobalt surface sites. Khodakov et al. [2] opined that the structure insensitivity is probably valid for only larger Co particles or when the particles contain different metal phases. The importance of the present investigation lies in enhancing the reducibility in larger particles by more than three folds. Higher reducibility normally means more number of active sites. Since metallic Co sites are supposed to be the active sites, this facile reducibility helps enhance the activity. Many authors [7, 9] have reported the effect of cobalt particle size on the activity. Sun et al. [13], studying the Co/SiO_2 catalysts, observed that the activity depends on the number of active sites. The existence of strong metal-support interaction decreases the reduction degree and the active site density.

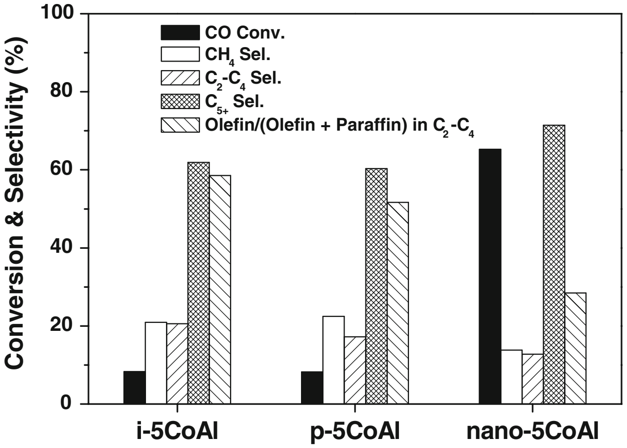

Fig. 3 Conversion of CO and products distribution. Reaction conditions: $T = 240$ °C; Pg = 10 kg f/cm^2; SV (L/kg_{cat}/h) = 6,000; feed compositions (H_2/CO/Ar = 63.2/31.3/5.5; mol%)

Figure 3 illustrates the CO conversion and the product distribution obtained on the three catalysts. Whereas nano-5CoAl reaches a conversion of 65%, the corresponding values for the other two catalysts are <10%. In the present investigation, even though the particle size of Co is larger for the nano catalyst compared to those of the conventionally prepared catalysts, the activity is much higher. This is an important observation. It could be explained that the influence of reducibility is more dominating than the dispersion in the case of the nano catalyst and the higher reducibility is a manifestation of the controlled particle size. It is necessary to understand how the controlled nano crystal deposition resists cobalt support interaction. In the case of alumina supported catalysts some amount of cobalt migrates in to the tetrahedral sites of γ-Al_2O_3 to form non-reducible (at temperatures <900 °C) spinel. This irreversible compound formation, as reported by Jongsomjit et al. [14], results in a decrease in the amount of reducible cobalt species. The same authors have also proposed the formation of a different kind of highly dispersed surface cobalt aluminate due to the migration of cobalt. In the present investigation, as stated above, the conventionally prepared catalysts show very low extent of reduction (about 20%) compared to the catalyst prepared by the controlled nano crystal deposition method. The easy mobility of the Co particles towards the tetrahedral sites of alumina leads to their stabilization and formation of cobalt aluminate. We feel that the reason for higher degree of reduction in the case of the nano catalyst could be the restricted mobility of the Co particles. Hence the Co-support interaction at the tetrahedral sites of alumina is decreased to a larger extent. This seems to be the major advantage of the controlled crystal deposition method.

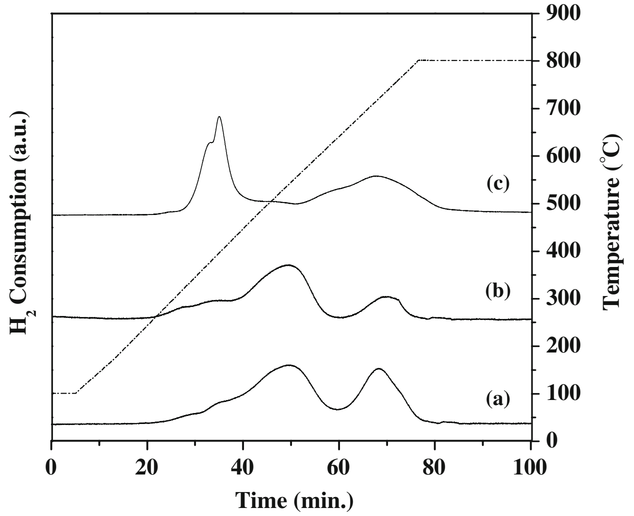

Fig. 4 Temperature-programmed reduction (TPR) profiles of Co/Al_2O_3 catalysts: **a** i-5CoAl, **b** p-5CoAl, **c** nano-5CoAl

The reduction behavior of the supported cobalt catalysts has been studied by TPR and the profiles are shown in Fig. 4. The TPR profiles of catalysts prepared by conventional methods such as impregnation and precipitation are shown as Fig. 4a, b, respectively. The peaks in the range of 350–650 °C, can be attributed to the reduction of Co_3O_4 to CoO and CoO to Co metal. Smaller Co_3O_4 crystallites are more difficult to be reduced than the bigger ones. The peak in the range of 650–800 °C can be attributed to the reduction of cobalt oxide surface species that interacted with the support surface. For the nano cobalt catalyst (Fig. 4c), a clear shift in the first peak is observed towards lower temperatures in the range of 250–450 °C. This pattern is thus very different from that of the conventionally prepared catalysts. The figure gives a clear indication that the formation of the aluminate phase is considerably decreased, thus giving support to our assumption of restricted mobility.

Figure 5 also illustrates the superiority of the controlled nano size catalyst. The catalyst exhibits steady activity over a period of 25 h. Longer hours of testing, planned in the laboratory, may throw more light on this aspect.

The selectivity to C_{5+} increased with the increase of reduction degree. The results of TPR, H_2 chemisorption and TEM analyses reveal that the nano catalyst contains the highly reducible cobalt oxide with the largest cluster size. The high selectivity to C_{5+} could be due to the easier dissociation of CO on the electron-rich cobalt cluster leading to the possible secondary reaction of olefins through chain-growth mechanism [15, 16] Interestingly, the rate of CH_4 formation is higher in the case of i-5CoAl and p-5CoAl catalysts which showed hard reducibility (Table 1). A comparison between the FTS functionalities of nano Co catalyst and the conventional catalysts reveals that the high CO conversion and selectivity to heavy hydrocarbons could be achieved on the catalyst showing a proper cobalt cluster size, above 10 nm, and high reducibility (electron-rich state) to enhance the facile dissociation of CO and secondary reaction of olefins.

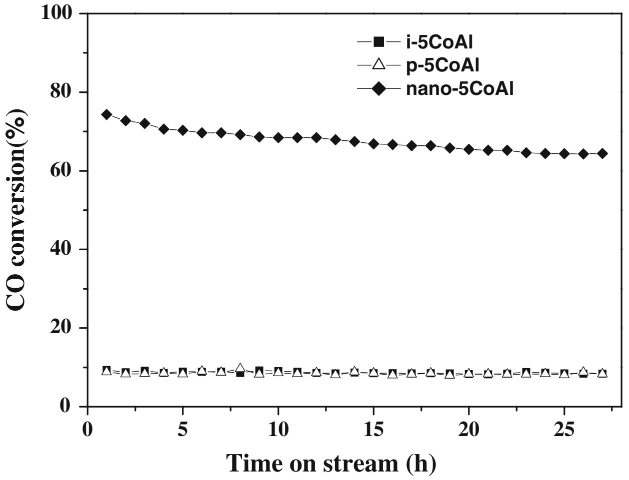

Fig. 5 Conversion of CO with time on stream (h). Reaction conditions: $T = 240$ °C; Pg = 10 kg f/cm^2; SV (L/kg$_{cat}$/h) = 6,000; feed compositions ($H_2/CO/Ar$ = 63.2/31.3/5.5; mol%)

4 Conclusions

The preparation of Co/Al_2O_3 catalyst by controlled nano crystal deposition method is a good approach for obtaining enhanced catalytic properties. The higher reducibility of the Co oxide stems from the lower mobility of the particles into the tetrahedral sites of alumina due to which the possibility for the formation of cobalt aluminate is decreased. Enhanced reducibility affords more number of active sites to increase the CO hydrogenation activity and C_{5+} selectivity.

Acknowledgments The authors would like to acknowledge the financial support of KEMCO and GTL Technology Development Consortium (Korea National Oil Corp., Daelim Industrial Co., LTD, Doosan Mecatec Co., LTD, Hyundai Engineering Co. LTD and SK Energy Co. LTD) under "Energy & Resources Technology Development Programs" of the Ministry of Knowledge Economy, Republic of Korea. PSSP thanks the Director, IICT, Hyderabad for sanctioning the sabbatical leave.

References

1. Khodakov AY, Chu W, Fongarland P (2007) Chem Rev 107:1692
2. Iglesia E, Soled SL, Fiato RA (1992) J Catal 137:212
3. Khodakov AY, Bechara R, Constant AG (2003) Appl Catal A 254:273
4. Hilmen AM, Schanke D, Hanssen KF, Holmen A (1999) Appl Catal A 186:169

5. Girardon JS, Quinet E, Griboval-Constant E, Chernavskii PA, Gengembre L, Khodakov AY (2007) J Catal 248:143
6. Reuel RC, Bartholomew CH (1984) J Catal 43:63
7. 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
8. Vada S, Hoff A, Adnanes E, Schanke D, Holmen A (1995) Top Catal 2:155
9. Martinez A, Prieto G (2007) J Catal 245:470
10. Lee YJ, Jun KW, Park JY, Potdar HS, Chikate RC (2008) J Ind Eng Chem 14:38
11. Kim SM, Lee YJ, Jun KW, Park JY, Potdar HS (2007) Mater Chem Phys 104:56
12. Rytter E, Eri S, Skagseth TH, Schanke D, Bergene E, Myrstad R, Lindvåg A (2007) Ind Eng Chem Res 46:9032
13. Sun S, Tsubaki N, Fujimoto K (2000) Appl Catal A 202:121
14. Jongsomjit B, Panpranot J, Goodwin JG Jr (2001) J Catal 204:98
15. Bae JW, Kim IG, Lee JS, Lee KH, Jang EJ (2003) Appl Catal A 240:129
16. Zhang J, Chen J, Ren J, Sun Y (2003) Appl Catal A 243:121