Catalytic Hydrodechlorination of 1,2,4,5-Tetrachlorobenzene over Various Supports Loaded Palladium Catalysts

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Water pollution by polychlorinated aromatic hydrocarbons has always been a global issue. In this work, we reported a synthesis of supported palladium catalysts Pd/C, Pd/CeO₂, Pd/SBA-15, Pd/ZrO₂, Pd/SiO₂, and Pd/Al₂O₃ as well as their catalytic activities on hydrodechlorination (HDC) of 1,2,4,5-tetrachlorobenzene (TeCB). These Pd catalysts were characterized by Brunauer-Emmett-Teller (BET) specific surface area, Transmission electron microscopy (TEM), X-ray diffraction (XRD), energy Dispersive X-ray Fluorescence (EDXRF), CO-chemisorption, and H₂-temperature programmed reduction (H₂-TPR) analysis. Pd/C, Pd/CeO₂ and Pd/SBA-15 catalysts showed relatively high catalytic activities. The catalytic activities were associated with dispersion of Pd, metal surface area, and reaction temperature, etc.

Keywords: Supported Pd catalysts; Catalytic hydrodechlorination; 1,2,4,5-Tetrachlorobenzene.

INTRODUCTION

Polychlorinated aromatic hydrocarbons (PCAH) are considered as the hazardous pollutants due to their acute toxicity and high bioaccumulation potential.¹ With the ever-increasing concerns for environmental protection and human health, the safe disposal of PCAH has attracted much attention.^{2,3} Various methods such as incineration and thermal oxidation were carried out to degrade the PCAH. However, incomplete oxidation usually leads to the formation of more toxic species such as dioxins, phosgene and chlorine etc.⁴ In contrast, catalytic hydrodechlorination (HDC) may become a promising method, by which PCAH can be converted into various valuable products.⁵ Furthermore, this reaction can be effectively carried out at room temperature and atmospheric pressure. Catalytic HDC can be conducted in both liquid and vapor phase using noble metal (Pd,⁶⁻¹⁴ Pt,^{15,16} Ru,¹⁷ Rh^{18,19}) or non-noble metal (Ni,^{6,20} Ni-Mo,^{21,22} Fe^{23,24}) as catalysts. Among all Group VIII metal catalysts, Pd is considered as the most effective catalyst for liquid phase HDC since it can selectively replace the chlorine element of substrate with hydrogen.^{23,25} These metal catalysts for HDC are usually loaded on various supports including carbon,^{11,15,17} Al₂O₃,^{13,17,20} SiO₂,^{17,20} MgO, 20 ZrO₂, 7,17 and CeO₂, 14,17 etc. The catalytic activity of catalysts is significantly dependent on the nature of support, metal particle size, reaction media, and reaction conditions. Shao *et al.*⁷ compared the catalytic behavior of Pd/ZrO₂ for gas phase HDC of chlorobenzene (CB) and found that catalysts with high Pd specific surface area and surface hydroxyl group content in ZrO₂ support exhibited a higher initial activity and stability. Gómez-Quero *et al.*²⁶ investigated the effect of metal particle size on liquid-phase HDC of 2,4-dichlorophenol over Pd/Al₂O₃ catalysts and found smaller particles (< 5 nm) possessed a higher activity.

As a member of PCAH family, 1,2,4,5-tetrachlorobenzene (TeCB) is one of 31 priority chemicals targeted by the United States Environmental Protection Agency for waste reduction.²⁷ The potential hazard of TeCB for human being possibly stemmed from the damage on liver, kidney, and thyroid.²⁸ However, the HDC of TeCB by the supported Pd catalysts in liquid phase has been rarely studied. Wee²⁹ reported that the HDC of TeCB by Pd/Al₂O₃ in water-ethanol mixtures and TeCB was converted rapidly and quantitatively into benzene. The impact of Pd catalysts loaded on different type supports has seldom been addressed, which promotes us to study the effects of different supports loaded Pd catalysts on HDC of TeCB in liquid phase. In this work, we described the preparation of various supports loaded Pd catalysts Pd/C, Pd/CeO₂, Pd/SBA-15, Pd/ZrO₂, Pd/SiO₂, and Pd/Al₂O₃ and evaluated their cata-

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lytic activities on HDC of TeCB at room temperature (Scheme I). The experimental results implied that the catalytic HDC activity of Pd catalysts was significantly dependent on the metal surface area, metal dispersion, and reaction temperature, etc. The product distribution was also discussed.



Scheme I The illustration of HDC of TeCB by various



EXPERIMENTAL

General: ZrO₂, SBA-15, and activated carbon used as supports were obtained from Adamas. PdCl₂, cerium (III) nitrate, γ-Al₂O₃, and other traditional chemicals were purchased from Sinopharm Chemical Reagent Company. SiO2³⁰ and CeO2³¹ supports were prepared according to the previously described methods. N₂ adsorption-desorption isotherms were obtained on a Micromeritics ASAP 2020M+C adsorption apparatus. The Pd content in supported catalysts was determined by Energy Dispersive X-ray Fluorescence (EDXRF, Skyray, 4500H). Transmission electron microscopy (TEM) investigations were performed with an FEI Tecnai G2 20 microscope operated at 200 kV. Room temperature XRD patterns were collected using a Philips X'Pert PRO powder diffractometer using a copper long fine focus X-ray diffraction tube operating at 40 kV and 40 mA as X-ray source. The intensity data were obtained in the 2θ range from 10° to 80° with a scan rate of 0.1°/s. H₂-temperature-programmed reduction (H₂-TPR) was performed using a continuous-flow apparatus equipped with a thermal conductivity detector (TCD). CO-chemisorption measurements were carried out on Auto Chem 2910 (Micromeritics, USA) instrument. Catalytic HDC activity of Pd catalysts was evaluated by gas chromatograph (GC-9790, Fuli, MD) equipped with a flame ionization detector (FID), a PEG-20M capillary column (30 m \times 0.25 mm \times 0.5 μm), and N_2 as carrier gas. The initial oven temperature was set at 50 °C for 3 min, and then was raised with a gradient of 10 °C/min until 200 °C and was held for 5 min. The temperature of the FID and the injection was 250 °C.

Preparation of Pd catalysts: It was reported that catalysts with low Pd loading on supports (5-10%) preferred to gain high

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catalytic activities.³²⁻³⁴ Gopinath et al.³⁵ investigated the HDC reaction on supported Pd catalysts and found that catalyst with 1 wt% Pd was more active and stable compared with traditional 10 wt% Pd catalysts. Considering the above finding, we decided to utilize 3 wt% Pd loading on various supports in this study. The Pd catalysts were prepared through an impregnation-deposition method with y-Al₂O₃, CeO₂, ZrO₂, SiO₂, SBA-15, and activated carbon as different supports, respectively. Typically, the PdCl₂ (0.1 g) aqueous solution (5 mL) was added to a support suspension (2.0 g of support in 100 mL of deionized water) under stirring. The suspension pH value was adjusted to 8.5 by adding 1 M of NaHCO3 solution and was maintained for 1.5 h during precipitation. Then a formaldehyde aqueous solution (37 wt%, 20 mL) was added to reduce Pd from Pd(II) to Pd(0).³⁶ After the reaction, the filter cake was collected by filtration and washed with deionized water followed by ethanol to remove excess chloride ions and dried open to air overnight at 353 K to get 3 wt% Pd catalysts.

Surface area and pore volume: N_2 adsorption-desorption isotherms were obtained at 77 K after all samples were degassed under vacuum at 473 K for 3 h. BET surface areas were calculated from the linear part of the BET plot.

Transmission electron microscopy (TEM): The catalyst sample was dispersed in ethanol by ultrasonic vibration, deposited on a lacey-carbon/Cu grid. For estimation of particle size, at least more than 100 individual particles were counted for each catalyst. The mean metal particle size was calculated as the surface-area-weighted average size (\overline{d}) according to the following expression:

$$\overline{d} = \frac{\sum_{i} n_i d_i^3}{\sum_{i} n_i d_i^2}$$

where n_i is the number of particles of diameter d_i , and $\Sigma n_i > 100$. These data were reported at 95% confidence interval.

Temperature-programmed reduction (TPR): Typically, 0.1 g of the as-prepared Pd catalyst was pretreated at 523 K in N₂ (mass flow controlled at 50 mL/min) for 2 h prior to a TPR measurement. For TPR experiment, H_2/N_2 gas (v/v = 1:9) with the rate of 50 mL/min was used and the temperature was ramped from room temperature to 873 K at 10 K/min while the effluent gas was analyzed with a TCD.

Pulse CO chemisorption: Prior to adsorption measurements, 0.1 g of Pd catalyst was firstly reduced in a H_2 flow (50 mL/min) at 573 K for 2 h and subsequently gas flow was changed to pure He flow at 573 K for 1 h. Then the sample was cooled down to room temperature in He stream. Then CO uptake was determined by injecting pulses of 10% CO balanced He from a calibrated on-line sampling valve into the He stream passing through the Pd catalyst system. Palladium surface area, dispersion percentage, and Pd average particle size were calculated by assuming the stoichiometric factor (CO/Pd (S)) as 1. Adsorption was deemed to be complete after three successive runs showed similar peak areas.

Catalytic activity: The HDC reactions were carried out at 298 K. Typically, a suspension containing one certain supported Pd catalyst (0.1 g), TeCB (0.1 g), and 100 mL of methanol/water (v/v = 1:9) was stirred for 20 min to reach the adsorption equilibrium between TeCB and Pd catalyst surface, after that the reactor was purged with pure H₂ three times and the H₂ atmosphere in reactor was maintained at standard atmosphere pressure. Then the HDC reaction started counting and aliquots of sample were taken at different time intervals for GC analysis. Usually, the HDC reactions were quenched within 10 h.

RESULTS AND DISCUSSION

The characterization of supported Pd catalysts

All the as-prepared supported Pd catalysts were firstly characterized by XRD analysis. However, no evident difference was observed in the powder XRD patterns between Pd/support and corresponding support possibly due to the relatively low Pd loading (3 wt%). Through transmission electron microscopy, we determined the presence of Pd (Fig. 1) and calculated palladium particle size. In order to verify the existence of Pd in catalyst systems, we performed the Pd content analysis by EDXRF technique and obtained a Pd content range from 1.9 to 2.3 wt%. The Pd content in all catalyst systems was smaller than 3 wt% stated above, which could result from the inadequate adsorption in reaction process. Nevertheless, the successful Pd loading in various supported Pd systems was quite obvious. The different supports-loaded Pd catalysts were also characterized by Brunauer-Emmett-Teller (BET) surface area analysis, particle size determination, and CO-chemisorption analysis and the results were comprised in Table 1. The Pd dispersion calculated from CO-chemisorption us-



Fig. 1. TEM micrographs of Pd/C, Pd/CeO₂, and Pd/ SBA-15.

ing the following equation assuming the spherical particle exposed to the gas plane was also shown in Table 1.

The % Dispersion = (number of surface Pd atoms) / (total number of Pd atoms) \times 100%. The palladium metal areas were calculated from CO consumption using the relationship $S_{Pd} = (n_{co} \times N_A \times \delta) / (W \times P)$, where n_{co} is the CO consumption, N_A is avogadro constant, δ is the cross-sectional area of the Pd atom, i.e. 8.33 Å². One way the Pd particle size (d_1, nm) was calculated from the estimated metal surface area (S_{Pd}) according to³⁷ $d_1 = 60000 / (\rho \times S_{Pd})$, where ρ is the density of Pd metal, i.e. 12.02 g·cm⁻³, another method the Pd particle size (d_2, nm) was calculated by TEM measurements. The results shown in Table 1 indicated that Pd/C, Pd/CeO₂, and Pd/SBA-15 Pd catalysts exhibited the high Pd dispersion (over 44%) suggesting a homogeneous distribution of active component on the corresponding supports compared with other catalyst systems. Generally, Pd dispersion decreased with the increase in particle size,¹¹ which was in good accord with the observation in present study. The higher CO-uptake values for Pd/C, Pd/CeO₂, and Pd/SBA-15 suggested that Pd particles were dispersed well on the corresponding support.

Temperature programmed reduction (TPR) was performed to provide necessary information about the nature of reduced Pd species in various supported Pd catalysts (Fig. 2). For all supported Pd catalyst systems, the absence of the negative peak in temperature range from 323 to 348 K implied the absence of β -PdH, which was usually formed in the presence of larger Pd particles.³⁸ This observation indicated the existence of smaller Pd particles in our catalyst systems (< 6 nm). All supported Pd catalysts exhibited a similar positive reduction peak at 378~385 K, which could be attributed to the reduction of support-inter-



Fig. 2. TPR profiles of various supported Pd catalysts.

Catalysts	Actual Pd loading (wt%)	BET Surface area (m ² /g)	CO uptake (µmol/g)	Dispersion (%)	$S_{\mathrm{Pd}} \left(\mathrm{m}^{2 \bullet} \mathrm{g}^{-1}\right)$	Particle size (nm)		$TOF \times 10^{-5}$	$S_{Pd} \bullet TOF \times$
						d_1^{a}	d_2^{b}	(s ⁻¹)	$10 (m \cdot g \cdot s^{-1})$
Pd/C	2.3	619.6	129	59.7	2813.6	1.8	2.2	1.7	4.8
Pd/SBA-15	2.0	421.2	103	54.8	224.6	2.2	2.5	1.9	4.2
Pd/CeO ₂	2.3	82.2	97	44.9	211.5	2.4	2.6	2.2	4.6
Pd/SiO ₂	1.9	439.3	75	42.0	163.5	3.1	3.6	2.3	3.7
Pd/ZrO ₂	2.3	23.2	60	27.8	130.8	3.8	4.0	2.5	3.2
Pd/Al_2O_3	2.0	129.4	42	22.3	91.6	5.5	5.9	3.0	2.7

Table 1. Physico-chemical properties of various supported Pd catalysts

^a d_1 : Particle size measured by CO chemsiorption. ^b d_2 : Particle size calculated by TEM measurements.

acted PdO species.³⁹ As for Pd/C and Pd/CeO₂, a broad reduction peak in high temperature range (> 600 K) was observed. It is rarely reported that PdO_x cannot be reduced at a temperature as high as 750 K. Thus, the peaks of Pd/CeO₂ at about 750 K could be associated with the partial reduction of CeO₂ support, while the high temperature reduction peaks of Pd/C might be related to the reduction of some PdCl₂ or Pd(OH)Cl that were not fully reduced by formaldehyde or not washed away during preparation.

Catalytic activity

The catalytic activity of the supported Pd catalysts was investigated by the HDC of TeCB at 298 K. The products in all HDC reactions included main product benzene together with a small amount of chlorobenzene (CB), dichlorobenzene (DCB), and trichlorobenzene (TCB) as determined by GC analysis. Fig. 3 showed the continuous concentration change of TeCB against reaction time over supported Pd catalysts. Initially, all Pd catalysts exhibited an appreciable catalytic activity. However, with the extension of reaction time, the catalytic activities of different Pd



Fig. 3. Activity profiles of various supported Pd catalysts.

of TeCB was converted in the initial 2.5 h. In the subsequent 7.5 h of reaction, TeCB was continuously degraded and the final concentration was less than 5%. Pd/SBA-15 and Pd/CeO₂ exhibited the similar catalytic behavior to Pd/C but with lower catalytic activities. The residual TeCB concentrations in these two cases were 16% and 9% after 10 h of reaction, respectively. Pd/SiO₂, Pd/Al₂O₃, and Pd/ ZrO₂ showed the worse catalytic activities and more than 40% of substrate was still remained even after 10h. In general, Pd/C, Pd/CeO₂, and Pd/SBA-15 catalysts exhibited relatively high catalytic HDC activities, which could be attributed to the high Pd dispersion (44.9-59.7%) and high metal surface area (211.5-281.3 m^2/g) that could provide more active sites for substrate accessibility. While the relatively low catalytic HDC activities exhibited over Pd/SiO₂, Pd/Al₂O₃, and Pd/ZrO₂ could be due to the low Pd dispersion and low Pd surface area (Table 1). On the other hand, as shown in Fig. 3, the gradually declined TeCB concentration lines were indicative of the catalyst deactivation during HDC process. The reaction solution (Pd/C as catalyst) pH is 6.25 before the experiment and down to 1.82. The deactivation of Pd catalysts generally originated from HCl formed during reaction, which increased the acidity of the catalysts and leaded to the poisoning of catalysts. Some authors have reported that C and SBA-15, as supports compared to other supports (SiO₂, ZrO₂, Al₂O₃) owing to their high surface area and pore size distribution which can absorb the formed HCl, show resistance to severe deactivation.¹⁷ In a word, the overall catalytic properties of various supported Pd catalysts in present study were greatly dependent on Pd metal dispersion, metal surface area, and the deactivation, where as independence with the property of supports.

catalysts decreased in different extent. Pd/C catalyst exhib-

ited the best catalytic performance, for example, over 70%

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To better understand the nature of the activity of the catalyst active sites, the TeCB HDC activity of the reaction was expressed in terms of turn-over frequency (TOF) which is defined as the number of TeCB molecules degraded per atom of exposed palladium on the surface per unit time. The results in Fig. 3 showed that the reactant conversion is more than 50% after 5h of reaction. To appropriately compare the activity of the active sites of different catalysts in the kinetic region, the TOFs were calculated on the basis of formed TeCB after 15 min of reaction (the data during the initial 15 min), and the results are listed in Table 1.

Fig. 4 showed the relationship between TOF and the mean particle size of Pd (d_1) calculated from CO-chemisorption. The results show that the TOF value increases with an increase in d_1 , that is to say, the larger Pd particles possess higher initial catalytic activities for the title reaction because the smaller Pd particles exhibit stronger interaction with support. This situation has been found in the Pd/SiO₂/AlPO₄, Pd/ZrO₂ and Pd/MgO catalyst for bromobenzene HDC to benzene³² and indicates also the structure-sensitive catalytic hydrogenation character of the title reaction. The similar phenomenon was also observed in the previous report.¹⁷

TOF against the metallic Pd surface area (S_{Pd}) was plotted in Fig. 5. The results show that TOF of TeCB decrease with an increase in S_{Pd} , which indicates a decrease in utilization of individual Pd atoms. This result suggests that the activity of the catalyst is not only related to S_{Pd} but also to other causes. JOURNAL OF THE CHINESE CHEMICAL SOCIETY

Herein, the Pd/C catalyst is the most efficient for the TeCB HDC, but its TOF is only 1.7×10^{-5} . This is because the activity of the Pd catalyst is not only related to the catalytic activity of the individual Pd atoms (TOF) but also to the total number of Pd atoms on the catalyst surface, namely, the surface area of Pd⁰ (S_{Pd}) on the catalyst. The larger the S_{Pd} is, the greater the number of active sites on the catalyst surface is. If the S_{Pd} ·TOF values of catalysts were compared, we found that S_{Pd} ·TOF of the Pd/C catalyst is the largest (4.8×10^{-3} m² s⁻¹ g⁻¹) among all of the Pd catalysts (Table 1).

Effect of temperature and kinetic analysis

In order to investigate the effect of reaction temperature on the HDC of TeCB, we performed the HDC reaction catalyzed by Pd/C at 293, 303, 313, and 323 K respectively, and the result was illustrated by plotting the conversion of TeCB against reaction time (Fig. 6). Under the four different temperature conditions, benzene was always formed as the major product together with a small amount of CB, DCB, and TCB as by-products. Repeated experiments gave the similar results showing the considerable reproducibility. For all cases, TeCB conversion always went up with time extension but the growing rate of conversion decreased with the prolonging of reaction time. Generally, increasing temperature is beneficial for chemical reactions. The catalytic HDC of TeCB in the present study was in accord with this rule. As for the reaction temperature we studied, high temperature always provided the higher TeCB conversion than those obtained at lower temperature under the same reaction conditions. By plotting $\ln(c_0/c)$ against



Fig. 4. The relationship between particle size and TOF for TeCB HDC over various supported Pd catalysts.





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Temperature (K)	The first order reaction rate equation	$k(h^{-1})$	R ²
293	$\ln(c_0/c) = 0.9469t + 0.0083$	0.9469	0.9937
303	$\ln(c_0/c) = 1.9973t + 0.0133$	1.9973	0.9928
313	$\ln(c_0/c) = 2.7595t - 0.3407$	2.7595	0.9904
323	$\ln(c_0/c) = 3.5694t - 0.7940$	3.5694	0.9920

Table 2. Rate constants (*k*) values for HDC of TeCB at different reaction temperatures

reaction time (t), we got a straight line showing a first order feature for the catalytic HDC of TeCB, which was similar to the previous result.²⁹ From the lines in Fig. 6 and $\ln(c_0/c) = kt$, we had calculated the values of rate constant *k* that were listed in Table 2. With higher reaction temperature, *k* corresponded to a larger value showing the dependence of reaction rate on reaction temperature. From Arrhenius equation, the overall apparent activation energy in the range 293-323 K was estimated to be 34.1 kJ/ mol.

Product distribution and possible reaction path

Fig. 7a shows the product distribution obtained by Pd/C catalyst at 303 K as a function of reaction time. As expected, benzene, the main product, appeared at the beginning of the reaction and its yield increased linearly with time, showing that benzene was considerably stable and could not be further degraded under the reaction conditions. Other products including CB, *p*-DCB, and *o*-DCB were always present in the reaction mixture and their yields gradually increased but their contents were relatively low (< 6%). For TCB, it appeared from the beginning of the reaction, but its yield passed through a maximum at 1.5 h of



Fig. 6. Temporal TeCB conversion profiles at 293, 303, 313, and 323 K using Pd/C as catalyst.





Fig. 7. Product yields of TeCB (a) and TCB (b) as a function of time at 303 K using Pd/C as catalyst. On the left: benzene. On the right: CB, *p*-DCB, *o*-DCB, and TCB (TCB was only present in Fig. 7a).

reaction time and then declined near to zero. This phenomenon implied that TCB would be a reaction intermediate, which was further converted into other products in later stage. A similar product distribution profile as Fig. 7a was also obtained at other studied temperatures. In order to determine whether TCB was the intermediate, we studied the reactivity of TCB under the same conditions (Fig. 7b). The result indicated that TCB was an intermediate in HDC of TeCB because of the quantitative conversion to benzene. Interestingly, the possible products such as *m*-DCB, cyclohexane, or chlorocyclohexane were not monitored throughout our experiments using TeCB or TCB as substrates. The possible reasons could be ascribed to the inductive and steric effects.⁴⁰ The similar phenomenon was also observed in previous report.⁴¹ Based on the above results, we supposed the possible main reaction path of HDC of TeCB (Scheme II).

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Scheme II The possible main reaction path of HDC of TeCB by Pd catalysts in this study



CONCLUSIONS

In this work, we investigated the catalytic activities of SiO_2 , γ -Al₂O₃, CeO₂, activated carbon, ZrO₂, and SBA-15 supported Pd catalysts for HDC of TeCB and found that different supports loaded Pd catalysts exhibited different catalytic HDC activities. Without consideration of support properties, the overall catalytic HDC activities of various supported Pd catalysts were greatly dependent on metal dispersion, metal surface area, metal particle size, and reaction temperature.

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REFERENCES

- Čvančarová, M.; Křesinová, Z.; Cajthaml, T. J. Hazard. Mater. 2013, 254, 116.
- 2. Morra, M. J.; Borek, V.; Koolpe, J. J. Environ. Qual. 2000, 29, 706.
- Alonso, F.; Beletskaya, I. P.; Yus, M. Chem. Rev. 2002, 102, 4009.
- Erickson, M. D.; Swanson, S. E.; Flora, J. J. D.; Hinshaw, G. D. *Environ. Sci. Tech.* **1989**, *23*, 462.
- Gaddalla, M. A.; Sommer, M. E. Chem. Eng. Sci. 1989, 44, 2825.
- Amorim, C.; Wang, X.; Keane, M. A. Chin. J. Catal. 2011, 32, 746.
- Shao, Y.; Xu, Z. Y.; Wan, H. Q.; Chen, H.; Liu, F. L.; Li, L. Y.; Zheng, S. R. J. Hazard. Mater. 2010, 179, 135.
- Kawabata, T.; Atake, I.; Ohishi, Y.; Shishido, T.; Tian, Y.; Takaki, K.; Takehira, K. *Appl. Catal. B.* **2006**, *66*, 151.
- Meng, B. C.; Sun, Z. Y.; Ma, J. P.; Cao, G. P.; Yuan, W. K. Catal. Lett. 2010, 138, 68.
- 10. Nakao, R.; Rhee, H.; Uozumi, Y. Org. Lett. 2005, 7, 163.
- Calvo, L.; Gilarranz, M. A.; Casas, J. A.; Mohedano, A. F.; Rodríguez, J. J. Appl. Catal. B. 2006, 67, 68.

- 12. Hildebrand, H.; Mackenzie, K.; Kopinke, F. D. *Environ. Sci. Tech.* **2009**, *43*, 3254.
- Kumar, J. V.; Lingaiah, N.; Babu, N. S.; Kumar, V. P.; Prasad, P. S. *Catal. Lett.* **2009**, *132*, 109.
- Gopinatha, R.; Lingaiaha, N.; Sreedhar, B. *Appl. Catal. B.* 2003, 46, 587.
- Yoneda, T.; Takido, T.; Konuma, K. J. Mol. Catal. 2007, 265, 80.
- Bonarowska, M.; Kaszkur, Z.; Kępiński, L.; Karpiński, Z. *Appl. Catal. B.* 2010, 99, 248.
- Srikanth, C. S.; Kumar, V. P.; Viswanadham, B.; Chary, K. V. R. *Catal. Commun.* **2011**, *13*, 69.
- Benítez, J. L.; Angel, G. D. Ind. Eng. Chem. Res. 2010, 50, 2678.
- Diaz, E.; Mohedano, A. F.; Casas, J. A.; Calvo, L.; Giarranz, M. A.; Rodriguez, J. J. *Appl. Catal. B.* **2011**, *106*, 469.
- 20. Keane, M. A.; Larsson, R. Catal. Commun. 2008, 9, 333.
- 21. Gryglewicz, S.; Piechocki, W. Chemosphere 2011, 83, 334.
- Gryglewicz, G.; Stolarski, M.; Gryglewicz, S.; Gryglewics, S.; Klijanienko, A.; Piechocki, W.; Hoste, S.; Driessche, I. V.; Carleer, R.; Yperman, J. *Chemosphere* 2006, *62*, 135.
- 23. Munoz, M.; de Pedro, Z. M.; Casas, J. A.; Rodriguez, J. J. *Water. Res.* **2013**, *47*, 3070.
- 24. Aristov, N.; Habekost, A. Chemosphere 2010, 80, 113.
- 25. Coq, B.; Ferrat, G.; Figueras, F. J. Catal. 1986, 101, 434.
- Gómez-Quero, S.; Cárdenas-Lizana, F.; Keane, M. A. Ind. Eng. Chem. Res. 2008, 47, 6841.
- U.S. Environmental Protection Agency. *Priority Chemicals* and Fact Sheets; http://www.epa.gov/epaoswer/hazwaste/ minimize/chemlist.htm (Accessed August 2010).
- den Besten, C.; Vet, J. J. R. M.; Besselink, H. T.; Kiel, G. S.; Berkel, B. J. M.; Beens, R.; Bladeren, P. J. *Toxicol. Appl. Pharm.* 1991, *111*, 69.
- 29. Wee, H. Y.; Cunningham, J. A. J. Hazard. Mater. 2008, 155, 1.
- Shen, S. D.; Gu, T.; Mao, D. S.; Xiao, X. Z.; Yuan, P.; Yu, M. H.; Xia, L. Y. *Chem. Mater.* 2011, 24, 230.
- 31. Feng, T.; Wang, X.; Feng, G. Mater. Lett. 2013, 100. 36.
- 32. Aramendía, M. A.; Boráu, V.; García, I. M.; Jiménez, C.; Lafont, F.; Marinas, A.; Marinas, J. M.; Urbano, F. J. J. *Catal.* **1999**, *187*, 392.
- Gopinath, R.; Lingaiah, N.; Suryanarayana, I.; Sai Prasad, P. S. React. *Kinet. Catal. Lett.* 2003, 79, 61.
- Berry, F. J.; Smart, L. E.; Sai Prasad, P. S.; Lingaiah, N.; Rao, P. K. *Appl. Catal. A.* 2000, 204, 191.
- 35. Gopinath, R.; Babu, N. S.; Kumar, J. V.; Lingaiah, N.; Prasad, P. S. S. *Catal. Lett.* **2008**, *120*, 312.
- Jin, Z. H.; Li, D.; Wang, X. Y.; Lu, G. Z. Chin. J. Chem. 2010, 28, 16.
- 37. Anderson, J. R. Structure and Metallic Catalysis; Academic

www.jccs.wiley-vch.de 123

- 38. Chang, T. C.; Chen, J. J.; Yeh, C. T. J. Catal. 1985, 96, 51.
- 39. Babu, N. S.; Lingaiah, N.; Gopinath, R.; Reddy, P. S. S.; Prasad, P. S. S. J. Phys. Chem. C 2007, 111, 6447.
- 40. Coq, B.; Figueras, F.; Bodnariuk, P.; Cossio, F.; Bermudez, O.; del Angel, G. In *Proceedings of the XI Symposium*;

Gomez, R., Ed.; Iberoamericano de Catalisis Guanajuato Mexico, 1988; p 1145.

 Meshesha, B. T.; Chimentão, R. J.; Medina, F.; Sueiras, J. E.; Cesteros, Y.; Salagre, P.; Figueras, F. *Appl. Catal. B* 2009, 87, 70.