ASIAN JOURNAL OF CHEMISTRY

One-Pot Synthesis of Gold Nanoparticles on N,O-Containing Organic Group Modified Silica and Its Catalytic Performance for Selective Hydrogenation of Acetylene

Kang-Jun Wang[1,*], Jing Wu[1] and Xin-Kui Wang[2]

[1]College of Chemical Engineering, Shenyang University of Chemical Technology, Shenyang 110142, P.R. China
[2]Laboratory of Plasma Physical Chemistry, Dalian University of Technology, Dalian 116024, P.R. China

*Corresponding author: Fax: +86 24 89383760; Tel: +86 24 89383902; E-mail: wangkj_dut@yahoo.com.cn

A novel *in situ* autoreduction and entrapment route has been developed, by which highly dispersed gold nanoparticles could be easily prepared on modified silica in one step. The aminopropyl groups were introduced onto silica *via* sol-gel condensation of tetraethoxylsilicate (TEOS) and aminopropyltriethoxysilane (APTES). The formaldehyde can be anchored on amino groups to form N,O-containing organic groups ($NHCH_2OH$). The resulted N,O-containing organic groups can directly reduce the $HAuCl_4$ to form highly dispersed gold nanoparticles on modified silica at room temperature. The as-synthesized novel gold catalyst, compared with gold supported on commercial silica prepared by conventional deposition-precipitation method, showed much better stability, activity and selectivity for selective acetylene hydrogenation.

Key Words: Gold, Nanoparticles, Organic groups modified silica, Acetylene hydrogenation.

INTRODUCTION

Gold has been always considered to be chemically inert and regarded as a poor catalyst. However, since the Haruta *et al.*[1] discovered the extraordinary activity of supported gold in CO low temperature oxidation, gold catalysts have been successfully applied to a variety of reactions such as hydrogenation of unsaturated substrates[2-5], oxidation of methanol[6], alcohol[7] and glucose[8] and synthesis of organic compounds[9,10]. It is generally agreed that the catalytic activity of gold catalysts strongly depends on the sizes of gold particles, but the nature of the support material, the preparation method and the activation procedure have also been suggest to play a key role[1,5,11-13]. As for so-called 'active' oxide supports, such as TiO_2[14,15], CeO_2[16], ZrO_2[17], Fe_2O_3[2,18,19] and Co_3O_4[20], high activity of gold catalysts can be achieved by traditional coprecipitation (CP) and deposition-precipitation (DP) methods due to the strong interaction between gold and supports. However, the preparation of silica-supported gold nanoparticles with high activity remains a challenge because of the weak interaction between gold and 'inert' silica[21,22]. To obtain high active and stable gold nanoparticles on silica, several strategies, such as modification of silica with other oxides[12,23,24], introduction of H_2N or R_4N^+-containing organic groups onto silica surface[25,26] and changing the charge property of gold precursor[21], have been demonstrated to be effective. But several separate steps are involved in the preparation processes and this sometimes results in poor reproducibility. In addition, during these processes the Cl^- anions, bound with gold ions, are difficult to completely remove in subsequent washing, calcination and reduction procedures, which not only causes agglomeration of gold particles during heat treatment, but also poisons the active sites[27]. Recently, Kumar *et al.*[28,29] found that the silanol groups present on the surface of fumed silica could directly reduce the aqueous chloroaurate ions to form gold nanoparticles after long reaction time (*ca.* 100 h). Moreover, addition of alkylamine into preparation solution or introducing $-NH_2$ or -SH groups onto silica surface were needed to control and stabilize the formed gold particles. In this report, a novel one-step synthesis of gold nanoparticles on modified silica has been developed. The N,O-containing groups prepared on silica function not only as reductant but also as capping agent, thereby, highly dispersed gold nanoparticles can be achieved on silica in several hours without adding external reducing reagent and stabilizer. The Cl^- anions can be easily removed by washing due to their chemical separation from metallic gold particles. The novel as-synthesized gold catalyst exhibited excellent stability, activity and selectivity for selective acetylene hydrogenation in contrast to gold sample supported on commercial silica prepared by conventional deposition-precipitation method.

EXPERIMENTAL

Gold nanoparticles supported on N,O-containing organic groups modified silica (denoted as Au/M-SiO$_2$) were prepared as follows. Firstly, 2.0 mL tetraethoxylsilicate (TEOS) was added into a mixture of 5.0 mL aminopropyltriethoxysilane (APTES), 10 mL of aqueous ammonia solution (27 wt. %) and 20 mL of deionized water. After stirring at room temperature for 30 h, the mixed solution was evaporated at 353 K and the obtained solid was further dried in air at 393 K for 12 h, leading to the formation of aminopropyl-functionalized silica (denoted as NH$_2$-SiO$_2$). After that, 1.0 g of the above prepared NH$_2$-SiO$_2$ was added into 50 mL of aqueous solution of formaldehyde and the mixture was stirred at 340 K for 8 h. The resulted suspension was filtered and washed with deionized water for several times and then dried under vacuum at 323 K for 5 h. The white solid containing HOCH$_2$HN- groups was thus obtained (denoted as HOCH$_2$-NH-SiO$_2$)[30]. To introduce gold onto support, 1.0 g of HOCH$_2$-NH-SiO$_2$ solid was mixed with 30 mL aqueous solution of HAuCl$_4$ (0.0017 M) and stirred at room temperature for 4 h. After filtering, the obtained deep pink sample was washed with deionized water and then dried under vacuum at room temperature for 5 h. The Au catalyst thus prepared was denoted as Au/M-SiO$_2$. The loading of gold was *ca.* 1 %. For comparison, a similar loading Au sample supported on a commercial SiO$_2$ (Qingdao Haiyang Chemical Co., China) was synthesized. Typically, 20 mL aqueous solution of HAuCl$_4$ (0.0029 M) was heated to 333 K. The pH was adjusted to 9-10 by dropwise addition of ammonia water (1 M) and then 2 g of commercial SiO$_2$ was added into the solution. The mixture was kept at 333 K and stirred for 4 h and then was further dispersed by ultrasonic at room temperature for 20 min. After filtering and washing with deionized water, the resulted yellow sample was dried at 333 K for 8 h (denoted as Au/C-SiO$_2$). When as-prepared Au/C-SiO$_2$ catalyst was further calcined at 393 K for 2 h and then at 673 K for 4 h, the red power obtained was denoted as Au/C-SiO$_2$-673.

The UV-VIS spectra were recorded on a Cintra 20 spectrometer. Transmission electron microscope images of the catalysts were recorded with a transmission electron microscope (TEM, Philips Tecnai G2 20). The chemical properties of the catalyst surface were analyzed by X-ray photoelectron spectrascopy (VG ESCALAB250) equipped with a monochromatic Al K$_\alpha$ (1486.6 eV) radiation source. To eliminate the effect of possible charge development in the sample during the XPS measurement, the observed peak position was calibrated using the C1s peak (284.6 eV) as a reference. FTIR spectra of catalyst samples were determined using a Bruker TENSOR 27 IR spectrometer.

The selective hydrogenation of acetylene was conducted in a quartz tube reactor (i.d. 4 mm) at 393 K with a gas hourly space velocity (GHSV) of 12000 mL h^{-1} (g cat.)$^{-1}$. The hydrocarbon concentrations in the effluent gas from the reactor were analyzed by an on-line gas chromatograph (Agilent 1790) equipped with a Porapak N column and a flame ionization detector. High-purity H$_2$ gas and 2 % C$_2$H$_2$ in Ar were employed for feeding. The flow rate of feeding gas was measured and controlled by mass flow controller. The selectivity of ethylene (SE) was defined as: selectivity of ethylene = ethylene formed/ acetylene converted.

RESULTS AND DISCUSSION

Synthesis and characterization of Au-based catalysts: Fig. 1 presents the UV-VIS spectra of commercial SiO$_2$ (curve a) and HOCH$_2$-NH-SiO$_2$ (curve b), Au/C-SiO$_2$ (curve c), Au/ M-SiO$_2$ (curve d) and Au/C-SiO$_2$-673 (curve e). It can be seen that one peak appears at around 520 nm, attributed to metallic gold[5], for Au/M-SiO$_2$ (curve d) and Au/C-SiO$_2$-673 (curve e) catalysts, while there is no peak observed for commercial SiO$_2$, HOCH$_2$-NH-SiO$_2$ and Au/C-SiO$_2$ between 400-800 nm, clearly confirming the presence of gold nanoparticles on silica for Au/M-SiO$_2$ and Au/C-SiO$_2$-673 catalysts.
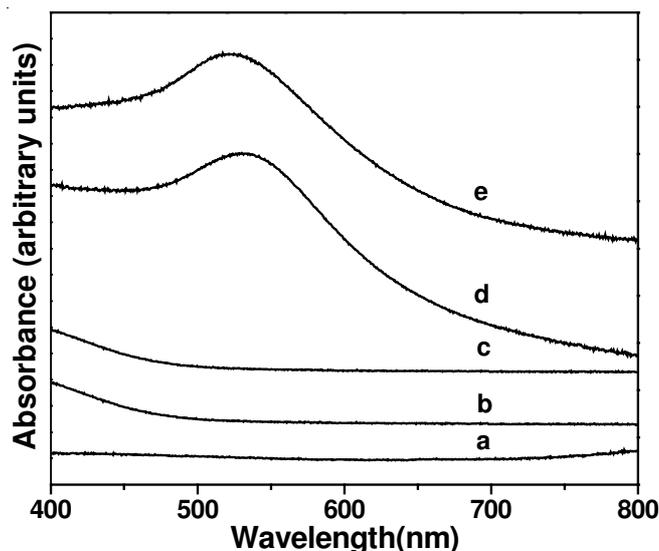

Fig. 1. UV-VIS spectra of (a) SiO$_2$, (b) HOCH$_2$-NH-SiO$_2$, (c) Au/C-SiO$_2$, (d) Au/M-SiO$_2$ and (e) Au/C-SiO$_2$-673

To estimate the size of gold particles, the typical TEM images of Au-based catalysts are shown in Fig. 2. For Au/ M-SiO$_2$ (Fig. 2a), it is clearly shown that the highly dispersed Au nanoparticles have been successfully prepared on modified silica with an average size of 5-7 nm. Previous works[31-33] have demonstrated that some organic groups could strongly interact with the metal nanoparticles, such as Pt, Pd and Au nanoparticles and prevent aggregation. In the present work, the N,O-containing organic groups were introduced onto silica, which has been demonstrated by FTIR spectra (Fig. 3). The appearance of the peaks at 3358 cm^{-1}, 3297 cm^{-1}, (assigned to N-H stretching), 1600 cm^{-1} (assigned to scissoring in-plane bending mode of the primary amine NH$_2$ group)[34], 2934 and 2880 cm^{-1} (assigning to the C-H of aminopropyl stretching) for NH$_2$-SiO$_2$ (Fig. 3b)[35], clearly indicates that aminopropyl groups are introduced onto the silica *via* sol-gel condensation of TEOS and APTES. After further reaction with HCHO to form HOCH$_2$-NH-SiO$_2$ (Fig. 3c) and introduction of gold to yield Au/M-SiO$_2$ (Fig. 3d), the FTIR spectra of the two samples show almost no strength change for the peaks associated with alkyl groups despite the peaks related to amino groups are weakened (Fig. 3c and 3d), which proves that the organic groups are maintained during these process. Due to the presence of N,O-containing organic groups on silica, which can strongly interact with formed Au nanoparticles, therefore, highly dispersed Au nanoparticles was prepared on modified silica without adding an external stabilizer.
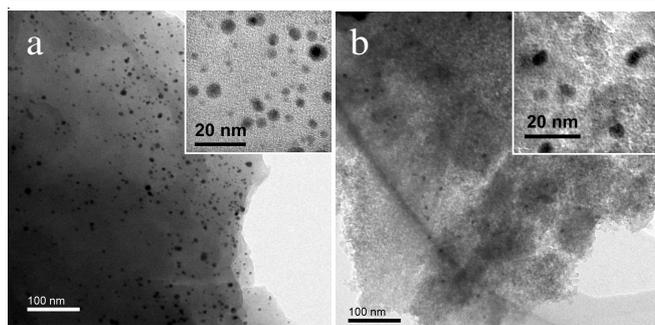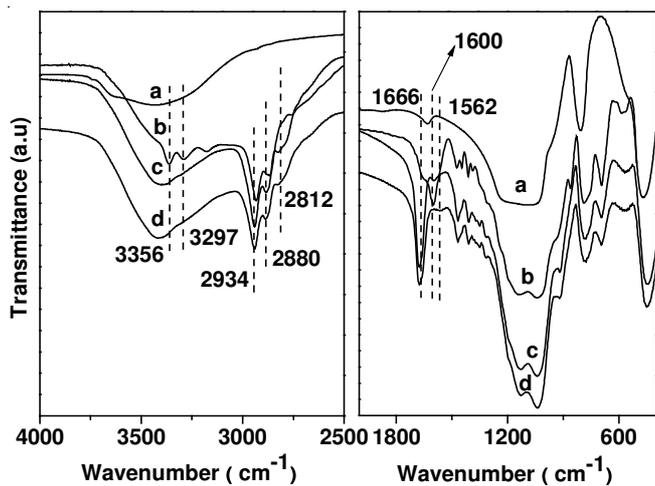
Fig. 2. TEM images of (a) Au/M-SiO$_2$ and (b) Au/C-SiO$_2$-673

Fig. 3.   FTIR spectra of (a) Au/C-SiO$_2$-673, (b) H$_2$N-SiO$_2$, (c) HO-CH$_2$-NH-SiO$_2$ and (d) Au/M-SiO$_2$

Fig. 4. Au 4f XPS spectra of (a) Au/M-SiO$_2$ and (b) Au/C-SiO$_2$-673

Fig. 4 shows the XPS spectra of the Au 4f state for the gold catalysts. Au/M-SiO$_2$ catalyst only showed the double peaks with binding energy of 83.9 eV (Au 4$f_{7/2}$) and 87.4 eV (Au 4$f_{5/2}$), indicating exclusively metallic Au particles with no significant amount of Au oxidized species (Fig. 4a)[6,12]. However, Au/C-SiO$_2$-673 catalyst gave the binding energy of 84.2 eV (Au 4$f_{7/2}$) and 87.7 eV (Au 4$f_{5/2}$) (Fig. 4b), which was up shift 0.3 eV compared with that of Au/M-SiO$_2$ catalyst. It is well known that as for the small size of metal particle, decrease of particle size will cause an increase of binding energy[36]. In the present work, part of the particle size of Au/M-SiO$_2$ is smaller than that of Au/C-SiO$_2$-673 catalyst and the size of some particles on Au/M-SiO$_2$ is similar to that of Au/C-SiO$_2$-673 catalyst (Fig. 2), so the size effect can be ruled out. The FTIR spectra of the Au/M-SiO$_2$ clearly showed the presence of the N,O-containing organic groups on Au/M-SiO$_2$ (Fig. 3d). According to the previous work[37], electron-rich N-containing organic groups and compounds could transfer electron to metal nanoparticles. Therefore the low binding energy of Au 4f of Au/M-SiO$_2$ may be attributed to the effect of the organic groups on the silica surface, which may also suggest that the gold particles can be stablized on the modified silica.

Selective acetylene hydrogenation: The above results clearly show that the highly dispersed gold nanoparticles have been prepared on modified silica by *in situ* autoreduction in one step. The catalytic acetylene hydrogention was used to test the catalytic performance of newly synthesized gold ca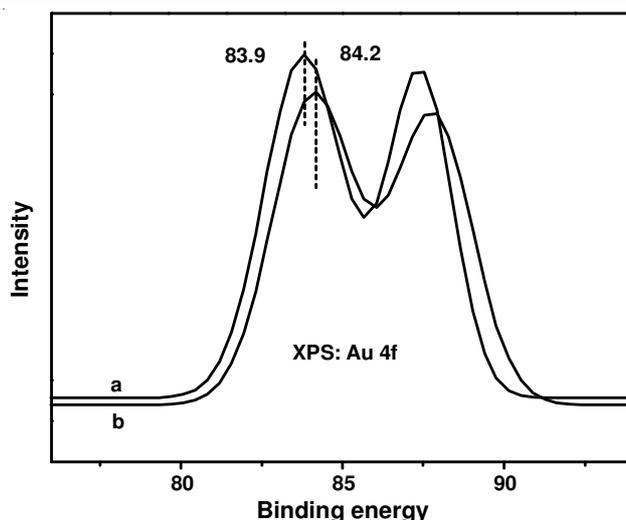talysts. Fig. 5 presents the time on stream acetylene hydro-genation on gold-based catalysts. For Au/C-SiO$_2$-673 catalyst prepared by traditional deposition-precipitation method, the activity decreased significantly with the time on stream, the acetylene conversion decreased from 100 % to 20 % over a period of 3 h. However, for Au/M-SiO$_2$ catalyst, time on stream studies showed stable activity for over 10 h under the same reaction conditions. This result clearly shows that Au/M-SiO$_2$ has much better activity and stability than Au/C-SiO$_2$-673 catalyst (Fig. 5). From the result of Fig. 5, it can be seen that Au/M-SiO$_2$ also exhibits better selectivity compared with Au/C-SiO$_2$-673 catalyst. It is well known that the coke deposition and the size of particles generally affect the activity and stability of catalyst for acetylene hydrogenation for Au-based catalyst. However, the size of Au particles on Au/C-SiO$_2$-673 catalyst was almost not changed with the time on stream for 3 h. This result indicates that the decrease of activity may be due to the coke deposition for Au/C-SiO$_2$-673 catalyst.
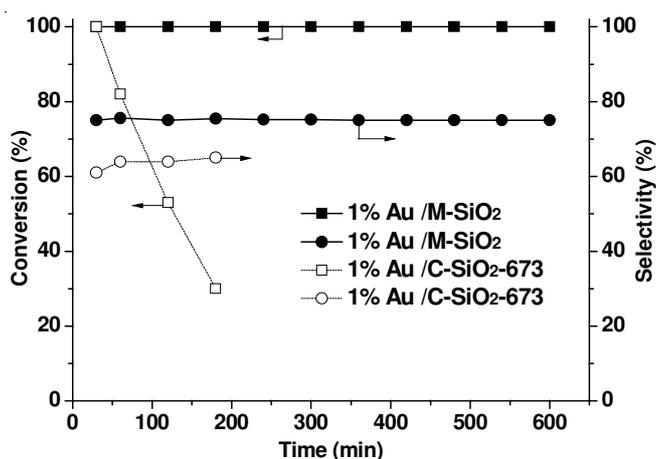

Fig. 5.   Time on stream acetylene hydrogenation activity and selectivity on Au/M-SiO$_2$ and Au/C-SiO$_2$-673 catalysts at 393 K. Gas hourly space velocity of 12000 mL h^{-1} (g cat.)$^{-1}$, H$_2$/C$_2$H$_2$ = 20

Conclusion

The novel one-step preparation of highly dispersed gold nanoparticles on N,O-containing organic group modified silica

was presented in this work. The N,O-containing organic groups (HO-CH$_2$-NH-) formed by treating the H$_2$N-group with formaldehyde, which function not only as a reductant but also as a stabilizer. The highly dispersed gold nanoparticles can be synthesized in aqueous solution using HAuCl$_4$ precursor without adding any other reductants and stabilizers. Compared with Au/C-SiO$_2$-673 catalyst prepared with deposition-precipitation method, the novel Au/M-SiO$_2$ catalyst exhibited excellent stability and selectivity for selective acetylene hydrogenation.

REFERENCES

1. M. Haruta, T. Kobayashi, H. Sano and N. Yamada, *Chem. Lett.*, **2**, 405 (1987).
2. F. Cardenas-Lizana, S. Gomez-Quero and M.A. Keane, *Catal. Commun.*, **9**, 475 (2008).
3. S.A. Nikolaev, N.A. Permyakov, V.V. Smirnov, A.Y. Vasil'kov and S.N. Lanin, *Kinet. Catal.*, **51**, 288 (2010).
4. E. Bus, R. Prins and J.A. van Bokhoven, *Catal. Commun.*, **8**, 1397 (2007).
5. Y.Y. Chen, J.S. Qiu, X.K. Wang and J.H. Xiu, *J. Catal.*, **242**, 227 (2006).
6. A. Nuhu, J. Soares, M. Gonzalez-Herrera, A. Watts, G. Hussein and M. Bowker, *Top. Catal.*, **44**, 293 (2007).
7. A. Abad, P. Conception, A. Corma and H. Garcia, *Angew. Chem. Int. Ed.*, **44**, 4066 (2005).
8. N. Thielecke, K.D. Vorlop and U. Prusse, *Catal. Today*, **122**, 266 (2002).
9. X. Zhang and A. Corma, *Chem. Commun.*, **29**, 3080 (2007).
10. A. Stephen, K. Hashmi and G.J. Hutchings, *Angew. Chem. Int. Ed.*, **45**, 7896 (2006).
11. N.F. Zheng and G.D. Stucky, *J. Am. Chem. Soc.*, **128**, 14278 (2006).
12. K. Qian, W.X. Huang, Zh. Q. Jiang and H.X. Sun, *J. Catal.*, **248**, 137 (2007).
13. F. Cardenas-Lizana, S. Gomez-Quero, N. Perret and M.A. Keane, *Gold Bull.*, **42**, 124 (2009).
14. B. Schumachera, V. Plzakb, M. Kinnea and R.J. Behm, *Catal. Lett.*, **89**, 109 (2003).
15. Y.F. Yang, P. Sangeetha and Y.W. Chen, *Int. J. Hydrogen Energ.*, **34**, 8912 (2010).
16. S. Carrettin, P. Conception, A. Corma, J.M. Lopez Nieto and V.F. Puntes, *Angew. Chem. Int. Ed.*, **43**, 2538 (2004).
17. G.J. Hutchings, *Catal. Today*, **72**, 11 (2002).
18. Z.Y. Zhong, J. Ho, J. Teo, S.C. Shen and A. Gedanken, *Chem Mater.*, **19**, 4776 (2007).
19. Y.F. Yang, P. Sangeetha and Y.W. Chen, *Ind. Eng. Chem. Res.*, **48**, 10402 (2010).
20. M. Haruta, S. Tsubota, T. Kobayashi, H. Kageyama, M.J. Genet and B. Delmon, *J. Catal.*, **144**, 175 (1993).
21. H.G. Zhu, C.D. Liang, W.F. Yan, S.H. Overbury and S. Dai, *J. Phys. Chem. B*, **110**, 10842 (2006).
22. G. Budroni and A. Corma, *Angew. Chem. Int. Ed.*, **45**, 3328 (2006).
23. W.F. Yan, S.M. Mahurin, B. Chen, S.H. Overbury and S. Dai, *J. Phys. Chem. B*, **109**, 15489 (2005).
24. A.M. Venezia, F.L. Liotta, G. Pantaleo, A. Beck, A. Horvath, O. Geszti, A. Kocsonya and L. Guczi, *Appl. Catal. A*, **310**, 114 (2006).
25. J.L. Gu, J.L. Shi, G.J. You, L.M. Xiong, S.X. Qian, Z.L. Hua and H.R. Chen, *Adv. Mater.*, **17**, 557 (2005).
26. C. Yang, H. Sheu and K. Chao, *Adv. Funct. Mater.*, **12**, 143 (2002).
27. Z.Y. Zhong, J.Y. Lin, S.P. Teh, J. Teo and F.M. Dautzenberg, *Adv. Funct. Mater.*, **17**, 1402 (2007).
28. A. Ghosh, C.R. Patraa, P. Mukherjeea, M. Sastry and R. Kumar, *Micropor. Mesopor. Mater.*, **58**, 201 (2003).
29. P. Mukherjee, C.R. Patra, A. Ghosh, R. Kumar and M. Sastry, *Chem. Mater.*, **14**, 1678 (2002).
30. J.M. Sun, D. Ma, H. Zhang, X.M. Liu, X.W. Han, X.H. Bao, G. Weinberg, N. Pfänder and D.S. Su, *J. Am. Chem. Soc.*, **128**, 15756 (2006).
31. J. Alvarez, J. Liu, E. Roman and A.E. Kaifer, *Chem. Commun.*, **13**, 1151 (2000).
32. S. Mandal, D. Roy, R.V. Chaudhari and M. Sastry, *Chem. Mater.*, **16**, 3714 (2004).
33. P. Mukherjee, C.R. Patra, R. Kumar and M. Sastry, *Phys. Chem. Commun.*, **5**, 1 (2001).
34. T. Ramanathan, F.T. Fisher, R.S. Ruoff and L.C. Brinson, *Chem. Mater.*, **17**, 1290 (2005).
35. T. Kasahara, K. Inumaru and S. Yamanaka, *Micropor. Mesopor. Mater.*, **76**, 123 (2004).
36. I. Lopez-Salido, D.C. Lim, R. Dietsche, N. Bertrom and Y.D. Kim, *J. Phys. Chem. B*, **110**, 1128 (2006).
37. H. Borchert, D. Fenske, J. Kolny-Olesiak, J. Parisi, K. Al-Shamery and M. Bäumer, *Angew. Chem. Int. Ed.*, **46**, 2923 (2007).