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DOI:
[10.1039/C8TA03018A](https://doi.org/10.1039/C8TA03018A)

Document Version

Accepted author manuscript

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Citation for published version (APA):

Li, M., Qi, T., Yang, R., Xiao, H., Fang, Z., Hodge, S. A., James, T. D., Wang, L., & Mao, B. (2018). Promoting magnesium sulfite oxidation via partly oxidized metal nanoparticles on graphitic carbon nitride (g-C₃N₄) in the magnesia desulfurization process. *Journal of Materials Chemistry A*, 6(24), 11296-11305.
<https://doi.org/10.1039/C8TA03018A>

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Journal of Materials Chemistry A

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PAPER

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Promoting magnesium sulfite oxidation via partly oxidized metal nanoparticles on graphitic carbon nitride (g-C₃N₄) in the magnesia desulfurization process

Meng Li, Tieyue Qi, Ruoxi Yang, Hui-Ning Xiao, Zhimo Fang, Stephen A. Hodge, Tony D. James, Lidong Wang* and Boyang Mao*

Sulfur dioxide (SO₂) emission has become a crucial problem, especially in developing countries since it is one of the main reasons for the formation of acid precipitation and the secondary formation of fine particulate matter (PM_{2.5}).

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PAPER

Promoting magnesium sulfite oxidation *via* partly oxidized metal nanoparticles on graphitic carbon nitride (g-C₃N₄) in the magnesia desulfurization process†Meng Li,^{‡a} Tieyue Qi,^{‡a} Ruoxi Yang,^{bc} Hui-Ning Xiao,^a Zhimo Fang,^a Stephen A. Hodge,^{id d} Tony D. James,^{id b} Lidong Wang^{id *a} and Boyang Mao^{*e}

Sulfur dioxide (SO₂) emission has become a crucial problem, especially in developing countries since it is one of the main reasons for the formation of acid precipitation and the secondary formation of fine particulate matter (PM_{2.5}). Wet magnesia desulfurization stands out as a widely used practical approach for the control of SO₂ due to its high removal efficiency, low operating cost and potential valuable by-products. However, the effluent of magnesium sulfite (main by-product) can reemit SO₂ and cause water pollution. Thus, it is important, but challenging, to enhance the oxidation rate to improve the utilization of MgSO₄ for sustainable resources and meanwhile downsize the absorbing tower. Herein, we report a series of graphitic carbon nitride (g-C₃N₄)-assembled transition metal catalysts (M-C₃N₄) for the first time *via* a facile and environmentally friendly synthetic route as a new generation of catalysts for the oxidation of magnesium sulfite. We have performed both theoretical evaluation and deep experimental validation of the series of M-C₃N₄ materials, and in particular, the cobalt-C₃N₄ material since it possesses the best catalytic activity reported to date, which is comparable to that of aqueous precious metal benchmarks but only with a 2.4 wt% cobalt loading. Additionally, the ability to recycle the Co-C₃N₄ complex is investigated to facilitate its practical application. This fabrication method is expected to provide a new concept for the construction of multifunctional nanocomposites for a large variety of industrially relevant desulfurization applications.

Received 2nd April 2018

Accepted 17th May 2018

DOI: 10.1039/c8ta03018a

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1. Introduction

Environmental pollution caused by sulfur dioxide (SO₂) emission has become a worldwide problem.^{1–3} This issue needs to be addressed for the treatment of exhaust gas due to the formation of acid precipitation and secondary formation of fine particulate matter (PM_{2.5}),^{4,5} which seriously damage the atmosphere and pose a risk to human health. Among the current practical solutions, wet magnesia desulfurization stands out as a promising approach for SO₂ control on the industrial scale, for instance in power stations and industrial boilers, due to its high

SO₂ removal efficiency (around 95–98%), low operating and capital cost and potential valuable by-products.⁶ The challenge for magnesia desulfurization is that MgSO₃ is the main by-product from this process; thus, the effluent of magnesium sulfite slurry can reemit SO₂ and cause water pollution by consuming dissolved oxygen. Thus, enhancement of the oxidation rate can improve the utilization of MgSO₄ and meanwhile downsize the absorbing tower.

In our previous studies, we have shown the catalytic effect of transition metals,^{7,8} such as Co²⁺, Mn²⁺, Fe²⁺, and Cu²⁺, on sulfite oxidation, among which, cobalt is considered to be the best solution for MgSO₃ oxidation. However, the application of homogeneous transition metal catalysts will result in serious secondary pollution, especially on an industrial scale. Hence, to develop this approach on an industrial scale, we have developed various nanoscale dispersed solid transition metal-based catalysts using wet impregnation. These supported hybrid materials can be fabricated as cobalt-based molecular sieves,⁹ cobalt-based multiwalled carbon nanotubes¹⁰ and cobalt-based mesoporous silica (SBA-15),¹¹ which exhibit remarkable catalytic efficiency and easy recovery when used for magnesium sulfite oxidation. By means of comprehensive experimental and

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† Electronic supplementary information (ESI) available. See DOI: 10.1039/c8ta03018a

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theoretical studies, it was determined that the oxidation reaction is controlled by both the properties of the scaffold materials and the dispersion of active species. Studies on the scaffold-metal interactions reveal that charge transfer across the support material-metal interface often occurs depending on the interface spacing and Fermi level difference between the scaffold materials and the metal. This charge transfer is presumed to be the main reason why certain nano-active species supported on scaffold surfaces display enhanced catalytic activity.

Herein, we design and fabricate graphitic carbon nitride ($g\text{-C}_3\text{N}_4$) as a platform and investigated a series of $g\text{-C}_3\text{N}_4$ organometallic catalysts as a new class of $M\text{-C}_3\text{N}_4$ materials for magnesium sulfite oxidation. Graphitic carbon nitride ($g\text{-C}_3\text{N}_4$), a graphite-like layered material,^{12–16} is composed of ordered triazine subunits connected through planar tertiary amino groups within a layer and weak van der Waals forces between each layer. The two-dimensional (2D) monolayer $g\text{-C}_3\text{N}_4$ nanosheets show many unique features, such as ultrahigh nitrogen content, large aspect ratios and high surface area,^{17–23} thus offering great potential as building blocks for the construction of 3D architectures with excellent thermal and chemical stability as well as environmental friendliness. Owing to the strong confinement effect of $g\text{-C}_3\text{N}_4$, transition metal species can be isolated to achieve atomic/nanoscale level dispersion, which enhances the energy interaction between $g\text{-C}_3\text{N}_4$ and transition metals^{24–27} and thus reinforce their catalytic ability. It is also worth noting that the C_3N_4 powder is a promising source for the mass production of freestanding and thin $g\text{-C}_3\text{N}_4$ nanosheets *via* liquid or thermal exfoliation approaches due to its low fabrication cost. In this study, melamine is applied as the reaction precursor.

2. Experimental

2.1 Chemicals and instruments

The reagents used in this study were as follows: isopropyl alcohol (Tianjin Bei Chen Fang Zheng Reagent, AR, purity $\geq 99.7\%$), cobaltous chloride hexahydrate (Tianjin Kermel Chemical Reagent, AR, purity $\geq 99.0\%$), copper chloride (Tianjin Guangfu Fine Chemical Research Institute, AR, purity $\geq 99.0\%$), manganese chloride (Tianjin Guangfu Fine Chemical Research Institute, AR, purity $\geq 99.0\%$), ferric chloride (Tianjin Guangfu Fine Chemical Research Institute, AR, purity $\geq 99.0\%$), iron chloride tetrahydrate (Tianjin Guangfu Fine Chemical Research Institute, AR, purity $\geq 99.7\%$), nickelous chloride (Tianjin Guangfu Fine Chemical Research Institute, AR, purity $\geq 99.0\%$), magnesium chloride hexahydrate (Tianjin Fuchen Chemical Reagent, AR, purity $\geq 98.0\%$), sodium sulfite (Tianjin Guangfu Technology, AR, purity $\geq 97.0\%$), barium chloride (Tianjin Bei Chen Fang Zheng Reagent, AR, purity $\geq 99.5\%$), sodium hydroxide (Tianjin Bei Chen Fang Zheng Reagent, AR, purity $\geq 96.0\%$), sodium chloride (Tianjin Bei Chen Fang Zheng Reagent, AR, purity $\geq 99.5\%$), hydrochloric acid (Tianjin Beilian Chemical, AR, purity $\geq 36.0\%$), glycerol (Tianjin Bei Chen Fang Zheng Reagent, AR, purity $\geq 99.0\%$),

and glacial acetic acid (Tianjin Fuchen Chemical Reagent, AR, purity $\geq 99.5\%$).

The instruments used for the reactions were as follows: mass flow meter; WSC21070 oil-less air compressor; AS07-03P dynamic distribution apparatus; 722G spectrophotometer; AMO-C thermostat water bath; PHS-3C pH meter; DF-101S heat collection-constant temperature magnetic stirrer, SHENGYANG ultrasonic cleaner, and ZONKIA SC-3612 centrifuge.

2.2 Characterization

The morphology of the catalysts was observed at the magnification of 2500–100000 times using a HitachiS-4800 SEM. The samples were ultrasonicated for 10–15 min and then dripped on a conductive adhesive film. The acceleration voltage was 0.5–30 kV. The elemental mapping of $\text{Co-C}_3\text{N}_4$ was conducted *via* energy dispersive X-ray spectroscopy (Bruker Quantax 400). A JEM-2100 transmission electron microscope (TEM) was used to observe the crystallization structure of the sample at an acceleration voltage of 200 kV.

The specific surface area and pore distribution of the prepared catalysts were determined *via* the N_2 adsorption method at a temperature of 77.3 K with a Quantachrome Instruments analyzer. The specific surface area and pore size distribution of the catalysts were obtained using the BET equation and BJH method, respectively. The crystalline phases of the prepared samples were characterized *via* X-ray diffraction (XRD, Bruker D8 Advance) under wide-angle ($10\text{--}90^\circ$) scanning with a step size of 0.01° . Thermogravimetric analysis was carried out on a NETZSCH STA 449 F3 thermal analyzer with heating from room temperature to 1000°C at a rate of 5°C min^{-1} . X-ray photoelectron spectroscopy (XPS) was conducted using an ESCALAB 250Xi energy spectrometer with a resolution of 0.48 eV ($\text{Ag } 3d_{5/2}$) and 0.68 eV ($\text{C } 1s$) to investigate the surface chemical composition and valence state of cobalt, respectively. The composition of the $\text{Co-C}_3\text{N}_4$ catalysts was determined using the ICP-OES technique (PE-7000DV, USA). A mixture of hydrofluoric acid and nitric acid was used to dissolve the sample at 100°C . The functional groups on the surface of the catalysts were determined *via* Fourier transform infrared spectroscopy (FT/IR-200, JASCO, Japan). For each sample, 50 mg of the spent adsorbent sample was scanned in the range of $4000\text{--}500\text{ cm}^{-1}$ with a wavenumber accuracy of 0.01 cm^{-1} .

2.3 Preparation of $\text{Co-C}_3\text{N}_4$ and fabrication of MgSO_3

The yellow graphitic carbon nitride ($g\text{-C}_3\text{N}_4$) bulk phase powder was prepared *via* the thermal annealing of melamine (Kermel Inc.) at 550°C for 2 h. 400 mg $g\text{-C}_3\text{N}_4$ was added to a 400 mL mixed solution of isopropanol and water (volume% 1 : 1). The suspension was sonicated for 12 h to obtain well dispersed $g\text{-C}_3\text{N}_4$ nanosheets (SHENGYANG Ultrasonic Cleaner, 0.4 kW). Then, CoCl_2 (6.4 g) was mixed and dissolved in the suspension. The reaction flask was then heated at 105°C and refluxed for 8 h. Then, the mixture was cooled to room temperature and the sample was rinsed with deionized (DI) water and collected by centrifugation at 1000 rpm for 30 min (ZONKIA SC-3612

centrifuge). The resultant precipitate was freeze dried under reduced pressure.

Magnesium sulfite (MgSO_3) was prepared by mixing saturated sodium sulfite (Na_2SO_3) and magnesium chloride ($\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$) solutions in a rotary evaporator at 60°C under vacuum (0.090 MPa).

2.4 Catalytic oxidation of MgSO_3

The oxidation of magnesium sulfite was carried out in an experimental-scale bubbling reactor with a gas flow rate of 1 L min^{-1} . The experiment lasted 30 min with sampling at fixed intervals (5 min, 10 min, 15 min, 20 min and 30 min). The SO_4^{2-} concentration at a fixed time was determined *via* barium sulfate spectrophotometry, which is outlined in our previous studies.^{10,11} The oxidation rate of sulfite can be gained from the slope of the graph of sulfate concentration *versus* reaction time.

2.5 Calculation of TOF value

The turnover frequency (TOF), which is the number of moles of oxidized sulfite per mole of active Co per second, was also calculated as follows:

$$\text{TOF} = \frac{n_{\text{sulfite}}}{n_{\text{Co}} d_{\text{Co}} t} \quad (1)$$

where, n_{sulfite} is the amount of sulfite oxidized, n_{Co} represents the Co content, d_{Co} is the dispersion of cobalt in the catalyst, and t is the reaction time.

3. Results and discussion

3.1 Characterization

Fig. 1a presents a digital image of the series of synthesised $\text{M-C}_3\text{N}_4$ powders. The fabrication procedure is described in the Experimental section. Generally, $\text{g-C}_3\text{N}_4$ was obtained by adding bulk C_3N_4 powder to a mixed solution of isopropanol and water (volume% 1 : 1), which gives the optimal dispersion behavior.²⁸ The suspension was sonicated in a 1 : 1 mixture of water and isopropyl alcohol for 12 hours (SHENGYANG Ultrasonic Cleaner, 0.4 kW) to obtain well dispersed and exfoliated $\text{g-C}_3\text{N}_4$ nanosheets. Subsequently, CoCl_2 was dissolved in the suspension and refluxed for 8 hours at 105°C . The resultant precipitate was collected by centrifugation at a speed of 1000 rpm for 30 min and then freeze dried under reduced pressure (other $\text{M-C}_3\text{N}_4$ were synthesised using a similar procedure with different metal salts, Experimental section). The morphology of $\text{Co-C}_3\text{N}_4$ was directly characterized *via* scanning electron microscopy (SEM) and transmission electron microscopy (TEM). From the SEM images in Fig. 1b and c (more from Fig. S1†), it can be seen that the $\text{Co-C}_3\text{N}_4$ nanosheets exhibit a lamellae structure, while $\text{g-C}_3\text{N}_4$ is observed to be a relatively amorphous aggregation with a small lamellae flake size. The TEM images of $\text{Co-C}_3\text{N}_4$ (Fig. 1d and S2) reveal a sheet-like monolayer structure. After metal decoration, Co was homogeneously distributed on the $\text{g-C}_3\text{N}_4$ surface in the form of nanoparticles. The particle size was analysed by measuring 100 Co particles in different areas of the TEM image. This procedure demonstrated that the Co particles

had a modal size distribution over the range of 4–4.5 nm (42%). Further investigation by high-resolution TEM with the insert fast Fourier transform (FFT) pattern in Fig. 1e–g reveals two distinct metal structural domains. The first is the interplanar spacing of 0.205 nm and dihedral angle of 90° corresponding to the (400) plane of cubic oxidised Co particles and the other the interplanar spacing of 0.216 nm and dihedral angle of 60° corresponding to the (001) oriented hexagonal Co particle. This indicates that the nanoscale Co particles are partially oxidized to form a more stable state. Subsequently, the homogeneous distribution of Co species in the $\text{g-C}_3\text{N}_4$ framework was further investigated using scanning transmission electron microscopy coupled with energy-dispersive X-ray spectroscopy (STEM-EDS) element mapping (Fig. 1h–k) to determine the elemental map of Co, O, and $\text{Co-C}_3\text{N}_4$. The STEM-EDS analysis supports the conclusion that Co metal and Co oxide co-exist on the surface of $\text{g-C}_3\text{N}_4$. Furthermore, the atomic force microscopy (AFM) analysis indicates that $\text{Co-C}_3\text{N}_4$ features highly dispersed island-like Co nanoparticles attached to the ultrathin $\text{g-C}_3\text{N}_4$ substrate, and the examined $\text{Co-C}_3\text{N}_4$ is about 4 nm in height (Fig. S3†), which is well consistent with the SEM and TEM observations.^{20b}

To further investigate the pore structure of $\text{Co-C}_3\text{N}_4$, its specific surface area of was measured using the Brunauer–Emmett–Teller (BET) method. The BET specific surface areas of $\text{g-C}_3\text{N}_4$ and $\text{Co-C}_3\text{N}_4$ presented similar values of 19.65 and $19.99\text{ m}^2\text{ g}^{-1}$, respectively, as shown in Table S1,† with a dominant pore diameter of 4.04 nm. The N_2 adsorption–desorption isotherms of the synthesized catalysts are presented in Fig. 2a, which are of type III with an identifiable H4-type hysteresis loop. This may be caused by the aggregation of the nanosheets during freeze drying.²⁹ The uniform adsorption curve indicates an unchanged structure after $\text{g-C}_3\text{N}_4$ interacts with the metal. It is noteworthy that after decoration with Co/oxide nanoparticles, the porosity of the structure gradually decreased and the whole structure became dense.

The XRD spectra of melamine, $\text{g-C}_3\text{N}_4$ and $\text{Co-C}_3\text{N}_4$ were characterized to probe the phase structures of the samples (Fig. 2b). The patterns of the three samples feature a small diffraction peak at 13° , which corresponds to the (100) plane in the structural packing motif.^{30–32} The other characteristic features of melamine were not observed in either $\text{g-C}_3\text{N}_4$ or $\text{Co-C}_3\text{N}_4$, which indicates a framework change after the calcination process. A strong peak at 27.8° was observed in both $\text{g-C}_3\text{N}_4$ and $\text{Co-C}_3\text{N}_4$, which is attributed to the (002) typical interlayer from graphite-like stacks,^{31,33–36} indicating that the prepared $\text{g-C}_3\text{N}_4$ and $\text{Co-C}_3\text{N}_4$ are both laminar in structure. The two weak diffraction peaks at 32.0° and 38.7° in $\text{Co-C}_3\text{N}_4$ match well with crystalline and oxidized Co with a face-centered cubic structure³⁷ (PDF#42-1467), respectively. Also, the weak peak at 44.2° matches elementary cobalt (PDF#15-0806), which proves the existence of cobalt species and its high dispersion within the $\text{Co-C}_3\text{N}_4$ sample. The XRD patterns for the other $\text{M-C}_3\text{N}_4$ complexes are shown in Fig. S4,† which indicate that all the $\text{M-C}_3\text{N}_4$ samples maintain the original chemical structure of $\text{g-C}_3\text{N}_4$. Additionally, the content of Co species in the product was calculated to be about 2.17 wt% from thermogravimetric analysis (TGA) measurements in air (Fig. 2c). TGA analysis was

Fig. 1 (a) Digital image of M-C₃N₄ powder, inset: 3D molecular structure of M-C₃N₄ nanosheet, (b) SEM image of exfoliated g-C₃N₄, (c) SEM image of Co-C₃N₄, (d) TEM image of Co-C₃N₄, inset: corresponding particle size distribution of the Co nanoparticles. (e–g) High-Resolution TEM image, insets: corresponding FFT pattern, (h) STEM image and (i–k) STEM-EDS element mapping of Co-C₃N₄.

performed to ascertain the thermal behavior of Co-C₃N₄. Its weight decreased by 5.71% owing to the decomposition of residual solvent (water and isopropanol) until a sharp loss at 570 °C, which is ascribed to the onset of the thermal decomposition of the graphitic nanosheets of Co-C₃N₄. Co-C₃N₄ decomposed with the release of heat, as indicated by the sudden increase the differential scanning calorimetric (DSC) curve. After the decomposition of Co-C₃N₄, about 1% of the sample was left as residual Co. The binding states of C, N and Co in this sample were investigated *via* X-ray photoelectron spectroscopy (XPS). The high resolution Co 2p spectra are presented in Fig. 2d. The spectra were split into 2p_{1/2} and 2p_{3/2} components with an energy separation of 16 eV due to the spin-orbit interaction, which indicates the existence of Co²⁺ in Co-C₃N₄. The peak at 780.6 eV is related to metallic cobalt, 781.9 eV is associated with bivalent cobalt (Co²⁺),³⁸ and 780.0 eV corresponds to trivalent cobalt (Co³⁺). The peaks at 786.9 eV and 803.2 eV are the shake-up satellite of Co 2p_{3/2} and 2p_{1/2}, respectively.

Together with the TGA measurements, it is concluded that Co and Co oxide grew on the surface of g-C₃N₄. In Fig. 2e, C 1s shows three peaks centered at 284.6 eV, 287.9 eV, and 288.5 eV, which are related to the sp² C–C bonds, C=N coordination, and sp²-bonded carbon (N–C=N), respectively.^{38–42} The XPS N 1s spectra in Fig. 2f display peaks at 398.6 eV, 399.3 eV, 400.7 eV, and 404.8 eV, corresponding to pyridinic N, pyrrolic N, graphitic N, and oxidized nitrogen compounds,^{41–45} respectively, which serve as anchor points for the cobalt nanoparticles. The Co content in this catalyst was up to 2.4 wt% loading according to inductively coupled plasma optical emission spectrometry (ICP-OES), which correlates well with the calculated TGA results. The Raman spectra of the exfoliated g-C₃N₄ and Co-C₃N₄ (Fig. S5†) show that there is no obvious structural change after Co metalisation. The poor Raman signal may due to the poor vibrational, rotational, and other low-frequency modes in the system.

Fig. 2 (a) N₂ adsorption–desorption isotherms and pore distribution of g-C₃N₄ and Co-C₃N₄, (b) X-ray diffraction pattern of melamine, g-C₃N₄ and Co-C₃N₄, (c) TGA curves of Co-C₃N₄, (d) Co 2p XPS spectra of Co-C₃N₄, (e) C 1s XPS spectra of Co-C₃N₄ and (f) N 1s XPS spectra of Co-C₃N₄.

3.2 Proposed mechanism of MgSO₃ catalytic oxidation

To gain insight into the nanoparticle formation mechanism, the interactions between the metal and g-C₃N₄ were investigated using electrostatic simulation. The crystal structure of monolayer g-C₃N₄ and its charge density are shown in Fig. 3a. The equilibrium crystal structure calculated by density functional theory (DFT) adopts a planar morphology, with the lattice parameter of 7.12 Å. Starting from the structure determined by XRD, the single layer g-C₃N₄ and its internal positions are fully relaxed within periodic boundary conditions. The charge density isosurfaces are shown next to the crystal structure. As the figure indicates, the charge primarily accumulates in the vicinity of the N atoms, suggesting the C–N bonds have ionic character. The negatively charged N atoms can absorb M⁺ ions through electrostatic interaction and then further capture the metal cations into their tri-s-triazine units by nitrogen-coordination, which leads to the *in situ* formation of metal (oxide) nanoparticles.⁴⁶

Fourier transform infrared (FTIR) spectroscopy was then employed to characterize the pristine g-C₃N₄ and M-C₃N₄ (Fig. 3b). The spectrum of g-C₃N₄ displays a peak at 810 cm⁻¹, which is typical for the out-of-plane bending mode of heptazine rings, while the peaks located between 900 and 1800 cm⁻¹ originate from the N–C=N heterorings.^{47,48} The multiple broad peaks in the range of 3000–3500 cm⁻¹ correspond to the N–H stretching vibrations.^{47,48} As discussed for the DFT calculation above, for the M-C₃N₄ samples, distinct changes can be observed in this range of the FTIR spectra, as highlighted by the yellow shaded regions in Fig. 3b, due to nitrogen-coordination confinements. The progressive decrease in the intensity of the N–H stretching peaks between 3000 and 3300 cm⁻¹ indicates the interaction of the metal and –N–H, and for Co-C₃N₄ these features almost disappear, suggesting the strong interaction of Co species with g-C₃N₄.

Furthermore, studies on the M-C₃N₄ interaction using fluorescence spectroscopy reveal that depending on the M-C₃N₄ spacing, there charge transfer often occurs across

Fig. 3 (a) Crystal structure and charge density isosurfaces of g-C₃N₄ from side- and top-view. Brown and blue circles represent C and N atoms, respectively. Regions of low and high electron density are shown in blue and red, respectively. Atoms are omitted in the isosurface for clarity. (b) IR spectra of the g-C₃N₄ conjugated transition metals (M-C₃N₄). (c) Fluorescence spectra of the g-C₃N₄ conjugated transition metals (M-C₃N₄) excited at 310 nm. (d) Proposed mechanism of the sulfite oxidation process catalysed by Co-C₃N₄.

the M-C₃N₄ interface (Fig. 3c). This charge transfer may be the main reason why certain nanoparticles supported on the g-C₃N₄ surface show enhanced catalytic activity. Thus, to investigate the interfacial spacing of the metal and g-C₃N₄, the fluorescence spectra of the g-C₃N₄ conjugated transition metals (M-C₃N₄) were measured. The fluorescence intensity decreased and the maximum emission wavelength shifted to a shorter wavelength after the conjugation with transition metals. Compared with the other M-C₃N₄, Co-C₃N₄ significantly blue shifts by 5 nm compared to the other transition metals, indicating that the cobalt nanoparticles more closely interact with the graphitic carbon nitride layer and this unique structure may facilitate electron transfer between the cobalt layer and g-C₃N₄.

As discussed above, Co-C₃N₄ should exhibit better catalytic behavior than other transition metals. Accordingly, the proposed mechanism of sulfite oxidation catalysed by Co-C₃N₄ is shown in Fig. 3d. According to the XRD and XPS analyses in the preceding section, the active component for Co-C₃N₄ consists of three types of cobalt species, including Co(II), Co(III) and metallic cobalt. Based on the multiple valence states of cobalt in Co-C₃N₄, Co-C₃N₄ acts as a reduction-oxidation type of catalyst in the oxidation of MgSO₃, where the oxidizing oxygen comes from the catalyst rather than directly from oxygen in the air. The metallic Co is easily oxidized to CoO (Co(II)) by oxygen, and Co₂O₃ (Co(III)) is reduced to CoO by the carbon in g-C₃N₄. Then, MgSO₃ is oxidized by the oxygen from Co_xO_y and oxygen in air acts to replenish the consumed oxygen from the Co_xO_y species.

3.3 Catalyst performance measurement

Our catalyst was applied in a demonstration project. Co-C₃N₄ was used in an oxidation pond established outside the desulfurization tower after the chemical adsorption of SO₂ by MgO. As shown in Fig. 4a, MgSO₃ as the by-product of desulfurization was sucked into the oxidation pond to be oxidized. In this pond, the Co-C₃N₄ catalyst was used as a fixed bed and the MgSO₃ was passed over the catalyst by a stream of air to achieve the rapid transformation of MgSO₃ to MgSO₄. The product MgSO₄ was then transferred to the concentration tank to be concentrated and recycled. The oxidation of MgO and concentration enhancement of MgSO₃ observed are very promising for practical application in magnesia desulfurization.

Furthermore, the catalysis performance of Co-C₃N₄ for magnesium sulfite oxidation was investigated. For comparison, the catalysis performance of Fe-C₃N₄, Cu-C₃N₄, Ni-C₃N₄ and Mn-C₃N₄ were also measured under the same test conditions. As shown in Fig. 4b, Co-C₃N₄ exhibited the best catalytic performance among all the catalysts, which was five-times better than the uncatalyzed condition. This enhancement is consistent with previous investigations on liquid-phase catalysis using transition metal ions.^{47,49} Cobalt was the most active constituent, causing Co-C₃N₄ to be a facile material for magnesium sulfite oxidation.

Subsequently, the effect of Co-C₃N₄ catalyst concentration (~0.25–0.75 g L⁻¹) on the oxidation of sulfite was investigated, as shown in Fig. 4c. The oxidation rate of sulfite increased with the catalyst concentration, which increased by 3.92 times when the Co-C₃N₄ catalyst concentration was increased from 0.25 to

Fig. 4 (a) Schematic of the magnesia wet flue-gas desulfurization process, (b) comparison of the catalytic performance of the g-C₃N₄ coordinated transition metals (M-C₃N₄) in magnesium sulfite oxidation, (c) effect of the Co-C₃N₄ catalyst on the oxidation rate of MgSO₃; inset: reaction order of the Co-C₃N₄ catalyst in MgSO₃ oxidation, (d) effect of oxygen partial pressure on the oxidation rate of MgSO₃; inset: reaction order of oxygen partial pressure in MgSO₃ oxidation, (e) comparison of the oxidation efficiency of other recently reported catalysts at a concentration of 0.5 g L⁻¹, and (f) effect of recycle times of the Co-C₃N₄ catalyst on the oxidation rate of MgSO₃.

0.75 g L⁻¹. The catalyst concentration and reaction rate values were converted to dimensionless values and the reaction order of the catalyst was calculated by logarithmic operations to be approximately 1.2. This reaction order is higher than that of the Co-CNTs (carbon nanotubes) (0.22)¹⁰ and Co-MS (molecular sieves) (0.39)⁹ in our previous study, implying the importance of the graphitic carbon nitride support on sulfite oxidation.

Moreover, the effect of oxygen partial pressure on sulfite oxidation was investigated, as shown in Fig. 4d. When the oxygen partial pressure increased from 0.1 atm to 1.0 atm, the oxidation rate of sulfite gradually increased to 0.22 mmol L⁻¹ s⁻¹, which is 20 times higher than that in the absence of catalyst. Also, the reaction order of oxygen partial pressure was calculated to be 0.66. The intrinsic reaction rate of the catalyzed magnesium sulfite oxidation was determined as follows:

$$R_{\text{in}} = k_{\text{in}} c_{\text{O}_2}^{\alpha} c_{\text{cat}}^{\beta} c_{\text{S(IV)}}^{\gamma} \quad (2)$$

Applying the steady-state assumption,⁵⁰ the diffusion rate is equal to the intrinsic reaction rate and the following equation can be achieved:

$$R_{\text{obs}} = D \frac{\partial^2 c_{\text{O}_2}}{\partial t^2} = k_{\text{in}} c_{\text{O}_2}^{\alpha} c_{\text{cat}}^{\beta} c_{\text{S(IV)}}^{\gamma} \quad (3)$$

Hence the mass transfer flux of oxygen, N , can be calculated as follows:

$$N = -D \frac{\partial c_{\text{O}_2}}{\partial t} = \sqrt{\frac{2Dk_{\text{in}} c_{\text{O}_2}^{\alpha+1} c_{\text{cat}}^{\beta} c_{\text{S(IV)}}^{\gamma}}{\alpha + 1}} \quad (4)$$

The results demonstrate that the observed reaction orders with respect to the catalyst and oxygen are 1.2 and 0.66, respectively. Therefore, the reaction order (α) with respect to the dissolved oxygen is 0.32. According to surface renewal theory, the diffusion coefficient (D)⁵¹ and liquid mass transfer coefficient (k_L)⁵² can be determined by eqn (5) and (6).

$$D = 7.87 \times 10^{-6} \exp(-2400/T) \quad (5)$$

$$k_L = 1.87 \times 10^{-5} \nu^{0.85} \quad (6)$$

The enhancement factor, E , is expressed as a function of the Hatta number:

$$E = \sqrt{1 + M} = \frac{1}{k_L} \sqrt{\frac{2Dk_{\text{in}}c_{\text{O}_2}^{\alpha-1}c_{\text{cat}}^{\beta}c_{\text{S(IV)}}^{\gamma}}{\alpha + 1}} \quad (7)$$

$$\text{Hatta} = \sqrt{M} \quad (8)$$

Thus, the enhancement factor can be determined by:

$$E = \frac{1}{k_L} \sqrt{\frac{2DR_{\text{in}}}{(\alpha + 1)c_{\text{O}_2}}} \quad (9)$$

By measuring the dissolved oxygen in the reaction slurry, the Hatta number for the dissolved oxygen concentration of 4.38, 5.31, 6.39, 9.26, and 9.69 mol L⁻¹ was calculated to be 3.47, 3.92, 4.06, 4.79, and 5.05, respectively. The reaction conditions are presented in Table 1.

Thus, the Hatta value was higher than 3 at 0.1–1.0 atm oxygen partial pressure, which indicates the magnesium sulfite catalytic oxidation reaction is fast under these reaction conditions.

Furthermore, a comparison of the oxidation rates of different types of catalysts is presented in Fig. 4e. Co-MS,⁹ Co-CNTs,¹⁰ Co-SBA-15 (ref. 11) and Co-TiO₂ were investigated as catalyst systems for the oxidation of magnesium sulfite, in which cobalt was loaded onto the support as the active agent. These catalysts with optimal cobalt loadings were compared for their catalytic performance in the oxidation of sulfite. It was found that our Co-C₃N₄ material composite displayed the best catalytic performance of up to 0.074 mmol L⁻¹ s⁻¹ for the oxidation of sulfite oxidation. Moreover, its TOF value was calculated to be 0.47 s⁻¹, which is 1.8 times that of Co-SBA-15 (0.26 s⁻¹),¹¹ certifying its supreme catalytic activity for the oxidation of magnesium sulfite.

Table 1 E and Hatta values at various oxygen partial pressures

P_{O_2} , atm	c_{O_2} , mol L ⁻¹	k_L , m s ⁻¹	D , m ² s ⁻¹	E	Hatta
0.1	4.38	7.34×10^{-5}	4.15×10^{-9}	3.61	3.47
0.2	5.31	7.34×10^{-5}	4.15×10^{-9}	4.05	3.92
0.4	6.39	7.34×10^{-5}	4.15×10^{-9}	4.18	4.06
0.8	9.26	7.34×10^{-5}	4.15×10^{-9}	4.89	4.79
1.0	9.69	7.34×10^{-5}	4.15×10^{-9}	5.15	5.05

Finally, the catalytic performance of the recycled Co-C₃N₄ (2.4 wt%) was determined, as shown in Fig. 4f. The catalytic performance of Co-C₃N₄ declined with each recycle. After the first recycle, the oxidation rate decreased by 22% compared to the fresh material. After the second and third recycling step, the oxidation rate decreased by 52%. However, the oxidation rate did not noticeably change after the second recycling step. Moreover, the oxidized cobalt from the recovered samples was analyzed by XPS (Fig. S6†), which indicates that the content of Co²⁺ (Table S2†) in each sample decreased with the number of recycles. Herein, it can be inferred that the decrease in catalytic activity after each recovery may have resulted from the loss of active cobalt. Although the catalytic activity of this heterogeneous catalyst decreased after each recycling step, the reaction rate after the recycling step was still enhanced by over 3.4 times compared that of the uncatalyzed system and was comparable to the performance of the fresh aqueous Co²⁺ catalyst. Furthermore, aqueous Co²⁺ cannot be reclaimed and can cause secondary pollution since it is a heavy metal, thus having an adverse impact on human health. Therefore, the solid catalyst developed in this work stands out as a promising alternative to facilitate the oxidation of sulfite. Furthermore, the leakage of cobalt from the Co-C₃N₄ catalyst was investigated by measuring the content of cobalt ions in the reaction medium with atomic absorption spectrometry. Cobalt ions were not detected in the reaction medium after recycling the catalyst, which might be due to its low concentration.

4. Conclusion

In summary, we evaluated M-C₃N₄ as a new class of non-precious metal catalysts for the oxidation of magnesium sulfite in industry, which is relevant in wet magnesia desulfurization. Co-C₃N₄ with only a 2.4 wt% Co loading is very promising, displaying comparable activity to that of precious metal benchmarks for the oxidation reaction. Physicochemical characterization combined with electrostatic simulation identified the active sites to be Co metal (oxide) nanoparticles on the g-C₃N₄ matrix. It was shown that g-C₃N₄ can act as a template to grow nanoscale metal (oxide) particles and the particle size can be controlled to around 4 nm. We further demonstrated the origin of the activity and established a design principle for different M-C₃N₄ complexes. It is worth noting that in future studies, recycled samples will be regenerated by refluxing and cobalt re-introduction to promote the catalyst performance back to its original level. This work opens up new opportunities for the application of high-efficiency and stable noble-metal-free catalysts to facilitate sulfite oxidation in wet desulfurization applications. More importantly, this cost-efficient hybrid structure can be successfully used as a nanostructured material for industrial scale applications.

Conflicts of interest

The authors declare no conflicts of interest.

Acknowledgements

Meng Li and Tiejue Qi contributed equally to this work. The present work is supported by the National Key Research and Development Program of China (Grant #: 2017YFC0210201 and 2016YFC0204102), the National Natural Science Foundation of China (Grant #: 21607044 and 51378204). This work was also supported by Natural Science Foundation of Hebei Province (Grant #: B2017502069 and E2016502096) and the Fundamental Research Funds for the Central Universities (Grant #: 2018MS113 and 2017XS130).

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