Dalton Transactions

PAPER



Cite this: DOI: 10.1039/c4dt01323a

Received 4th May 2014, Accepted 2nd July 2014 DOI: 10.1039/c4dt01323a

www.rsc.org/dalton

Introduction

The quality of indoor air is very important for human health because people often spend more than 80% of their time in indoor space. Formaldehyde is a major indoor pollutant and long-time exposure to HCHO-containing air may cause serious health problems including nasal tumors, eye and skin irritation, nasopharyngeal cancer, etc.^{1,2} In order to clean the indoor air, many strategies have been developed to remove HCHO, for instance, adsorption,³⁻⁷ photocatalytic oxidation,^{8,9} plasma technology,¹⁰ and thermal catalytic oxidation.¹¹⁻¹⁶ However, adsorption has a disadvantage of a short lifetime due to its limited adsorption capacity. And photocatalytic oxidation, plasma technology and high-temperature thermal catalytic oxidation all need extra equipment (such as a light source for photocatalytic oxidation, plasma equipment for plasma technology, heating equipment for high-temperature thermal catalytic oxidation), which brings more complicated processes and additional operating cost.

E-mail: jiaguoyu@yahoo.com; Fax: +86-27-87879468; Tel: +86-27-87871029 ^bSchool of Chemistry and Chemical Engineering, Hubei University of Technology, Wuhan 430068, P. R. China

^cFaculty of Science, King Abdulaziz University, Jeddah 21589, Saudi Arabia

Efficient decomposition of formaldehyde at room temperature over Pt/honeycomb ceramics with ultra-low Pt content

Longhui Nie,^{a,b} Yingqiu Zheng^a and Jiaguo Yu*^{a,c}

Pt/honeycomb ceramic (Pt/HC) catalysts with ultra-low Pt content (0.005–0.055 wt%) were for the first time prepared by an impregnation of honeycomb ceramics with Pt precursor and NaBH₄-reduction combined method. The microstructures, morphologies and textural properties of the resulting samples were characterized by X-ray diffraction (XRD), field-emission scanning electron microscopy (FE-SEM), and transmission electron microscopy (TEM). The obtained Pt/HC catalysts were used for catalytic oxidative decomposition of formaldehyde (HCHO) at room temperature. It was found that the as-prepared Pt/HC catalysts can efficiently decompose HCHO in air into CO₂ and H₂O at room temperature. The catalytic activity of the Pt/HC catalysts increases with increasing the Pt loading in the range of 0.005–0.013 wt%, and the further increase of the Pt loading does not obviously improve catalytic activity. From the viewpoint of cost and catalytic performance, 0.013 wt% Pt loading is the optimal Pt loading amount, and the Pt/HC catalyst with 0.013 wt% Pt loading also exhibited good catalytic stability. Considering practical applications, this work will provide new insights into the low-cost and large-scale fabrication of advanced catalytic materials for indoor air purification.

However, room-temperature catalytic oxidative decomposition of HCHO into CO₂ and H₂O can overcome the above shortcomings and is considered the most promising strategy for removal of indoor HCHO, because it is environmentally friendly and energy saving.^{11,13–15} In the case of room-temperature catalytic oxidation, various supported noble metal catalysts have been developed by some research groups.^{11,13–15,17–22} For example, Zhang et al.¹¹ firstly found that HCHO could be completely oxidized into CO2 and H2O over various supported noble metal (Pt, Rh, Pd and Au) catalysts with 1 wt% loading at room temperature. Then, Ma et al.²⁰ reported that HCHO could be partly oxidized into CO2 and H2O on about 1 wt% Au/Co₃O₄-CeO₂ at 25 °C. Huang *et al.*¹⁴ also found that HCHO could be completely oxidized into CO2 and H2O on Pd/TiO2 with ≥ 0.1 wt% loading at room temperature. In our recent study, our work indicated that HCHO was also completely oxidized into CO2 and H2O over Pt-supported catalysts with \geq 0.1 wt% loading.^{21,22} Among the above noble metal-supported catalysts, the Pt-supported catalyst exhibited a better catalytic performance for decomposition of HCHO than other noble metal catalysts at room temperature. However, most of the Pt-supported catalysts were prepared in powder form, which brings much trouble in actual applications because they need to be pressed into tablets or attached to other big-block supports. At the same time, it also opens the possibility of high air resistance, and catalysts' falling off from the tablets or

Published on 02 July 2014. Downloaded by University of Windsor on 17/07/2014 11:00:33.



View Article Online

^aState Key Laboratory of Advanced Technology for Materials Synthesis and Processing, Wuhan University of Technology, Wuhan 430070, P. R. China.

big-block supports. Furthermore, the high cost of noble metals prevents their actual applications because most of the reported Pt-supported catalysts have high Pt content (most ≥ 0.5 wt%, the lowest Pt content is 0.1 wt%). So, there is an urgent need to develop a high-performance HCHO room-temperature oxidative catalyst with low noble metal loading content. Further, to overcome the abovementioned drawbacks of powder catalysts, monolith-type catalytic materials can be considered.

Honeycomb ceramics (HC) are widely used as catalysts,²³ catalyst carriers²⁴ and reactors²⁵ due to their unique mechanical and thermal properties. Also, the macropore structure of HC will help to greatly reduce air resistance in gas phase reactions. So, in this work, for the first time, we report the fabrication of novel and easily applied Pt/HC catalysts with an ultralow Pt content (0.005–0.055 wt%) and their application to room temperature catalytic oxidation decomposition of HCHO from air. The prepared Pt/HC catalysts exhibit good catalytic activity and stability.

Experimental

Sample preparation

All reagents were of analytical grade and were used without further purification. The honeycomb ceramics (mainly composed of α -Al₂O₃) used were commercially available from Wuhan University of Technology. The Pt/HC catalysts were prepared by equivalent-volume impregnation of the honeycomb ceramic (see Fig. 1a, diameter: 4.75 cm, height: 1.2 cm, weight: 21.0 g, 300 mesh) with Pt precursor solution followed by reduction with NaBH4.21 In a typical preparation, one honeycomb ceramic support was immersed in 12 mL of H₂PtCl₆ aqueous solution with different concentrations (from 0.8, 1.6, 3.2, 6.5, to 12.9 mM) under shaking. After impregnation for 10 min, the mixed solution (10 mL) of NaBH₄ solution (from 4.8, 9.6, 19.2, 39.0, to 77.4 mM) and NaOH solution (from 24, 48, 96, 195, to 387 mM) was quickly added onto the immersed support for 10 min (NaOH: NaBH₄: Pt = 25:5:1, molar ratio) under shaking, and it should be noted that the mixed solution can contact uniformly with the whole surface of the support. After reduction, the samples were dried at 80 °C for 12 h. The nominal weight ratios of Pt to HC in obtained Pt/HC catalysts were 0.009, 0.018, 0.036, 0.072 and 0.144 wt%, respectively.



Fig. 1 Photographs of the HC and Pt/HC (Pt13) samples.

The real content of Pt (the weight ratio of Pt to HC) in the Pt/HC catalysts measured by inductively coupled plasma atomic emission spectrometry (ICP-AES) was 0.005, 0.008, 0.013, 0.032 and 0.055 wt%, respectively. The Pt/HC samples with real Pt content of 0.005, 0.008, 0.013, 0.032 and 0.055 wt% were named as Pt5, Pt8, Pt13, Pt32 and Pt55, respectively.

Characterization

Pt/HC catalysts were analyzed using a D/Max-RB X-ray diffractometer (Rigaku, Japan) with Cu K_{α} radiation at a scan rate (2 θ) of 0.05° s⁻¹. A scanning electron microscopy (SEM) image was obtained on an S-4800 field emission SEM (FESEM, Hitachi, Japan) at an accelerating voltage of 10 kV. The elemental mapping over a desired region of the selected sample was carried out by an energy-dispersive X-ray analyzer (EDX) attached to the SEM. Transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM) images were collected on a JEM-2100F microscope at an accelerating voltage of 200 kV. X-ray photoelectron spectroscopy (XPS) measurements were performed on a VG ESCA-LAB250xi with X-ray monochromatisation. All binding energies (BE) were referenced to the C 1s peak at 284.8 eV of the surface adventitious carbon. The dispersion of Pt was measured and calculated on the basis of CO chemisorption performed by a BELCAT catalyst analyzer (BELCAT-B-293, BEL Japan). The sample (0.1117 g) was firstly pretreated in hydrogen (50 SCCM) at 200 °C for 15 min and purged with helium (50 SCCM) for 15 min at the same temperature. Then, the catalyst was cooled to room temperature and CO pulses were injected from a calibrated on-line sampling valve. CO adsorption was assumed to be complete after three successive peaks showed the same peak areas. A CO/Pt stoichiometry of 1 was used for calculations.

Catalytic activity test

Formaldehyde is widely used by industry to manufacture building materials and numerous household products. It is also a by-product of combustion and certain other natural processes. Thus, it is always present in substantial concentrations both indoors and outdoors. The room-temperature catalytic oxidation of HCHO was performed in a dark organic glass box covered by a layer of aluminum foil on its inner wall at 25 °C and 50% relative humidity in the same way as our previously reported work.²¹ The Pt/HC sample was placed on the bottom of a glass Petri dish with a diameter of 14 cm. After placing the sample dish on the bottom of the reactor with a glass slide cover, 6 µL of condensed HCHO solution (38%) was injected into the reactor and a 5 watt fan was placed on the bottom of the reactor. After 2 h, the HCHO solution was volatilized completely and the concentration of HCHO was stabilized. The analysis of HCHO and CO2 was on-line conducted by a photoacoustic IR multigas monitor (INNOVA AirTech Instruments Model 1412). The HCHO vapor was allowed to reach adsorption-desorption equilibrium within the reactor prior to catalytic activity experiments. The initial concentration of HCHO after adsorption equilibrium was controlled at about 140 ppm,

which remained constant until the glass slide cover on the Petri dish was removed to start the catalytic oxidation reaction of HCHO. Each set of experiments was followed for about 60 min. The CO₂ concentration increase (Δ CO₂, which is the difference between CO₂ concentration at *t* reaction time and initial time, ppm) and the HCHO concentration decrease were used to evaluate the catalytic performance.

Results and discussion

Phase structures, morphology and element composition

The photographs of HC and Pt/HC (Pt13) were taken by a digital camera. Fig. 1a shows the photograph of HC used in this study. The diameter and height of HC are about 4.75 and 1.2 cm, respectively. It can be seen that many triangular-shaped channels (300 meshes) were patterned in the HC, which are beneficial to the deposition of the small Pt nano-particles (NPs) on the interior surface of HC. HC not only provides more active contact sites for HCHO but also reduces the air resistance of the gaseous reaction. Further observation indicates that the color of HC changed from white to grey black of Pt/HC (see Fig. 1b) after Pt deposition, implying the presence of Pt NPs.

The XRD patterns of the HC and Pt/HC (Pt13) samples are presented in Fig. 2. The XRD results indicate that all the diffraction peaks of the HC and Pt/HC samples can be indexed to alpha-alumina, which are consistent with the JCPDS file of Al₂O₃ (JCPDS no. 43-1484), indicating that the HC sample is mainly composed of alpha-alumina. Also, no obvious change can be observed in the height and position of Al₂O₃ diffraction peaks before and after the deposition of Pt NPs (for the HC and Pt/HC samples). Further observation shows that the diffraction peaks of Pt cannot be observed in the XRD pattern of the Pt/HC sample, mainly due to its extremely low loading $(0.005-0.055 \text{ wt%}).^{21,26}$

SEM, TEM and HRTEM results of the HC and Pt13 samples are shown in Fig. 3. The SEM image (Fig. 3a) of HC shows that



Fig. 2 XRD patterns of the HC and Pt/HC (Pt13) samples.

the HC sample is composed of a large number of Al₂O₃ grains with the size of about 0.5–5 μ m. After the deposition of Pt, the Al₂O₃ grain size of the Pt13 sample (see Fig. 3b) shows no obvious change. In order to further analyse the element composition of the Pt13 sample, the area element mappings of Al, O and Pt of Fig. 3b were obtained by an energy-dispersive X-ray analyzer attached to the SEM and the corresponding results are shown in Fig. 3c, d and e, respectively. Fig. 3c, d and e clearly show that a large number of uniform small dots in the elemental area mappings of Al, O and Pt species are well distributed on the whole bulk catalyst and the density of dots for Al and O elements is much bigger than that for the Pt element. This is not surprising, because the Pt loading amount of the Pt13 sample is 0.013%. The above elemental analysis indicates that the deposited Pt is highly dispersed on the surface of Al₂O₃ grains in the Pt13 sample, which was further confirmed by CO chemisorption with about 33.1% of Pt dispersion.

Fig. 3f and g present TEM and HRTEM images of the Pt13 sample, respectively. It can be seen from Fig. 3f that some small black dots marked in white circle, dispersed on the surface of Al_2O_3 grains, are clearly observed, implying the presence of Pt NPs. Their size is about 4–5 nm. The HRTEM image (Fig. 3g) of Pt NPs shows that the lattice spacing in white circle is *ca*. 0.224 nm, which is consistent with the lattice spacing of the (111) planes of metallic Pt,²⁷ also further confirming that the black NPs are Pt NPs. Combining the above results of the TEM image (Fig. 3f) and area element mapping of Pt (Fig. 3e) as well as the results reported in the literature,²⁸ it can be inferred that Pt may have two existence forms: one is in the form of Pt NPs, and the other is some metallic Pt atoms uniformly deposited on the surface of Al_2O_3 grains.

XPS analysis

The composition and element chemical state of the prepared samples were investigated by XPS and the results are shown in Fig. 4. It is difficult to detect a Pt signal by XPS due to the extremely low Pt content of 0.005-0.055 wt%. Therefore, in order to detect a Pt XPS signal more easily, a 1 wt% Pt/HC sample was prepared by the above Pt deposition method using the ground HC powder as the support. XPS survey spectra (see Fig. 4a) of HC and Pt/HC show that the elements Al, O, Sm, Na, Si, and C exist in the HC sample and the XPS peaks of Pt also appear in the Pt/HC sample after deposition of Pt. It can be observed that the peak of Na 1s for Pt/HC is much stronger than that of HC. This is because the deposition of Pt introduces some Na element into the Pt/HC sample because of using NaOH and NaBH₄ as precursors. Because the Al 2p line of the support overlaps with the Pt 4f line of the active component usually used for the spectroscopic analysis of platinum, the Pt 4d line was chosen to identify Pt species in this study. The high-resolution XPS spectra of Pt 4d, O 1s and C 1s regions are shown in Fig. 4b, c and d, respectively. The peak observed at 314.4 eV for the Pt/HC sample is assigned to Pt 4d5/2 of metal Pt,^{29,30} further confirming the presence of Pt(0). A high-resolution XPS spectrum of O 1s is shown in



Fig. 3 SEM image (a) of the HC sample, SEM image (b) and EDX element mappings (c: Al Kα, d: O Kα, and e: Pt Mα) of the prepared Pt13 sample, and TEM (f) and HRTEM (g) images of the Pt13 sample.

Fig. 4c. Two fitted peaks located at 530.8 and 532.2 eV are observed for both HC and Pt/HC, which can be assigned to the lattice oxygen (O 1s) of Al_2O_3 and the oxygen of the surface hydroxyl (OH) groups, respectively.²² An extra peak at 536.0 eV is also observed for Pt/HC, which can be attributed to Na KLL.³¹ The high-resolution C 1s spectra of HC and Pt/HC are shown in Fig. 4d. The peak located at 284.8 eV (C–C bond) can be assigned to the adventitious carbon. Compared to HC, a new peak at 289.0 eV appears in the spectra of Pt/HC, which is

assigned to C of Na $_2$ CO $_3$, mainly resulting from the reactions between NaOH and CO $_2$.³²

Catalytic activity

Fig. 5 shows a comparison of the catalytic performance of the HC, Pt5, Pt8, Pt13, Pt32 and Pt55 samples towards HCHO oxidation at room temperature. As can be seen in this figure, the Pt loading content exhibits a significant influence on the HCHO oxidation catalytic activity of the prepared samples.

Paper



Fig. 4 Typical survey spectra (a) of the HC and Pt/HC samples, high-resolution XPS spectra for Pt 4d (b) of the Pt/HC sample and O 1s (c), C 1s (d) of the HC and Pt/HC samples.



Fig. 5 Changes in formaldehyde concentration (a) and ΔCO_2 (the difference between CO_2 concentration at t reaction time and initial time, ppm) (b) as a function of reaction time for the HC and Pt/HC samples with different Pt contents.

In the absence of Pt, for the HC sample, the HCHO concentration decreases in the initial 10 min and then remains almost unchanged during the subsequent 50 min. Accordingly, the CO_2 concentration has no obvious increase in the whole process, implying that the HC sample is not active for HCHO oxidation and HCHO is mainly adsorbed on the surface of HC. Therefore, it can be reasonably inferred that the presence of Pt is indispensable for room temperature HCHO oxidation decomposition. However, in the presence of a small amount of Pt, the activity of the Pt5 sample was obviously enhanced. нсно

The HCHO concentration (shown in Fig. 5a) decreases with increasing reaction time; meanwhile, the CO_2 concentration (shown in Fig. 5b) increases, indicating that the Pt5 sample is active for HCHO oxidation and HCHO is oxidized into CO_2

ÇH,

HC

Π

HC

III



Fig. 6 Proposed mechanism for the catalytic oxidation of HCHO over Pt/HC.



Fig. 7 Illustration of the Pt/HC (1) and Pt/particles (2) catalysts for HCHO oxidation.

and H₂O. The catalytic activity of the Pt/HC samples shows a tendency to increase with increasing Pt loading content. However, when the Pt loading content is higher than 0.013 wt%, a further increase in the content of Pt loading does not cause a great increase in the catalytic activity. This is because a further increase in the Pt loading would lead to the aggregation of Pt NPs and the growth of Pt particles (the results are not shown here). Thus, there is no obvious increase in the number of reactive sites for the Pt32 and Pt55 samples. So, considering Pt cost and catalytic activity, the optimal Pt loading was determined to be 0.013 wt% for Pt/HC catalysts. The catalytic oxidation activity of Pt/HC toward HCHO can be understood by the following suggested mechanism (see Fig. 6) based on the previously reported results.^{11,21,33} In the case of catalytic oxidation of HCHO over Pt/HC, HCHO and O2 are firstly adsorbed onto the HC and Pt surface (step I), respectively. The O2 molecule was dissociated into two adsorbed active O atom species on the surface of Pt NPs.³³ After that, HCHO is oxidized to formate species by the adsorbed active O atom at the Pt NPs surface (step II). Then, the surface formate species are further oxidized into carbonic acid species (H_2CO_3) (step III), and finally, carbonic acid will decompose into CO₂ and H₂O (step IV).

Why can the Pt/HC catalysts with ultra-low Pt content (0.005-0.013 wt%) exhibit high catalytic performance for oxidation decomposition of HCHO at room temperature? One possible explanation is when the HC is used as the support to deposit the Pt NPs. The Pt NPs are mainly deposited on the outer surface of HC due to its big Al2O3 grain size and compact structure. Therefore, the HCHO molecules are much easier to contact with the Pt NPs on the surface of HC than those in powder-like catalysts. Because most Pt NPs in powderlike catalysts are deposited on the inner surface of porous catalysts, the inner Pt NPs are not easily approached by HCHO molecules. The difference between Pt/HC and Pt/particle catalysts in HCHO oxidation is illustrated in Fig. 7. It is notable that the increase of CO₂ concentration is larger than the decrease of HCHO concentration for all Pt/HC catalysts. This is because some adsorbed HCHO molecules on the reactor



Fig. 8 Changes in formaldehyde concentration (a) and ΔCO_2 (b) as a function of reaction time for the Pt13 sample in five recycle tests.

surface will gradually desorb with decreasing the concentration of HCHO in the reactor, and these desorbed HCHO molecules are then oxidized into CO_2 , thus resulting in the increase of CO_2 concentration.

The stability of catalysts is also very important for their practical application. The stability of the Pt13 sample in oxidative decomposition of HCHO at room temperature was further investigated by performing the recycle experiments five times (see Fig. 8). After five recycles, the oxidation rate of HCHO shown in Fig. 8a and the generation rate of CO_2 shown in Fig. 8b over Pt13 do not show any significant changes as compared with those obtained in the first-cycle, suggesting that the Pt13 catalyst can keep a stable and efficient catalytic performance.

Conclusions

In summary, Pt/honeycomb ceramic (Pt/HC) catalysts with ultra-low Pt loading content (0.005-0.055 wt%) were first prepared and used for catalytic decomposition of formaldehyde (HCHO) at room temperature. The catalytic activity of the Pt/HC samples increases with increasing the Pt loading amount in the range of 0.005-0.013 wt%, and the further increase in the Pt loading does not obviously increase catalytic activity when the Pt loading amount is higher than 0.013 wt%. Considering the catalyst cost and catalytic performance studied, the optimal Pt loading was determined to be 0.013 wt%. Owing to honeycomb ceramics having good mechanical and thermal properties, low air resistance for a gas phase reaction and extremely low Pt loading content, the prepared Pt/honeycomb ceramic catalyst is expected to be widely used in the removal of indoor HCHO and the purification of indoor environments. This work will provide new insights into the design and fabrication of low-cost and high-performance indoor air purification catalysts.

Acknowledgements

This work was supported by the 863 Program (2012AA062701), NSFC (21177100, 51272199 and 51320105001), Fundamental Research Funds for the Central Universities (WUT: 2014-VII-010), Self-determined and Innovative Research Funds of SKLWUT (2013-ZD-1 and 2013-KF-10) and Young and Middle-aged Project in Hubei Province Department of Education (Q20121403).

Notes and references

- 1 J. J. Collins, R. Ness, R. W. Tyl, N. Krivanek, N. A. Esmen and T. A. Hall, *Regul. Toxicol. Pharmacol.*, 2001, 34, 17.
- 2 T. Salthammer, S. Mentese and R. Marutzky, *Chem. Rev.*, 2010, **110**, 2536.
- 3 Z. H. Xu, J. G. Yu, G. Liu, B. Cheng, P. Zhou and X. Y. Li, *Dalton Trans.*, 2013, **42**, 10190.

- 4 Z. H. Xu, J. G. Yu and W. Xiao, *Chem. Eur. J.*, 2013, **19**, 9592.
- 5 Y. Le, D. P. Guo, B. Cheng and J. G. Yu, *Appl. Surf. Sci.*, 2013, 274, 110.
- 6 Z. H. Xu, J. G. Yu, J. X. Low and M. Jaroniec, ACS Appl. Mater. Interfaces, 2014, 6, 2111.
- 7 P. Zhou, X. F. Zhu, J. G. Yu and W. Xiao, *ACS Appl. Mater. Interfaces*, 2013, **3**, 8165.
- 8 R. C. W. Lama, M. K. H. Leung, D. Y. C. Leung, L. L. P. Vrijmoedb, W. C. Yamc and S. P. Ng, *Sol. Energy Mater. Sol. Cells*, 2007, 91, 54.
- 9 J. G. Yu, S. H. Wang, J. X. Low and W. Xiao, *Phys. Chem. Chem. Phys.*, 2013, 15, 16883.
- 10 W. J. Liang, J. Li, J. X. Li, T. Zhu and Y. Q. Jin, J. Hazard. Mater., 2010, 175, 1090.
- 11 C. B. Zhang and H. He, Catal. Today, 2007, 126, 345.
- 12 L. L. Liu, H. Tian, J. H. He, D. H. Wang and Q. W. Yang, J. Environ. Sci., 2012, 24, 1117.
- 13 B. T. Liu, C. H. Hsieh, W. H. Wang, C. C. Huang and C. J. Huang, *Chem. Eng. J.*, 2013, 232, 434.
- 14 H. B. Huang and D. Y. C. Leung, ACS Catal., 2011, 1, 348.
- 15 N. H. An, W. L. Zhang, X. L. Yuan, B. Pan, G. Liu, M. J. Jia and W. F. Yan, *Chem. Eng. J.*, 2013, 215–216, 1.
- 16 S. Scirè, S. Minicò, C. Crisafulli, C. Satriano and A. Pistone, *Appl. Catal.*, B, 2003, 40, 43.
- 17 B. B. Chen, C. Shi, M. Crocker, Y. Wang and A. M. Zhu, *Appl. Catal.*, *B*, 2013, **132–133**, 245.
- M. Ikegami, T. Matsumoto, Y. Kobayashi, Y. Jikihara, T. Nakayama, H. Ohashi, T. Honma, T. Takei and M. Haruta, *Appl. Catal.*, *B*, 2013, 134–135, 130.
- 19 D. Chen, Z. P. Qu, S. J. Shen, X. Y. Li, Y. Shi, Y. Wang, Q. Fu and J. J. Wu, *Catal. Today*, 2011, **175**, 338.
- 20 C. Y. Ma, D. H. Wang, W. J. Xue, B. J. Dou, H. L. Wang and Z. P. Hao, *Environ. Sci. Technol.*, 2011, 45, 3628.
- 21 L. H. Nie, J. G. Yu, X. Y. Li, B. Chen, G. Liu and M. Jaroniec, *Environ. Sci. Technol.*, 2013, 47, 2777.
- 22 (a) L. H. Nie, A. Y. Meng, J. G. Yu and M. Jaroniec, *Sci. Rep.*, 2013, 3, 3215; (b) L. H. Nie, P. Zhou, J. G. Yu and M. Jaroniec, *J. Mol. Catal. A: Chem.*, 2014, 390, 7; (c) L. H. Nie, J. G. Yu and J. W. Fu, *ChemCatChem*, 2014, DOI: 10.1002/cctc.201301105.
- 23 L. Zhao, J. Ma, Z. Z. Sun and H. L. Liu, *Appl. Catal., B*, 2009, **89**, 326.
- 24 L. Zhao, J. Ma, Z. Z. Sun and X. D. Zhai, *Appl. Catal., B*, 2008, **83**, 256.
- 25 Y. T. Wu, Y. H. Yu, V. H. Nguyen, K. T. Lu, J. C. S. Wu, L. M. Chang and C. W. Kuo, *J. Hazard. Mater.*, 2013, 262, 717.
- 26 J. X. Peng and S. D. Wang, Appl. Catal., B, 2007, 73, 282.
- 27 N. Shang, P. Papakonstantinou, P. Wang, S. Ravi and P. Silva, J. Phys. Chem. C, 2010, 114, 15837.
- 28 (a) C. B. Zhang, F. D. Liu, Y. P. Zhai, H. Ariga, N. Yi, Y. C. Liu, K. Asakura, M. Flytzani-Stephanopoules and H. He, Angew. Chem., Int. Ed., 2012, 51, 9628; (b) B. Qiao, A. Wang, X. Yang, L. F. Allard, Z. Jiang, Y. Cui, J. Liu, J. Li and T. Zhang, Nat. Chem., 2011, 3, 634.

- 29 J. W. Jeong, B. Choi and M. T. Lim, *J. Ind. Eng. Chem.*, 2008, 14, 830.
- 30 A. S. Ivanova, E. M. Slavinskaya, R. V. Gulyaev, V. I. Zaikovskii, O. A. Stonkus, I. G. Danilova, L. M. Plyasova, I. A. Polukhina and A. I. Boronin, *Appl. Catal.*, *B*, 2010, **97**, 57.
- 31 *Handbook of X-ray Photoelectron Spectroscopy*, ed. J. F. Moulder, W. F. Stickle, P. E. Sobol, K. D. Bomben and J. Chastain,

Perkin-Elmer Inc., Physical Electronics Division, Eden Prairie, MN, 1992.

- 32 J. G. Yu, X. Y. Li, Z. H. Xu and W. Xiao, *Environ. Sci. Technol.*, 2013, 47, 9928.
- 33 J. Szlachetko, D. Ferri, V. Marchionni, A. Kambolis, O. V. Safonova, C. J. Milne, O. Kröcher, M. Nachtegaal and J. Sá, J. Am. Chem. Soc., 2013, 135, 19071.