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Synthesis of three crystalline forms of Al_2O_3 featuring rod-like fibers and their effect on the gaseous degradation of 1-chloronaphthalene†

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Three crystalline forms of Al_2O_3 featuring rod-like fibers are synthesized, to perform the gaseous degradation of 1-chloronaphthalene (CN-1), a model compound. The degradation efficiency (DE) decreases as follows: micro/nano- γ - Al_2O_3 > micro/nano- η - Al_2O_3 > regular α - Al_2O_3 . The high DE of 92.2% attained over γ - Al_2O_3 is attributed to its specific defective spinel structure, resulting in its large surface area and pore volume, large amounts of surface-adsorbed oxygen species, and Brønsted and Lewis acid sites. The degradation products, naphthalene and 1,4/1,6-dichloronaphthalene (DiCN), with yield ratios of 7.3–13.3, are detected, indicating the occurrence of hydrodechlorination and side chlorination reactions. 1,6-DiCN is believed to be the most favored DiCN isomer product based on the calculated ΔH_r and ΔG_r . However, the percentage values of intermediates formed via these two reactions, in the degradation of CN-1, are 9.1%, 4.5% and 4.4%, over α -, η - and γ - Al_2O_3 , respectively. The oxidative degradation pathway possibly dominantly occurs especially over micro/nano- γ - Al_2O_3 with oxidative species such as O_2^- , O^- and O^{2-} , following the Mars–van Krevelen mechanism. Oxidation intermediates containing $-\text{CH}_2-$, $-\text{CH}_3$, and $\text{C}-\text{O}$ groups are produced, which can be subsequently oxidized to low-molecular-weight products, such as formic, acetic and propanoic acids, and eventually completely oxidized to CO_2 .

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Environmental significance

The unintentional emissions from industrial thermal processes are important sources of PCNs in the gaseous phase, thus it is of environmental significance to develop elaborate cleaning measures to lower their levels. The crystal form of a material influences its catalytic performance greatly while reports on the effects of different structures of Al_2O_3 on newly listed PCNs are particularly scarce. In this study, three crystalline forms of Al_2O_3 (α -, η -, and γ - Al_2O_3) featuring rod-like fibers are synthesized to degrade gaseous 1-chloronaphthalene (CN-1). Among the three crystal forms, γ - Al_2O_3 possesses a defective spinel structure with vacancies at cation positions, resulting in better efficiencies towards CN-1 degradation. The oxidative degradation pathway possibly dominantly occurs especially over γ - Al_2O_3 , and the related degradation mechanism is explored based on the detection of a series of oxidative intermediates. The present work provides a promising method to reduce the emission of PCNs.

1. Introduction

Polychlorinated naphthalenes (PCNs) are a new class of persistent organic pollutants listed in the Stockholm Convention in 2015, and characteristically have two fused benzene rings featuring one to eight chlorine substituents.¹ The Conference of the Parties listed and specified related control measures

for PCNs in Annexes A and C of the Stockholm Convention.² PCNs are highly toxic, with toxic equivalents at 5.88 pg g^{-1} lipid higher than those of polychlorinated dibenzo-*p*-dioxins at 5.22 pg g^{-1} lipid in human sera from Korea.³ The manufacture and use of technical PCN formulations have almost ceased globally. However, unintentional emissions of PCNs from industrial thermal processes are expected to become an important source of PCNs. The International Programme on Chemical Safety considered waste incineration and disposal of PCN-containing items as the major current sources of PCN release into the environment.⁴ PCN emissions have also been reported from other industrial thermal processes such as the ore sintering industry at 3–983 pg m^{-3} and secondary nonferrous aluminum smelting industry at 59.5–635 ng m^{-3} .^{5,6} These industrial processes have also been recognized as

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important sources of PCNs in the gaseous phase. Therefore, it is essential to develop elaborate cleaning measures to lower the levels of gaseous PCNs. However, progress in this particular area is relatively poor.

Compared with adsorption, catalytic destruction is more effective and advantageous as it allows complete decomposition of hazardous organics.^{7–11} As reported, Co_3O_4 – CeO_2 composite oxide showed superior performance in the degradation of 1,2,4-trichlorobenzene (1,2,4-TrCB).⁷ A high level of degradation activity for decachlorobiphenyl (CB-209) and hexachlorobenzene (HCB) was achieved over as-prepared Fe_3O_4 micro/nano-material.^{12,13} Furthermore, Yang *et al.* showed that high degradation efficiencies for 2,2',4,4'-tetrabromodiphenyl ether of above 92% could be attained over Fe–Al composite oxides prepared with different urea dosages.¹⁴ Jia *et al.* reported a HCB degradation efficiency of 99.9% over a Fe_xO_y – CeO_2 composite at 300 °C.¹⁰

It is known that the crystal form of a material, which relates to the physical and chemical properties of the material, influences the catalytic performance of the material.^{15,16} For instance, as reported, the amount of 1,2-epoxydecane formed by the photocatalyzed epoxidation of 1-decene in the presence of hydrogen peroxide over rutile was 13.3 μmol , which was higher than that over anatase (2.5 μmol).¹⁷ MnO_2 nano-rods, featuring different crystal phases, *i.e.*, α -, β -, γ -, and δ -phases, displayed different catalytic performances toward CO oxidation, which decreased in the order of α - $\approx$ δ - > γ - > β - MnO_2 .¹⁸ Al_2O_3 has three main crystalline forms, namely, α - Al_2O_3 , η - Al_2O_3 and γ - Al_2O_3 . Among them, corundum α - Al_2O_3 , which features a hexagonal close-packed structure, is the most thermodynamically stable form.¹⁹ In contrast, spinel η - and γ - Al_2O_3 belong to the transition aluminas and have a cubic structure.²⁰ Previous research studies have pointed out that Al_2O_3 has important applications as a catalyst and/or a high-surface catalyst support for eliminating organic pollutants.^{14,21,22} However, reports on the effects of different crystal forms of Al_2O_3 on the catalytic activity of newly listed PCNs are particularly scarce. Investigating the relationship between the different crystalline forms of Al_2O_3 and the catalytic activity toward PCN degradation is important to clarify the factors influencing the catalytic properties of Al_2O_3 and elucidate the degradation mechanism.

Recently, a wealth of methods including coprecipitation,⁷ sol-gel,²³ solid-state chemical reaction,²⁴ template-assisted,²⁵ electrodeposition,²⁶ and hydrothermal treatment have been developed for controlled synthesis of micro/nano-materials.^{27,28} In particular, hydrothermal synthesis is a powerful technique to prepare micro/nano-materials with different crystalline forms. Zhang *et al.* reported that several manganese oxides with different crystalline forms, such as δ - MnO_2 nanosheets, γ - MnO_2 microspheres and β - MnO_2 distinct rods, were controllably synthesized from the same precursor Na-BirMO *via* a facile, direct hydrothermal method.²⁸ Therefore, with an appropriate choice of the temperature, time, and reactants for the hydrothermal process, the desired micro/nano-crystalline forms can be controllably synthesized.

In this study, three crystalline forms of Al_2O_3 (α -, η -, and γ - Al_2O_3) featuring rod-like fibers were prepared using a simple and cost-effective hydrothermal process. The catalytic degradation of 1-chloronaphthalene (CN-1) as a model compound over the Al_2O_3 samples at 300 °C was investigated on a pulsed-flow microreactor with a fixed bed quartz-tube reactor. The effect of the crystalline structure on the CN-1 degradation efficiencies was addressed based on the surface area and pore volume, surface-adsorbed oxygen species, and Brønsted and Lewis acid sites. The degradation products were identified by gas chromatography-mass spectrometry (GC-MS), ion chromatography (IC) and *in situ* Fourier transform infrared spectroscopy (FTIR). Based on these determined products, the related degradation mechanism was explored in combination with the crystal physical properties.

2. Experimental

2.1 Materials

Naphthalene, CN-1, 2-chloronaphthalene, 1,2-dichloronaphthalene (1,2-DiCN), 1,4-DiCN, 1,5-DiCN, 1,6-DiCN and 1,8-DiCN were purchased from Supelco Inc. (Bellefonte, PA, USA). These standards were mixed together for identification of the degradation products. Pesticide-grade hexane was purchased from Dika Technologies (Lake Forest, CA, USA). Other chemicals were purchased from Beijing Chemical Co. (Beijing, China).

2.2 Catalyst preparation

Three crystalline Al_2O_3 samples, *i.e.*, α -, η -, and γ - Al_2O_3 , were prepared using the same hydrothermal method. Poly(ethylene glycol) (PEG; 16 g, $M_n = 20\,000$) was dissolved in distilled water (35 mL). $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (8 g) was added to the PEG solution, and urea (20 g) was added to the mixed solution. The solution system was stirred magnetically to form a homogeneous solution and then transferred to a Teflon-lined stainless steel autoclave (100 mL). The autoclave was heated in an oven at 120 °C for 24 h. The product was collected, washed, filtered, and dried at 80 °C under vacuum for 8 h to obtain the catalyst precursor. The precursor was then calcined in air at 1100 °C for 5 h, 1100 °C for 3 h and 900 °C for 3 h, to obtain α - Al_2O_3 , η - Al_2O_3 and γ - Al_2O_3 , respectively.

2.3 Characterization

X-ray diffraction (XRD, Rigaku, Tokyo, Japan) patterns of the samples were scanned on a Rigaku D/max 2500 diffractometer using Cu K α radiation ($\lambda = 0.154056$ nm, 40 kV, 200 mA). Field-emission scanning electron microscopy (FE-SEM) images were obtained on an SU-8020 scanning electron microscope (Zeiss Supra 55, Zeiss, Oberkochen, Germany). The samples for FE-SEM were prepared by depositing the powder sample on conductive tape using N_2 vertical purging. High-resolution transmission electron microscopy (HRTEM, JEM-2100, JEOL, Tokyo, Japan) images were obtained using a TECNAI G2 F20 microscope, operating at 200 kV. For

analysis, the sample was dispersed in ethanol, treated ultrasonically for 5 min, and deposited on a copper grid coated with a preformed holey carbon film. N₂ adsorption-desorption isotherms were obtained at 77 K using a Quantachrome NOVA 2000e sorption analyser (Quadrastorb SI-MP, Quantachrome, Boynton Beach, FL, USA); the samples were degassed at 200 °C for 6 h before measurements were performed. The specific surface areas of the samples were obtained using the multipoint Brunauer-Emmett-Teller (BET) procedure. The pore size distribution of the samples was determined from the desorption branch of the N₂ adsorption-desorption isotherms using the Barrett-Joyner-Halenda method. X-ray photoelectron spectroscopy (XPS, VG Instruments Group Ltd., UK) was performed using an AXIS Ultra system equipped with Al K α radiation ($h\nu = 1486.6$ eV) and an anode operating at 200 W and 15 kV. The binding energy values were calibrated using the C 1s peak (284.8 eV). The surface relative compositions were estimated from the integrated intensities corrected with atomic sensitivity factors.

The Brønsted and Lewis acid sites of the catalysts were investigated using FTIR spectroscopy (Varian 3100, Varian Inc., Palo Alto, CA) with ammonia as a probe molecule. The spectra were recorded using a Bruker Equinox 55 spectrometer at a resolution of 4 cm⁻¹ (average of 50 scans). Using a Harrick Scientific "Praying Mantis" diffuse-reflectance infrared Fourier transform spectroscopy cell, *in situ* recording of the spectra at ambient temperature and at higher temperatures were conducted. The cell was equipped with a heater and connected to a gas flow system. The temperature was monitored using a thermocouple placed in direct contact with the sample. Powder samples (~20 mg) were loaded into the diffuse-reflectance infrared Fourier transform spectroscopy cell for the FTIR spectroscopic studies. A KBr spectrum was used as a background reference. Before surface characterization was performed, the samples were activated by heating at 673 K for 30 min, cooled to room temperature, and saturated with ammonia (500 ppm, Airgas) for 60 min. The gas flow was then switched to N₂ (40 mL min⁻¹) for 30 min to remove physically adsorbed ammonia, and the spectrum was monitored until no change was observed (~30 min). The samples were then heated in a N₂ flow (40 mL min⁻¹) at 673 K for 60 min to remove chemically adsorbed ammonia.

2.4 Activity measurements and product analysis

The degradation experiments were performed using a pulsed flow microreactor (Fig. S1†). Activity tests on the prepared catalysts were performed in a fixed bed quartz-tube reactor. Typically, the catalyst (50 mg) was introduced into the reactor, and a mixture of 10 vol% O₂ with balance N₂ was fed into the reactor system using mass flow controllers set at a total flow rate of 80 mL min⁻¹. After a balance of the mixed gaseous reactants and a reaction temperature of 300 °C were attained, CN-1 (0.5 μ L, 3684.6 nmol) was spiked in the quartz

tube and evaporated promptly. Vapors of CN-1 and the mixed carrier gas were allowed to react with the catalyst for 30 min at the predetermined temperature. Al₂O₃ has an average density of ~4 g cm⁻³. Therefore, 50 mg of catalyst powder corresponds to a gas hourly space velocity of 384 000 h⁻¹. All experiments were performed in triplicate to ensure reproducibility of the results.

After the degradation experiments, residual CN-1 and other products were extracted ultrasonically with hexane. The quartz tube was rinsed with hexane, and the rinsing solutions were combined with hexane in a wash bottle. The residual CN-1 and other products were analyzed using an Agilent 6890 gas chromatograph equipped with a DB-5MS capillary column (30 m $\times$ 0.25 mm internal diameter; 0.25 μ m film thickness) and a mass-selective detector (Agilent 5973N). The qualitative analysis was based on the *m/z* values of the ions detected by mass spectrometry, as well as the retention times of the available standards, and quantitative analyses were performed in selected ion-monitoring mode using the two most abundant ions of the molecular ion clusters (Table S1†). Helium ($\geq 99.999\%$) passed through the column as the carrier gas at a flow rate of 1 mL min⁻¹. The injector was set at 260 °C. The column temperature was initially set at 75 °C for 2 min, then gradually increased to 150 °C at 20 °C min⁻¹, and to 205 °C at 1.5 °C min⁻¹, and finally to 270 °C at 2.5 °C min⁻¹. The diluted sample (1.0 μ L) was injected in splitless mode. An electron ionization system with an ionization energy of 70 eV was used.

For the detection of other intermediates, the surface reaction products of CN-1 over the catalyst were determined using a Varian 3100 *in situ* FTIR spectrometer equipped with a liquid N₂-cooled mercury-cadmium-telluride detector. The analysis of organic acids formed during the reaction between CN-1 and γ -Al₂O₃ at 300 °C was undertaken by ion chromatography (IC). The degradation product samples obtained from the reaction of CN-1 (0.5 μ L, 3684.6 nmol) and γ -Al₂O₃ (50 mg) were extracted three times with 15 mL deionized water for 10 min each time under ultrasonication. The combined extracts were then filtered through a 0.45 μ m mesh membrane for IC measurement. The analysis was conducted using a Dionex AS 5000 column equipped with an AS-AP automated sampler. A Dionex AS11-HC guard column (50 mm $\times$ 4 mm i.d.) and a Dionex AS11-HC analytical column (250 mm $\times$ 4 mm i.d.) were used. The analysis was performed at 30 °C, using potassium hydroxide generated from an online Dionex EG as the eluent, with a linear gradient and at a flow rate of 1.0 mL min⁻¹. The produced organic acid products were identified from their retention times compared with available individual organic acid standards.

2.5 Theoretical calculation

All the theoretical calculations were carried out with the software package Gaussian 09.²⁹ Molecular geometries were optimized using the density functional theory method MPWB1K/6-31+G(d,p),^{30,31} and the vibrational frequency was used to

calculate the thermodynamic parameters of geometries. The isodesmic reaction was designed to calculate the thermodynamics of PCNs.^{32,33}

3. Results and discussion

3.1 Catalyst characterization

Three types of Al_2O_3 with different crystal structures were obtained by varying the precursor calcination conditions during synthesis. The crystal structures of the samples were identified using XRD and the patterns are shown in Fig. 1a. The diffraction peaks of the three crystalline forms of Al_2O_3 could be well indexed to $\alpha\text{-Al}_2\text{O}_3$ (JCPDS 01-075-1864), $\eta\text{-Al}_2\text{O}_3$ (JCPDS 01-077-0396), and $\gamma\text{-Al}_2\text{O}_3$ (JCPDS 00-050-0741). Employing calcination conditions of 1100 °C and 5 h led to the formation of $\alpha\text{-Al}_2\text{O}_3$. The corresponding XRD pattern featured sharp and well-resolved peaks. When the calcination time was set at 3 h, $\eta\text{-Al}_2\text{O}_3$ was formed and the associated XRD pattern featured broader peaks, with a reduced degree of resolution, indicating a high degree of structural disorder in the Al_2O_3 sample.²⁰ Further, when the calcination temperature was also changed to 900 °C, $\gamma\text{-Al}_2\text{O}_3$ was obtained. The associated XRD pattern featured peaks with a slightly lower degree of resolution when compared with those of $\eta\text{-Al}_2\text{O}_3$. These results indicate that $\alpha\text{-Al}_2\text{O}_3$ had the highest crystallinity, followed by $\eta\text{-Al}_2\text{O}_3$ and $\gamma\text{-Al}_2\text{O}_3$. A positive correlation between crystallite size and XRD peak intensity has previously been reported in the preparation of iron-based spinels.¹² The different crystal forms of Al_2O_3 possess different unit cell properties, as shown in Fig. 1b. $\alpha\text{-Al}_2\text{O}_3$ has a hexagonal close-packed structure, which is usually described as a hexagonal close packing of O atoms, with Al occupying two thirds of the octahedral interstices.^{34,35} In contrast, η - and $\gamma\text{-Al}_2\text{O}_3$ feature similar unit cell properties, with a face-centered cubic

structure.²⁰ In this structure, the oxygen ions form a cubic close-packed sublattice, and the aluminum ions partially occupy both octahedral and tetrahedral sites.^{20,36} Furthermore, η - and $\gamma\text{-Al}_2\text{O}_3$ are more appropriately described as having a defective spinel structure,²⁰ which may result in their structural disorder and lower crystallinity. However, the bulk structures of γ - and $\eta\text{-Al}_2\text{O}_3$ differ primarily in the distribution of the cations over the two sublattices.³⁷ John and Hays reported $75 \pm 4\%$ Al-coordinated O_h in $\gamma\text{-Al}_2\text{O}_3$ (wherein the sublattice is occupied by octahedrally coordinated Al) and $65 \pm 4\%$ Al-coordinated O_h in $\eta\text{-Al}_2\text{O}_3$ by Al NMR studies.³⁸ These results were further supported by the detailed X-ray and neutron scattering studies which revealed that vacancies were preferentially found at tetrahedral sites in $\gamma\text{-Al}_2\text{O}_3$ and at octahedral sites in $\eta\text{-Al}_2\text{O}_3$.³⁹

The detailed morphologies and structures of the three crystalline Al_2O_3 samples are shown in Fig. 2. Interestingly, the morphologies of the three crystalline Al_2O_3 samples, as examined by SEM, were similar owing to the same precursor involved during preparation. As an example, $\gamma\text{-Al}_2\text{O}_3$ consisted of many uniform rod-like fibers with lengths of 10–15 μm and diameters of 1.0–1.5 μm (Fig. 2a and b). In contrast, HRTEM analysis enabled closer examination of the crystalline properties of the Al_2O_3 samples that differed. Specifically, $\alpha\text{-Al}_2\text{O}_3$ featured much higher crystallinity (Fig. 2c and d) which is followed by $\eta\text{-Al}_2\text{O}_3$ (Fig. 2e and f) and $\gamma\text{-Al}_2\text{O}_3$ (Fig. 2g and h), and the rod-like fibers of η - and $\gamma\text{-Al}_2\text{O}_3$ were built up from many nanoparticles, which suggested that both η - and $\gamma\text{-Al}_2\text{O}_3$ featured micro/nano-structures. It can be seen that few crystalline regions and numerous amorphous areas could be observed for $\gamma\text{-Al}_2\text{O}_3$. These results agreed with the XRD results.

The BET surface areas (S_{BET}), average pore sizes, and total pore volumes of the Al_2O_3 samples with different crystal structures were determined using the N_2 adsorption-desorption isotherms (Table S2†). The S_{BET} of Al_2O_3 crystals was in the order of $\gamma\text{-Al}_2\text{O}_3$ at $135.0 \text{ m}^2 \text{ g}^{-1} > \eta\text{-Al}_2\text{O}_3$ at $34.9 \text{ m}^2 \text{ g}^{-1} > \alpha\text{-Al}_2\text{O}_3$ at $5.2 \text{ m}^2 \text{ g}^{-1}$. Meanwhile, the total pore volume increased with increasing S_{BET} and was dependent on the Al_2O_3 crystal structure. These trends indicated that sintering might occur during preparation with the increase of the calcination temperatures and times from $\gamma\text{-Al}_2\text{O}_3$ to $\alpha\text{-Al}_2\text{O}_3$ through $\eta\text{-Al}_2\text{O}_3$. A similar case about sintering as the calcination temperature increased has been found during the preparation of a NiFe composite oxide.¹²

The XPS patterns of the three crystalline Al_2O_3 samples are shown in Fig. 3a. The O 1s spectra featured three peaks labeled O_α , $\text{O}_{\alpha'}$ and O_β . The O_α and $\text{O}_{\alpha'}$ at 531.1 and 532.2–532.5 eV were attributed to surface-adsorbed oxygen species, such as O_2^{2-} and O^- , corresponding to defect oxide or hydroxyl groups, and chemisorbed water ($\text{O}_{\alpha'}$), respectively.^{8,40} O_β , which was observed at the lower binding energy of 530–530.5 eV, was assigned to lattice oxygen O^{2-} .⁴¹ The oxygen species associated with O_α are usually more reactive than those associated with O_β or $\text{O}_{\alpha'}$ in oxidation reactions because of their higher mobilities.⁴² In this study, the

Fig. 1 (a) XRD patterns and (b) unit cell schematics of α -, η -, and $\gamma\text{-Al}_2\text{O}_3$.

Fig. 2 Detailed morphologies and structures of the Al_2O_3 samples: (a and b) high-resolution SEM images of $\gamma\text{-Al}_2\text{O}_3$, and HRTEM images of (c and d) $\alpha\text{-Al}_2\text{O}_3$, (e and f) $\eta\text{-Al}_2\text{O}_3$, and (g and h) $\gamma\text{-Al}_2\text{O}_3$.

proportions of O_α in the samples, calculated as $\text{O}_\alpha/(\text{O}_\beta + \text{O}_\alpha + \text{O}_\alpha')$ in Table S2,† were 31.3% ($\gamma\text{-Al}_2\text{O}_3$), 10.5% ($\eta\text{-Al}_2\text{O}_3$), and 14.0% ($\alpha\text{-Al}_2\text{O}_3$). These results indicate that a high proportion of O_α species in $\gamma\text{-Al}_2\text{O}_3$ could enhance the oxidation of CN-1.

Ammonia FTIR spectroscopy was carried out to investigate the Lewis and Brønsted acidities of the three crystalline Al_2O_3 samples, as shown in Fig. 3b. The bands at 1625, 1587, 1255, and 1172 cm^{-1} were assigned to the asymmetric and symmetric vibrations of N–H bonds in ammonia which coordinated to Lewis acid sites.^{43–45} The bands at 1682, 1480, and 1453 cm^{-1} attributed to NH_4^+ corresponded to Brønsted acid sites.^{43,45,46} Detailed assignments of the IR bands (cm^{-1}) are presented in Table S3.† In $\alpha\text{-Al}_2\text{O}_3$, the Al ions can display

only octahedral coordination. The low-intensity band observed at 1587 cm^{-1} indicates that only one type of Lewis acid site is present in $\alpha\text{-Al}_2\text{O}_3$. Similar cases were previously reported by Claudio Morterra *et al.* and Claudio Morterra *et al.*^{47,48} In contrast, in η - and $\gamma\text{-Al}_2\text{O}_3$, the valence-unsaturated surface Al atoms are a source of surface Lewis acidity, which is central to catalysis.⁴⁹ As reported,⁵⁰ up to four types of Lewis acid-coordinating species can be observed on the surface of transition aluminas, displaying characteristic IR bands at 1625, 1587, 1255, and 1172 cm^{-1} . Both η - and $\gamma\text{-Al}_2\text{O}_3$ additionally featured Brønsted acid sites. However, the intensities of the peaks corresponding to Lewis and Brønsted acid sites on $\eta\text{-Al}_2\text{O}_3$ were significantly lower than those on $\gamma\text{-Al}_2\text{O}_3$, and the band at 1682 cm^{-1} , corresponding to a type of Brønsted acid site, was not detected in $\eta\text{-Al}_2\text{O}_3$. These results indicated that the total amount of acid sites should be the largest on $\gamma\text{-Al}_2\text{O}_3$, followed by η - and $\alpha\text{-Al}_2\text{O}_3$. It could be deduced that the amorphous structure of $\gamma\text{-Al}_2\text{O}_3$, as observed in the TEM images, created numerous surface defects, which are responsible for the acidity of a sample.⁵¹ Ma *et al.* reported that the catalytic oxidation of chlorinated volatile organic compounds is closely associated with both Lewis and Brønsted acid sites on the catalyst surface.⁵² It is therefore expected that the highest abundance of acid sites on $\gamma\text{-Al}_2\text{O}_3$ would improve the degradation of CN-1.

3.2 Activity measurements

The activities of the materials were evaluated based on the degradation efficiency (DE) calculated as follows: $\text{DE} = (1 - R_{\text{CN-1}}/I_{\text{CN-1}}) \times 100\%$, where $I_{\text{CN-1}}$ is the initial number of moles of CN-1 (before degradation) and $R_{\text{CN-1}}$ is the number of moles of CN-1 remaining after the reaction.

The degradation of CN-1 was performed over the Al_2O_3 samples at 300 °C for 30 min. Fig. 4a shows the DEs for CN-1 over the three crystalline Al_2O_3 samples. Micro/nano- $\gamma\text{-Al}_2\text{O}_3$ showed the highest DE (92.2%), followed by micro/nano- $\eta\text{-Al}_2\text{O}_3$ (65.7%) and regular $\alpha\text{-Al}_2\text{O}_3$ (26.6%). The catalytic activity of a material is primarily related to the amount of active sites on the material surface, which in turn depends on the physical and chemical properties of the material such as surface area, pore volume, and acid sites. For instance, Fan *et al.* reported that catalysts with high BET surface areas and large pore volumes showed higher activities.⁵³ de Rivas *et al.* found that the high total acidity of nanocrystalline Co_3O_4 promoted the conversion of a chlorinated feed and resulted in 100% selectivity for CO_2 during the oxidation of 1,2-dichloroethane.⁵⁴ Furthermore, in another study,⁵⁵ the authors demonstrated that increasing the surface acidity of metal oxides that could be considered as the adsorptive sites for chlorinated volatile organic compounds could increase the catalytic activity. Albonetti *et al.* evaluated the effects of Lewis and Brønsted acid sites on the performances of $\text{V}_2\text{O}_5/\text{TiO}_2$ and $\text{V}_2\text{O}_5\text{-WO}_3/\text{TiO}_2$ in the total oxidation of *o*-dichlorobenzene (*o*-DCB).⁵⁶ The Brønsted acid sites significantly improved *o*-DCB conversion and promoted the

Fig. 3 (a) O 1s XPS patterns and (b) FTIR spectra recorded after ammonia adsorption at room temperature of the prepared α -, η -, and γ - Al_2O_3 samples.

Fig. 4 (a) CN-1 degradation efficiencies attained over α -, η -, and γ - Al_2O_3 . The degradation process was conducted at 300 °C for 30 min. (b) GC-MS chromatogram and associated full-scan mass spectrometry of the degradation products of CN-1 over γ - Al_2O_3 at 300 °C for 30 min. (c) IC of organic acids generated following degradation of CN-1 over γ - Al_2O_3 . (d) FTIR spectra of products formed during CN-1 degradation over γ - Al_2O_3 at 50, 150, 200, 250, and 300 °C.

formation of partial oxidation products. In contrast, the Lewis acid sites acted as adsorption sites and enhanced the oxidation of intermediates to CO and CO_2 . Furthermore, Su

et al. reported that high O_α ratios of $\text{Ce}_{0.2}\text{TiAlO}_x$ are beneficial for the oxidation of 1,2,4-TrCB and enable fast SCR reactions.⁸ Ma *et al.* also found that surface active oxygen species,

especially O_α , could contribute to the oxidation reaction of 1,2-dichlorobenzene over Ca-doped FeO_x hollow microspheres.⁴¹ Accordingly, $\gamma\text{-Al}_2\text{O}_3$, which featured the highest surface area and O_α content and abundant acid sites among the three Al_2O_3 samples, displayed the highest DE. However, although the proportion of O_α in $\alpha\text{-Al}_2O_3$ was higher than that in $\eta\text{-Al}_2O_3$, the DEs for CN-1 over the former were lower than those achieved by the latter catalyst. Similar results have been reported in the NO_x conversions over $Ce_{0.2}W_{0.2}TiO_x$ and $Ce_{0.2}TiO_x$.⁵⁷ These similar trends suggest that the catalytic activities of the Al_2O_3 samples depend on a combination of factors including the surface area, pore volume, and number of surface-adsorbed oxygen species and acid sites.¹² In summary, the catalytic performance of $\gamma\text{-Al}_2O_3$ toward CN-1 degradation was better than those of α - and $\eta\text{-Al}_2O_3$.

3.3 Degradation product analysis

The degradation products of CN-1 over the three crystalline Al_2O_3 samples were identified by GC-MS. As an example, Fig. 4b shows the GC-MS chromatogram and full-scan mass spectra of the degradation products of CN-1 obtained over $\gamma\text{-Al}_2O_3$ at 300 °C for 30 min. Naphthalene and 1,4/1,6-DiCN were identified from the full-scan MS analysis and their standards. Their presence indicated the occurrence of hydrodechlorination and chlorination reactions during the degradation of CN-1 over the three crystalline Al_2O_3 samples. Hydrodechlorination often occurs during the catalytic degradation of halogenated aromatics such as polychlorinated biphenyls,¹² polybrominated diphenyl ethers,⁵⁸ and chlorobenzene.⁵⁹ On the other hand, Jiang *et al.* reported that 1,4/1,6-DiCN were the dominant DiCN congeners obtained in the chlorination of naphthalene to octachloronaphthalene during heating of fly ash sourced from secondary copper smelting.⁶⁰ However, 1,4/1,6-DiCN could not be separated because of the coelution of their peak. The released enthalpy and Gibbs free energy values during the reaction can be used to assess the degree of difficulty of the reaction. Accordingly, these values can be used to determine the ease of formation of

products during the reaction. To identify the specific DiCN product, the enthalpies and Gibbs free energies of formation of seven 1-substituted DiCNs were calculated using the isodesmic reaction.³² The enthalpy and Gibbs free energy (ΔH_r and ΔG_r) of the isodesmic reaction are calculated using the absolute enthalpies and Gibbs energies (H° and G°), respectively, as computed by the Gaussian 09 program package²⁹ with the MPWB1K/6-31+G(d,p) method.^{30,31} The obtained ΔH_r and ΔG_r values are presented in Fig. 5. The ΔH_r values associated with the formation of 1-substituted DiCNs including 1,6-, 1,7-, 1,3-, 1,5-, 1,4-, 1,2-, and 1,8-DiCNs were 1.12, 1.40, 4.01, 4.91, 5.83, 8.17, and 11.56 kJ mol⁻¹, respectively. When compared with the ΔH_r to form 1,4-DiCN, the one associated with generating 1,6-DiCN was lower. And among all ΔH_r values for the seven 1-substituted DiCNs, the value associated with producing 1,6-DiCN was the lowest. Moreover, the ΔG_r values associated with the formation of 1-substituted DiCNs showed a similar trend—the formation of 1,6-DiCN required the lowest ΔG_r value (1.04 kJ mol⁻¹). This result indicates that 1,6-DiCN is the most easily formed among the 1-substituted DiCNs in the chlorination reaction. Accordingly, it can be deduced that 1,6-DiCN is the most favored DiCN product formed while 1,4-DiCN is less or not formed, during the degradation of CN-1 over the three crystalline Al_2O_3 samples.

The amounts of the products obtained from the degradation of CN-1 over the three crystalline Al_2O_3 samples are presented in Table 1. The yield ratios of the produced naphthalene and 1,4/1,6-DiCN (*i.e.*, naphthalene-to-1,4/1,6-DiCN) over α -, η -, and $\gamma\text{-Al}_2O_3$ were calculated to be 7.3, 13.3, and 8.2, respectively. This result indicates that the chlorination route is a less prominent reaction pathway than the hydrodechlorination route. However, the percentage values of the produced naphthalene in the consumed CN-1 after the degradation reaction over α -, η -, and $\gamma\text{-Al}_2O_3$ were 8.0%, 4.2%, and 3.9%, respectively. Moreover, these values for the produced 1,4/1,6-DiCN were 1.1%, 0.3% and 0.5%, respectively. Both of them together were only 9.1%, 4.5%, and 4.4%, respectively. Obviously, the contribution of the hydrodechlorination

Fig. 5 Enthalpy (ΔH_r) and Gibbs free energy (ΔG_r) associated with the isodesmic reaction.

Table 1 The compound analysis for CN-1 degradation over the three types of Al₂O₃

Compounds	α -Al ₂ O ₃	η -Al ₂ O ₃	γ -Al ₂ O ₃
Initial CN-1 (nmol)	3684.6	3684.6	3684.6
Consumed CN-1 after reaction (nmol)	980.1	2420.8	3397.2
Produced naphthalene (nmol)	78.0	101.4	132.6
Produced DiCN (nmol)	10.7	7.6	16.2
Yield ratio of naphthalene to DiCN	7.3	13.3	8.2
Percentage of naphthalene in consumed CN-1 (%)	8.0	4.2	3.9
Percentage of DiCN in consumed CN-1 (%)	1.1	0.3	0.5
Percentage of other products in consumed CN-1 (%)	91.0	95.5	95.6

with chlorination reaction toward the overall CN-1 degradation was rather low in the presence of the three crystalline Al₂O₃ samples. There is a large mass imbalance in the carbon content of the consumed CN-1 and the detected products. Other products with the percentages of 91.0%, 95.5%, and 95.6% in the consumed CN-1 were deduced to be produced increasingly over α -, η -, and γ -Al₂O₃, respectively. Other degradation pathways associated with the generation of other products may dominate during the degradation of CN-1 over γ -Al₂O₃, followed by η - and α -Al₂O₃. It has been reported that competition between hydrodechlorination and oxidation reactions often occurs during the degradation of chlorinated aromatic hydrocarbons over metal oxides.^{10,61,62} Several studies have reported that the surface oxygen of metal oxides can attack the aromatic ring, thereby resulting in oxidation reactions.^{8,12} Based on the characteristics of the XPS spectra, reactive oxygen species, such as O²⁻, O₂⁻, and O⁻, were detected over the Al₂O₃ samples, especially over γ -Al₂O₃. Therefore, it is speculated that the oxidation reaction pathway may be dominant during the thermal degradation of CN-1 over the Al₂O₃ samples, especially over γ -Al₂O₃ with abundant reactive oxygen species.

In order to further determine the oxidation products, the produced organic acid products after the degradation of CN-1 over γ -Al₂O₃ were detected by IC. As shown in Fig. 4c, formic, acetic and propanoic acids were determined as degradation products, which further confirmed the occurrence of oxidation reactions. Su *et al.* reported that 1,2,4-TrCB in the presence of NO could be also oxidized to the organic acid products over Ce_{0.2}TiAl_{0.6}O_x at 300 °C.⁸ Huang *et al.* found the generation of formic, acetic and propanoic acids during the oxidation degradation of CB-209 over iron-based spinels.¹² This result indicated that γ -Al₂O₃ appeared to be able to facilitate the ring-cracking oxidation of CN-1, resulting in the formation of low-molecular-weight products.

The oxidative degradation pathway was further clarified by investigating the degradation of CN-1 over γ -Al₂O₃ using *in situ* FTIR spectroscopy. Fig. 4d shows the FTIR spectra recorded during the degradation of CN-1 over γ -Al₂O₃ at various reaction temperatures from 50 to 300 °C. The peaks observed within the 3400–3800 cm⁻¹ region were assigned to different types of surface hydroxyl groups.⁴⁰ The peaks ob-

served at 1690, 1596, 1507, and 1458 cm⁻¹ were attributed to the stretching of the aromatic rings of naphthalene.^{63,64} The peaks observed at 2967, 2933, and 1466 cm⁻¹ were ascribed to the stretching of C–H in –CH₂– and –CH₃.⁶³ The band at 2350 cm⁻¹ was assigned to CO₂.⁶⁵ The weak peak at 1242 cm⁻¹ was associated with C–O stretching.⁴⁰ The peaks corresponding to the naphthalene aromatic rings and surface hydroxyl groups weakened with increasing temperature, indicating that PCNs decomposed continuously while hydroxyl groups were consumed. Peaks associated with intermediates containing –CH₂–, –CH₃, and C–O groups gradually appeared, thus confirming the occurrence of oxidation reactions. Furthermore, the formation of oxidation products containing those structures was reported by Huang *et al.* while examining the degradation of polychlorinated biphenyls over mesoporous iron-based spinels.¹² The presence of those oxidation products indicates the partial splitting of the naphthalene ring during the degradation of CN-1. Interestingly, the positive CO₂-associated peak weakened with increasing temperatures, indicating that CO₂ was formed during the reaction. Therefore, it is speculated that the partial oxidation products formed during the degradation of CN-1 were eventually oxidized to CO₂.

3.4 Proposed degradation mechanism

Scheme 1 shows a proposed mechanism for CN-1 degradation over γ -Al₂O₃ based on the identification of intermediate products. The γ -Al₂O₃ structure can be regarded as a face-centered cubic packing of oxygen atoms, with Al³⁺ cations filling octahedral (Al_{Oct}) and tetrahedral (Al_{Tet}) interstitial sites among the oxygen atoms.⁶⁶ It is a defective spinel structure with vacancies at cation positions to accommodate the stoichiometric requirements.⁶⁷ The presence of vacancies at some cation sites leads to a more complex structure,⁶⁸ resulting in an amorphous phase, larger surface area and pore volume, and a higher number of active sites, all of which can improve adsorption abilities and the catalytic activity. Based on Scheme 1, dissociated CN-1 is first adsorbed on the Al³⁺ Lewis acid and Brønsted acid sites *via* the complex interaction and hydrogen bonding. In the presence of a proton donor (such as surface hydroxyl groups originating from the adsorbed water on γ -Al₂O₃), CN-1 is possibly protonated to naphthalene as part of the hydrodechlorination pathway.⁶⁹ The effect of water acting as a hydrogen donor on hydrodehalogenation of organohalogen compounds has been reported by a number of authors.^{70,71} Stach *et al.* studied the dechlorination of HCB on municipal waste incinerator fly ash within the temperature range of 150–350 °C.⁷¹ After the fly ash was previously dried by heating at 260 °C for 3 h, a considerable decrease in the hydrodechlorination efficiency for HCB from 33.9% to 14.5% was observed as compared with that over the corresponding untreated fly ash. This result proved the hydrogen donor role which water plays in the hydrodechlorination process. Matheson *et al.* presented that alkylhalides could undergo reductive dehalogenation in the

Scheme 1 Proposed mechanism of CN-1 degradation over γ - Al_2O_3 .

presence of a proton donor like water.⁷² However, the identification of water as a hydrogen source needs to be very carefully validated by other techniques. In addition, the free chloride species formed during CN-1 degradation can combine with residual CN-1 to form small amounts of 1,4/1,6-DiCN, instigating minor chlorination reactions. Both the hydrodechlorination and chlorination pathways during the degradation process accounted for 3.9% and 0.5%, respectively, of the total degradation process. The other pathway, mostly including the oxidation degradation pathway, accounts for 95.6%. The nucleophilic attack of the C-Cl bond by reactive O^{2-} species proceeds.^{8,73} The large surface area of γ - Al_2O_3 can weaken the Al-O bonds and facilitate lattice oxygen desorption from γ - Al_2O_3 , thereby facilitating the reduction process.⁷⁴ Simultaneously, the reactive electrophilic O_2^- and O^- species attack the π -electron cloud of the naphthalene ring, which has a highly dense electron population.⁷⁵ The oxidation intermediates containing $-\text{CH}_2-$, $-\text{CH}_3$, and C-O groups were produced, which can be subsequently oxidized to low-molecular-weight products, such as formic, acetic and propanoic acids, and eventually completely oxidized to CO_2 . The reaction pathways, involving the formation of oxidation species, follow the Mars-van Krevelen mechanism. In this mechanism, the consumed active O^{2-} species can be replenished by stepwise electron gain by O_2 adsorbed on the surface of γ - Al_2O_3 as follows: $\text{O}_2 \rightarrow \text{O}_2^- \rightarrow 2\text{O}^- \rightarrow 2\text{O}^{2-}$.⁸ A similar degradation mechanism has been reported for the oxidation of CO at the interface of Au nanoclusters and a stepped CeO_2 (111) surface,⁷⁶ and the oxidation of 1,2,4-TrCB over synthesized $\text{Ce}_{0.2}\text{TiAl}_x\text{O}_x$ micro/nano-material.⁸

Conclusions

Three crystalline Al_2O_3 samples, *i.e.*, α -, η -, and γ - Al_2O_3 , featuring rod-like fibers were prepared using the same hydro-

thermal method but with different calcination conditions. The degradation of gaseous CN-1 was investigated at 300 °C over three Al_2O_3 samples with different Al^{3+} filling in octahedral and tetrahedral sites. The DE for CN-1 over micro/nano- γ - Al_2O_3 was 92.2%, which was higher than those obtained over micro/nano- η - Al_2O_3 (65.7%) and regular α - Al_2O_3 (26.6%). The excellent catalytic performance of micro/nano- γ - Al_2O_3 can be attributed to its specific defective spinel structure resulting in its large surface area and pore volume, large amounts of surface-adsorbed oxygen species, and Brønsted and Lewis acid sites. Naphthalene and 1,4/1,6-DiCN were detected as products, indicating that hydrodechlorination and side chlorination reactions were involved in the overall degradation process. However, there is a large mass imbalance in the carbon content of the consumed CN-1 and the detected products. Other products with percentages of 91.0%, 95.5%, and 95.6% in the consumed CN-1 were deduced to be produced increasingly over α -, η -, and γ - Al_2O_3 , respectively. Formic, acetic and propanoic acids were determined by ion chromatography during the CN-1 degradation. *In situ* Fourier transform infrared spectroscopy revealed the presence of intermediates containing CO_2 , and $-\text{CH}_2-$, $-\text{CH}_3$, and C-O groups. This indicated that the other oxidation degradation pathway is possibly more favored to occur especially over γ - Al_2O_3 with more abundant reactive oxygen species.

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References

- 1 Seventh meeting of the Persistent Organic Pollutants Review Committee, <http://chm.pops.int/Convention/POPsReviewCommittee/POPRCMeetings/POPRC7/POPRC7Documents/tabid/2267/language/en-US/Default.aspx>, (accessed June 2016).
- 2 Seventh meeting of the conference of the parties to the Stockholm Convention, <http://synergies.pops.int/2015COPs/MeetingDocuments/tabid/4243/language/en-US/Default.aspx>, (accessed June 2016).
- 3 H. Park, J. H. Kang, S. Y. Baek and Y. S. Chang, *Environ. Pollut.*, 2010, **158**, 1420–1427.
- 4 Ninth meeting of the Persistent Organic Pollutants Review Committee, <http://chm.pops.int/TheConvention/POPsReviewCommittee/Meetings/POPRC9/Overview/tabid/3280/mctl/ViewDetails/EventModID/871/EventID/407/xmid/10326/Default.aspx>, (accessed June 2016).
- 5 G. R. Liu, M. H. Zheng, B. Du, Z. Q. Nie, B. Zhang, W. B. Liu, C. Li and J. C. Hu, *Chemosphere*, 2012, **89**, 467–472.
- 6 X. X. Jiang, G. R. Liu, M. Wang, W. B. Liu, C. Tang, L. Li and M. H. Zheng, *J. Hazard. Mater.*, 2015, **286**, 545–552.
- 7 S. J. Lin, G. J. Su, M. H. Zheng, D. K. Ji, M. K. Jia and Y. X. Liu, *Appl. Catal., B*, 2012, **123–124**, 440–447.
- 8 G. J. Su, L. Y. Huang, S. Liu, H. J. Lu, F. Yang and M. H. Zheng, *Catal. Sci. Technol.*, 2015, **5**, 1041–1051.
- 9 S. Kim, O. Byl and J. T. Yates, Jr., *J. Phys. Chem. B*, 2005, **109**, 3507–3511.
- 10 M. K. Jia, G. J. Su, M. H. Zheng, B. Zhang and S. J. Lin, *Sci. China: Chem.*, 2010, **53**, 1266–1272.
- 11 Y. Y. Ahn, E. T. Yun, J. W. Seo, C. Lee, S. H. Kim, J. H. Kim and J. Lee, *Environ. Sci. Technol.*, 2016, **50**, 10187–10197.
- 12 L. Y. Huang, G. J. Su, A. Q. Zhang, Y. L. Shi, C. B. Xia, H. J. Lu, L. W. Li, S. Liu and M. H. Zheng, *J. Hazard. Mater.*, 2013, **261**, 451–462.
- 13 M. K. Jia, G. J. Su, M. H. Zheng, B. Zhang and S. J. Lin, *J. Nanosci. Nanotechnol.*, 2011, **11**, 2100–2106.
- 14 F. Yang, Q. Q. Li, G. J. Su, X. C. Huang, B. K. Li, Y. H. Zhao, X. Miao and M. H. Zheng, *Chemosphere*, 2016, **150**, 445–452.
- 15 G. L. Chiarello, A. Zuliani, D. Ceresoli, R. Martinazzo and E. Selli, *ACS Catal.*, 2016, **6**, 1345–1353.
- 16 T. Montini, M. Melchionna, M. Monai and P. Fornasiero, *Chem. Rev.*, 2016, **116**, 5987–6041.
- 17 T. Ohno, Y. Masaki, S. Hirayama and M. Matsumura, *J. Catal.*, 2001, **204**, 163–168.
- 18 S. H. Liang, F. Teng, G. Bulgan, R. L. Zong and Y. F. Zhu, *J. Phys. Chem. C*, 2008, **112**, 5307–5315.
- 19 J. Temuujin, T. Jadambaa, K. J. D. Mackenzie, P. Angerer, F. Porte and F. Riley, *Bull. Mater. Sci.*, 2000, **23**, 301–304.
- 20 B. H. Kear, Z. Kalman, R. K. Sadangi, G. Skandan, J. Colaizzi and W. E. Mayo, *J. Therm. Spray Technol.*, 2000, **9**, 483–487.
- 21 S. Kim, O. Byl and J. T. Yates, Jr., *J. Phys. Chem. B*, 2005, **109**, 6331–6333.
- 22 C. H. Li, S. H. Qi and D. N. Zhang, *J. Appl. Polym. Sci.*, 2010, **115**, 3675–3679.
- 23 M. Penchal Reddy, W. Madhuri, K. Sadhana, I. G. Kim, K. N. Hui, K. S. Hui, K. V. Siva Kumar and R. Ramakrishna Reddy, *J. Sol-Gel Sci. Technol.*, 2014, **70**, 400–404.
- 24 C. W. Duan, L. X. Hu, Y. Sun, H. P. Zhou and H. Yu, *Phys. Chem. Chem. Phys.*, 2015, **17**, 22152–22159.
- 25 J. Yan, Q. Wang, T. Wei, L. L. Jiang, M. L. Zhang, X. Y. Jing and Z. J. Fan, *ACS Nano*, 2014, **5**, 4720–4729.
- 26 Y. Xiao, J. Wu, J.-Y. Lin, S.-Y. Taib and G. Yue, *J. Mater. Chem. A*, 2013, **1**, 1289–1295.
- 27 Y. H. Yang, J. H. Cui, M. T. Zheng, C. F. Hu, S. Z. Tan, Y. Xiao, Q. Yang and Y. L. Liu, *Chem. Commun.*, 2012, **48**, 380–382.
- 28 L. C. Zhang, Z. H. Liu, H. Lv, X. Tang and K. Ooi, *J. Phys. Chem. C*, 2007, **111**, 8418–8423.
- 29 M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, G. V. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski and D. J. Fox, *Gaussian 09 (Revision B.01)*, Gaussian Inc., Wallingford, CT, 2010.
- 30 Y. Zhao and D. G. Truhlar, *J. Phys. Chem. A*, 2004, **108**, 6908–6918.
- 31 W. J. Hehre, R. Ditchfield and J. A. Pople, *J. Chem. Phys.*, 1972, **56**, 2257–2261.
- 32 X. Yang, H. Liu, H. F. Hou, A. Flamm, X. S. Zhang and Z. Y. Wang, *J. Hazard. Mater.*, 2010, **181**, 969–974.
- 33 G. R. Liu, J. Y. Zhan, Y. Y. Zhao, L. Li, X. X. Jiang, J. J. Fu, C. P. Li and M. H. Zheng, *Chemosphere*, 2016, **155**, 348–357.
- 34 J. Lewis, D. Schwarzenbach and H. D. Flack, *Acta Crystallogr., Sect. A: Cryst. Phys., Diff., Theor. Gen. Crystallogr.*, 1982, **38**, 733–739.
- 35 C. Morterra, G. Cerrato and G. Meligrana, *Langmuir*, 2001, **17**, 7053–7060.
- 36 J. Gangwar, A. Chandran, T. Joshi, R. Verma, A. M. Biradar, S. K. Tripathi, B. K. Gupta and A. K. Srivastava, *Mater. Res. Express*, 2015, **2**, 075013.
- 37 K. Sohlberg, S. T. Pantelides and S. J. Pennycook, *J. Am. Chem. Soc.*, 2001, **123**, 26–29.
- 38 C. S. John, N. C. M. Alma and G. R. Hays, *Appl. Catal.*, 1983, **6**, 341–346.
- 39 R. S. Zhou and R. L. Snyder, *Acta Crystallogr., Sect. B: Struct. Sci.*, 1991, **47**, 617.
- 40 X. D. Ma, Q. Sun, X. Feng, X. He, J. Guo, H. W. Sun and H. Q. Cao, *Appl. Catal., A*, 2013, **450**, 143–145.
- 41 X. D. Ma, X. Feng, J. Guo, H. Q. Cao, X. Y. Suo, H. W. Sun and M. H. Zheng, *Appl. Catal., B*, 2014, **147**, 666–676.
- 42 X. Y. Wang, Q. Kang and D. Li, *Appl. Catal., B*, 2009, **86**, 166–175.

- 43 W. M. Zhang, P. G. Smirniotis, M. Gangoda and R. N. Bose, *J. Phys. Chem. B*, 2000, **104**, 4122–4129.
- 44 R. Q. Long and R. T. Yang, *Appl. Catal., B*, 2000, **24**, 13–21.
- 45 L. Chen, J. H. Li and M. F. Ge, *Environ. Sci. Technol.*, 2010, **44**, 9590–9596.
- 46 Y. C. Fu, T. Hong, J. P. Chen, A. Auroux and J. Y. Shen, *Thermochim. Acta*, 2005, **434**, 22–26.
- 47 C. Morterra, C. Emanuel, G. Cerrato and G. Magnacca, *J. Chem. Soc., Faraday Trans.*, 1992, **88**, 339–348.
- 48 C. Morterra, S. Coluccia, A. Chiorino and F. Boccuzzi, *J. Catal.*, 1978, **54**, 348–364.
- 49 D. Coster, A. L. Blumenfeld and J. J. Fripiat, *J. Phys. Chem.*, 1994, **98**, 6201–6211.
- 50 C. Morterra and G. Magnacca, *Catal. Today*, 1996, **27**, 497–532.
- 51 Y. Yang, J. Huang, S. W. Wang, S. B. Deng, B. Wang and G. Yu, *Appl. Catal., B*, 2013, **142–143**, 568–578.
- 52 X. D. Ma, J. S. Shen, W. Y. Pu, H. W. Sun, Q. Pang, J. Guo, T. Zhou and H. Q. Cao, *Appl. Catal., A*, 2013, **466**, 68–76.
- 53 Y. Fan, X. B. Lu, Y. W. Ni, H. J. Zhang, M. W. Zhu, Y. Li and J. P. Chen, *Appl. Catal., B*, 2011, **101**, 606–612.
- 54 B. de Rivas, R. López-Fonseca, C. Jiménez-González and J. I. Gutiérrez-Ortiz, *J. Catal.*, 2011, **281**, 88–97.
- 55 B. de Rivas, C. Sampedro, M. García-Real, R. López-Fonseca and J. I. Gutiérrez-Ortiz, *Appl. Catal., B*, 2013, **129**, 225–235.
- 56 S. Albonetti, S. Blasioli, R. Bonelli, J. E. Mengou, S. Scirè and F. Trifirò, *Appl. Catal., A*, 2008, **341**, 18–25.
- 57 W. P. Shan, F. D. Liu, H. He, X. Y. Shi and C. B. Zhang, *Appl. Catal., B*, 2012, **115–116**, 100–106.
- 58 Q. Q. Li, F. Yang, G. J. Su, L. Y. Huang, H. J. Lu, Y. Y. Zhao and M. H. Zheng, *Environ. Sci. Pollut. Res.*, 2016, **23**, 1540–1551.
- 59 G. J. Su, Y. X. Liu, L. Y. Huang, H. J. Lu, S. Liu, L. W. Li and M. H. Zheng, *Chemosphere*, 2014, **99**, 216–223.
- 60 X. X. Jiang, G. R. Liu, M. Wang and M. H. Zheng, *Chemosphere*, 2015, **119**, 1091–1098.
- 61 S. J. Lin, G. J. Su, M. H. Zheng, M. K. Jia, C. S. Qi and W. Li, *J. Hazard. Mater.*, 2011, **192**, 1697–1704.
- 62 G. J. Su, L. Y. Huang, R. F. Shi, Y. X. Liu, H. J. Lu, Y. Y. Zhao, F. Yang, L. R. Gao and M. H. Zheng, *Chemosphere*, 2016, **144**, 81–90.
- 63 L. Q. Guo, Y. B. Zeng, A. H. Guan and G. N. Chen, *React. Funct. Polym.*, 2011, **71**, 1172–1176.
- 64 M. Wei, S. X. Shi, J. Wang, Y. Li and X. Duan, *J. Solid State Chem.*, 2004, **177**, 2534–2541.
- 65 K. P. Rao, M. Higuchi, J. Duan and S. Kitagawa, *Cryst. Growth Des.*, 2013, **13**, 981–985.
- 66 E. J. Peterson, A. T. DeLaRiva, S. Lin, R. S. Johnson, H. Guo, J. T. Miller, J. Hun Kwak, C. H. F. Peden, B. Kiefer, L. F. Allard, F. H. Ribeiro and A. K. Datye, *Nat. Commun.*, 2014, **5**, 4885.
- 67 M. Y. Sun, A. E. Nelson and J. Adjaye, *J. Phys. Chem. B*, 2006, **110**, 2310–2317.
- 68 S. Blonski and S. H. Garofalini, *Surf. Sci.*, 1993, **295**, 263–274.
- 69 G. J. Su, Y. X. Liu, L. Y. Huang, Y. L. Shi, A. Q. Zhang, L. X. Zhang, W. B. Liu, L. R. Gao and M. H. Zheng, *Chemosphere*, 2013, **90**, 103–111.
- 70 H. Vogg, M. Metzger and L. Stieglitz, *Waste Manage. Res.*, 1987, **5**, 285–294.
- 71 J. Stach, V. Pekárek, R. Endršt and J. Hetflejš, *Chemosphere*, 1999, **39**, 2391–2399.
- 72 L. J. Matheson and P. G. Tratnyek, *Environ. Sci. Technol.*, 1994, **28**, 2045–2053.
- 73 L. F. Zhang, M. H. Zheng, W. B. Liu, B. Zhang and G. J. Su, *J. Hazard. Mater.*, 2008, **150**, 831.
- 74 C. B. Wang, C. W. Tang, S. J. Gau and S. H. Chien, *Catal. Lett.*, 2005, **101**, 59–63.
- 75 G. J. Su, H. J. Lu, L. X. Zhang, A. Q. Zhang, L. Y. Huang, S. Liu, L. W. Li and M. H. Zheng, *Environ. Sci. Technol.*, 2014, **48**, 6899–6908.
- 76 H. Y. Kim and G. Henkelman, *J. Phys. Chem. Lett.*, 2013, **4**, 216–221.