Graphene Oxide/ Mixed Metal Oxide Hybrid Materials for Enhanced Adsorption Desulfurization of Liquid Hydrocarbon Fuels

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HIGHLIGHTS

- The adsorption of sulfur from liquid hydrocarbons using mixed metal oxides unsupported and supported on graphene oxide was studied for the first time
- Sulfur adsorption capacity and thermal stability of mixed metal oxides is enhanced by the presence of graphene oxide
- The GO supported adsorbents show good selectivity for organosulfur compounds over sulfur-free aromatic hydrocarbons

KEYWORDS

Graphene oxide, mixed metal oxide, dibenzothiophene, adsorption, desulfurization

ABSTRACT

A series of mixed metal oxides (MMOs) adsorbents (MgAl-, CuAl- and CoAl-MMOs) were supported on graphene oxide (GO) through in-situ precipitation of layered double hydroxides (LDHs) onto exfoliated GO, followed by thermal conversion. The study shows that GO is an excellent support for the LDH-derived MMOs due to matching geometry and charge complementarity, resulting in a strong hybrid effect, evidenced by significantly enhanced adsorption performance for the commercially important removal of heavy thiophenic compounds from hydrocarbons. Fundamental liquid-phase adsorption characteristics of the MMO/GO hybrids are quantified in terms of adsorption equilibrium isotherms, selectivity and adsorbent regenerability. Upon incorporation of as little as 5wt% GO into the MMO material, the organosulfur uptake was increased by up to 170%, the recycling stability was markedly improved and pronounced selectivity for thiophenic organosulfurs over sulfur-free aromatic hydrocarbons was observed.

1. Introduction

Exfoliated graphene has attracted enormous attention due to its unique combination of extraordinary properties.[1] Among intense research activity across many disciplines,[2] the utilization of graphene-related materials as support frameworks for functional nanoparticles has emerged as a promising research area, utilizing a combination of properties such as high specific surface area, light weight, chemical inertness, mechanical robustness and excellent electrical and thermal conductivity. Hybrid materials based on inorganic nanoparticles and graphene or its hydrophilic derivative, graphene oxide (GO), have been shown to significantly boost the functional performance in a wide range of applications,[3] such as heterogeneous,[4] electro-[5] and photo-catalysis,[6] energy storage,[7] CO_2 adsorption,[8] and sensing.[9]

This study focuses on the utilization of GO as support for two-dimensional functional nanoparticles, specifically for mixed metal oxides (MMOs) that are produced from two-dimensional layered double hydroxide (LDH) nanoparticles. GO is expected to be particularly efficient as a support for LDH-derived MMOs due to the matching 2D geometry and the charge complementarity of the initial (positively-charged) LDH nanoplatelets and the exfoliated (negatively-charged) GO sheets. The functionality of the resulting MMO/GO hybrids is assessed for the commercially important adsorption of thiophenic organosulfur contaminants from hydrocarbons, the first example of applying inorganic GO hybrids to adsorption from non-aqueous systems.

Molecular adsorption from the liquid phase onto solid state adsorbents is a key step in many large-scale processes, including purification and liquid separation technologies. However so far, liquid-phase adsorption studies involving graphene and its derivates have mainly focused on water purification, e.g. the removal of toxins, such as heavy metal ions,[10] oxyanions, dyes and organic pollutants from aqueous systems.[11] In this context, most studies have dealt with pure graphene and GO powders,[11] and, recently, graphene aerogels[12],[13] where non-specific adsorption is usually prevalent. One approach to improve adsorption selectivity and capacity is the introduction of specific functional groups to the graphitic surface, for example via chemical functionalization of GO with thiol groups for the selective and efficient removal of Hg^{2+} ions from water.[14] A small number of studies have also explored the potential of metal-oxide/GO hybrids for enhancing adsorption from aqueous systems. Flower-like TiO2 nanostructures grown on GO were shown to be efficient, but non-specific adsorbents of heavy metal ions.[15] Further, iron-oxide/GO composites have been investigated for the removal of organic dyes[14] and arsenates[16],[17] from water.

In this paper, the removal of sulfur-containing aromatics, such as dibenzothiophene (DBT), from hydrocarbons is investigated. Organic sulfur derivatives are major contaminants in petroleum and a source of SOx emission, which results in air pollution, acid rain and catalyst poisoning issues.[18] Currently, the most widely employed desulfurization technology for petroleum derived hydrocarbons is the hydrodesulfurization (HDS) process. However, for heavy thiophenic derivatives, such as DBT and its substituted derivatives, desulfurization via HDS is slow and inefficient.[19],[20] Selective adsorption desulfurization provides a promising, alternative approach for removing thiophenic derivatives from hydrocarbon fuels with the potential to achieve low sulfur levels at relatively low environmental impact. There are two main types of adsorption desulfurization processes: reactive adsorption that occurs at high temperature and, non-reactive adsorption operating at <100°C. In the latter case, the organosulfur compounds are adsorbed as unchanged molecular species on the surface, simplifying the regeneration and cycling of the adsorbent. A range of adsorbent materials are currently under study, including zeolites,[21] metal organic frameworks (MOF),[22] mixed metal oxides,[18] activated carbon,[23],[24] and molecularly imprinted polymers.[25] In general, the development of a scalable adsorbent composed of inexpensive materials, but

possessing a large capacity and the ability to regenerate for a significant number of cycles, would be ideal for continuous operation in a desulfurization unit.[18]

In this paper, readily available, cost-effective LDH-derived MMOs are investigated which have been shown to be effective adsorbents due to their basic character that generates acid-base Lewis interactions with the organic molecules.[26] In addition, MMOs show promising features for adsorption due to their regenerability and adjustable elemental composition.[18] In this study, MgAl-LDH, a cost effective and well-studied LDH compound, was loaded with small weight fractions of GO, followed by thermal conversion into MgAl-MMO/GO hybrids. The pure and hybrid MgAl-MMO materials were tested in batch experiments to assess the non-reactive adsorption of dibenzothiophene (DBT) from dodecane, a typical heavy organosulfur contaminant of petroleum. Crucial adsorption parameters such as DBT uptake capacity, adsorption equilibrium isotherms and DBT selectivity in the presence of sulfur-free aromatics, as well as the adsorbent recyclability were quantified. In order to validate the findings of the MgAl-MMO model system, two other MMO systems with altered chemical composition were synthesized, based on the substitution of Mg^{2+} ions by sulphur-affine Cu^{2+} and Co^{2+} ions, that have the potential to strongly bind aromatic organosulfur compounds via sulfur-metal σ-bonds and π-interactions.[27],[28]

2. Results and Discussion

Synthesis of MMO/GO hybrids. MgAl-MMO can be easily synthesized from cheap reagents through straightforward co-precipitation of MgAl-LDH at basic conditions, followed by simple thermal conversion into MgAl-MMO. The parent CuAl-LDH and CoAl-LDH materials required slightly more complex synthesis approaches, namely co-precipitation at constant pH and slow, urea-mediated co-precipitation under inert conditions, respectively.[29] Incorporation of GO is easily achieved for all three co-precipitation methodologies through simple addition of GO to the basic precipitation medium. The basic pH of the precipitation medium promotes the deprotonation of carboxylic acid groups at the GO surface, facilitating the exfoliation of GO into individual nanosheets through electrostatic stabilization. Further, the negatively-charged carboxylate groups on the GO sheets form ideal nucleation sites for the formation of the positively-charged LDH nanocrystals. These effects facilitate the full utilization of the high surface area of the GO, resulting in an intimate mixture of the GO and LDH nanostructures on the nanoscale. For this study, hybrid materials were loaded with only 5 wt% GO, identified as the optimum nanocarbon loading to enhance the CO_2 storage performance.[30],[31] Considering, the order-of-magnitude difference between the theoretical specific surface area of fully exfoliated GO (~2650 m^2/g) and the measured specific surface area of the MgAl-MMO nanoparticles (135 m^2/g, Table 1), small quantities of the more expensive GO should be sufficient to promote the formation of true hybrid materials.

Materials Characterization. The bulk chemical composition of the synthesized pure MgAl-MMO and the MgAl-MMO/GO hybrid was determined by ICP-OES, confirming the presence of $Mg^{2+}$and Al^{3+} in ratio of 2.2:1 for both materials (Table 1). This ratio is very close to the nominal molar ratio (2:1) of the original metal salts and shows that the presence of GO during synthesis does not affect the chemical MMO composition significantly. In all the adsorbents, sodium was detected only at trace levels by ICP, indicating that the NaOH and Na_2CO_3 used during the synthesis were successfully removed.

Table 1. Chemical composition and textural characterization of the MMO and MMO/GO adsorbents.

Sample name	wt% GO actual[a]	Metal:Al ratio[b] (mol:mol)	SBETc (m2/g)	Vporec (cm3/g)
MgAl-MMO	0	2.20	135	0.52
MgAl-MMO/GO	4	2.20	195	0.57
CuAl-MMO	0	2.50	53	0.13
CuAl-MMO/GO	3	2.60	56	0.15
CoAl-MMO	0	1.90d	65	0.12
CoAl-MMO/GO	3	1.60d	85	0.20

[a] as determined by TGA; [b] as determined by ICP-OES; [c] as determined by nitrogen adsorption; [d] determined by XPS.

SEM imaging (Figure 1a) indicates that the initially precipitated MgAl-LDH nanoparticles are present as small, thin individual nanoplatelets, suggesting a good geometric match between the two two-dimensional components in the initial MgAl-LDH/GO hybrid. After thermal conversion, SEM showed that aggregates of very small MMO particles had formed (Figure 1b); the exact size and shape of the individual MMO nanoparticles cannot be discerned due to the resolution limitation of the SEM. It is noteworthy that SEM fails to visualize any indication for GO in the hybrid materials (Figures 1a and 1b), suggesting the presence of well-exfoliated GO sheets, fully covered by the functional nanoparticles.

TGA in oxidative air atmosphere was used to estimate the actual GO content of the MgAl-LDH/GO adsorbent (Figure 2a). The smaller TGA residue weight of the hybrid materials compared to pure MgAl-MMO, indicated the presence of combustible nanocarbons in the hybrid adsorbent; simple, rule-of-mixture analysis of the residue values suggests a carbon content of about 4 wt% (Table 1). This slightly lower value compared to the nominal GO weight fraction (5 wt%) is consistent with the loss of highly oxidized polyaromatic debris present in the original GO material but known to be solubilized and removed under the basic conditions of the LDH/GO synthesis and washing.[32] Powder XRD shows that the MgAl-LDH and MgAl-LDH/GO parent materials are phase-pure, exhibiting the typical diffractions of hydrotalcite-like compounds (Figure 1d). Upon thermal conversion, the pure and hybrid material show the typical diffractions of periclase-type MMOs (Figure 1e). Analysis of the broadening of the (200) peaks yields very similar crystal domain sizes for the pure and hybrid MgAl-MMO materials (3.4 and 3.3 nm respectively), indicating that GO incorporation has no significant impact on the crystallinity of the MMO adsorbent. It is noteworthy that no diffraction features related to GO are observed, most likely due to the small loading fraction of GO, its relative disorder, and its high degree of exfoliation. Nitrogen adsorption measurements, however, reveal differences between the pure MMO and hybrid MMO/GO adsorbents. Nitrogen adsorption and desorption follow a clear Type IV isotherm shape, typical for mesoporous materials with strong adsorbate-adsorbent interactions (Figure 1f). Previous studies showed that the incorporation of GO is a simple route to increase the specific surface area of LDHs and MMOs, although other means are possible.[8] In this study, the inclusion of 4 wt% GO in the hybrid material leads to an increase in specific surface area, as determined by BET analysis, by more than 40% (Table 1). This observation confirms the formation of a true MMO/GO hybrid material. Similarly to the MgAl-MMO system, the incorporation of 5 wt% GO into CuAl-MMO and CoAl-MMO also leads to increases in specific surface area (Table 1).

Liquid-phase DBT adsorption. The liquid-phase adsorption properties of the MgAl-MMO and MgAl-MMO/GO materials were assessed through batch adsorption experiments at 323 K, based on exposure of the adsorbent powders to dilute DBT solutions in dodecane for 5 days. The adsorption equilibrium isotherms measured in a concentration range between 250-10000 ppm DBT clearly demonstrate marked enhancement of DBT uptake upon incorporation of GO into the MMO adsorbent (Figure 2). At all DBT concentrations studied, DBT adsorption onto the MgAl-MMO/GO hybrid is significantly larger than adsorption onto the pure MgAl-MMO. For both pure and hybrid adsorbent, the experimental data were adequately described by the Freundlich isotherms indicating DBT sorption onto a heterogeneous MMO surface. The Freundlich parameters of both materials were found to be similar indicating that the presence of GO does not modify significantly the nature of the adsorption sites (ESI, Table S2). It is worth noting that pure (thermally-treated) GO did not adsorb any detectable DBT (ESI, Table S3). Further, a simple physical mixture of MgAl-MMO with 5 wt% GO exposed to 1500 ppm DBT showed virtually identical adsorption capacity as the pure MgAl-MMO (0.031 mol DBT/kg MMO). These controls confirm that the intimate mixture of LDH particles and GO sheets during the in-situ synthesis process is a prerequisite for the increased DBT capacity, resulting in the formation of a true hybrid material that clearly outperforms its individual components. This intimate mixture of the components allows for maximum utilization of the large surface area and negative surface charge of the GO. Exfoliated GO sheets can therefore act effectively as spacers between individual MMO particles, enhancing overall particle dispersion and significantly improving accessibility to the adsorption sites.

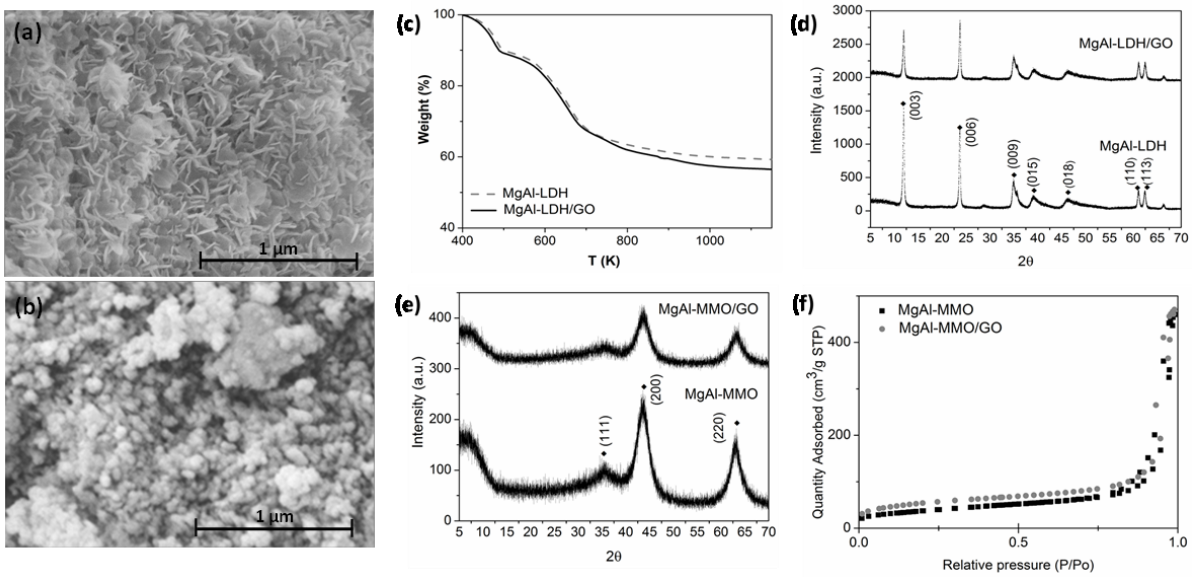

Figure 1. Materials characterization. (a) SEM of the as-synthesised LDH/GO hybrid; (b) SEM image of thermally-converted MMO/GO hybrid; (c) Thermograms of MgAl-LDH and MgAl-LDH/GO, (d) XRD diffraction patterns of MgAl-LDH/GO and MgAl-LDH, (e) XRD diffraction patterns of MgAl-MMO/GO and MgAl-MMO, (f) N_2 adsorption equilibrium isotherms of MgAl-MMO and MgAl-MMO/GO.

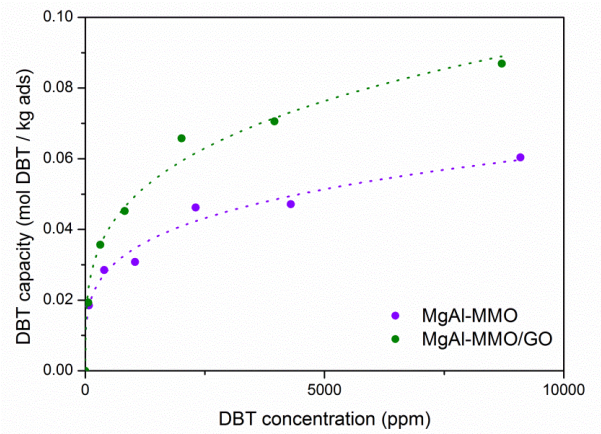

Figure 2. Adsorption equilibrium isotherms for the liquid-phase adsorption of DBT in dodecane solution onto MgAl-MMO and MgAl-MMO/GO, respectively; the dotted lines indicate isotherm fits according to the Freundlich model. Temperature 323 K.

The regeneration of the MgAl-MMO and MgAl-MMO/GO hybrid was assessed by carrying out 5 multicycle tests (ESI, Figure S1). The spent adsorbents were regenerated by washing with dodecane at 373 K. Then the MMOs were centrifuged, recovered, dried and exposed again to 1500 ppm DBT at 323 K. The unsupported adsorbent reduced its initial capacity by 10% in the first cycle and then remained constant over 5 adsorption-desorption cycles. On the other hand, the hybrid lost only 2% of its initial capacity in the first cycle and then its capacity remained stable. The improved stability of the supported material is consistent with observations of improved thermal cycling stability of MgAl-MMO/GO adsorbents used for CO_2 adsorption. Similarly to the CO_2 adsorption case, the improved DBT regeneration stability is due to the robust anchoring of the MMO particles on the exfoliated GO, preventing sintering of the small MMOs particles during DBT desorption at increased temperatures and during drying of the regenerated adsorbent materials.

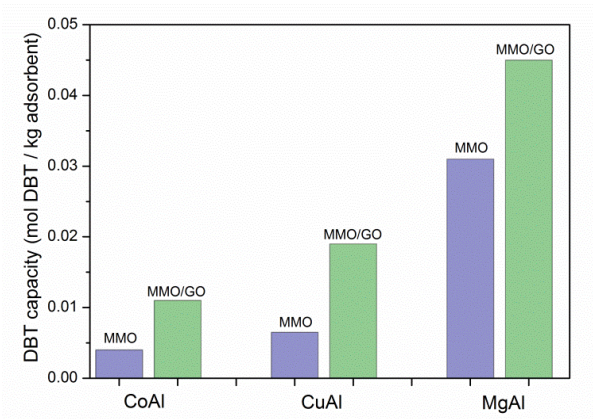

Figure 3. DBT uptake from dodecane (initial DBT concentration 1500 ppm) by CoAl-MMO, CuAl-MMO and MgAl-MMO in their pure (MMO) and hybrid (MMO/GO; containing 5 wt% GO) form.

In order to test the generality of the GO-hybrid enhancement, the DBT uptake (at an intermediate initial DBT concentration of 1500 ppm) was also tested over CuAl-MMO/GO and CoAl-MMO/GO adsorbents (Figure 3, Table 2). The batch adsorption measurements clearly showed that the incorporation of small GO quantities markedly enhances the DBT uptake for all three MMO systems.

The DBT capacity per mass of MMO and per total mass of adsorbent of the transition-metals is lower than for the MgAl-MMOs. However, when the uptake is normalized by surface area of the adsorbents (Table 2), the CuAl-MMO/GO shows the highest capacity. Analogous trends have been found for MOFs and zeolites when the effect of different transition metals

was investigated.[27],[28] The adsorption capacities per mass of total adsorbent presented in this study are comparable to values reported for some zeolites (~ 0.3 - 3 mg S/g ads) when differences in concentration and temperature are taken into account.[27] However, they are lower than those reported for some activated carbons and MOFs materials (~ 5 - 20 mg S/g ads), which have much higher surface area.[28],[33] The fact that MMOs show adsorption capacities per m^2 of the same order of magnitude to those obtained for MOFs suggests that the capacity of MMOs (and in particular MMO/GO hybrids) can be enhanced by further increasing their intrinsic surface area. Therefore, the challenge is to find alternative methods to synthesize MMOs with higher surface area, in particular for the CuAl- and CoAl-MMOs. It is worth noting that, in the transition-metal containing MMO systems, the large increase in DBT uptake per unit area upon GO incorporation (up to 170% in the case of the CuAl-MMO/GO hybrid, Table 2) cannot be explained by an increase in available MMO surface area alone. In these adsorbents, GO appears to exhibit additional functionality, most likely associated with the generation and stabilization of otherwise labile, highly-active adsorption sites. Further studies to elucidate the underlying, mechanistic details and to fully utilize this GO functionality for further organosulfur adsorption enhancement are currently underway.

Table 2. DBT uptake from dodecane (initial DBT concentration 1500 ppm, adsorption temperature 50°C) by MgAl-MMO/GO, CuAl-MMO/GO and CoAl-MMO/GO hybrids.

Sample name	mol DBT/ kg MMO[A]	mol DBT/ kg ads[B]	mg S/ g ads[A]	μmol DBT/ m^2 ads[B]
MgAl-MMO	0.0308	0.0308	0.987	0.228
MgAl-MMO/GO	0.0471	0.0452	1.449	0.232
CuAl-MMO	0.0065	0.0065	0.209	0.123
CuAl-MMO/GO	0.0192	0.0187	0.598	0.333
CoAl-MMO	0.0042	0.0042	0.133	0.064
CoAl-MMO/GO	0.0111	0.0107	0.344	0.126

[A] Intrinsic adsorption capacity (kg MMO), [B]Total adsorption capacity (kg MMO + kg GO)

An important practical aspect in the context of liquid hydrocarbon fuel purification is the impact of sulfur-free aromatics on the DBT uptake. Conventional, non-specific adsorbents, such as activated carbons, have been observed to show reduced DBT capacity in the presence of pure hydrocarbon aromatics due to competitive adsorption. As a model for the influence of aromatics, the uptake of DBT in the presence of biphenyl (BP), a structurally similar aromatic hydrocarbon, was measured for both MgAl-MMO and CuAl-MMO systems. While adsorption of DBT and BP occurred simultaneously (Figure 4), BP uptake was significantly smaller and did not compete with or inhibit DBT uptake. In fact, for all the adsorbent systems, the DBT uptake in presence of equimolar concentrations of BP (Figure 4) remained as high as the uptake from DBT-only dodecane solution (Figure 3). These results confirm a marked affinity and selectivity towards sulphur-containing compounds, most clearly observed for the CuAl-MMO/GO adsorbent.

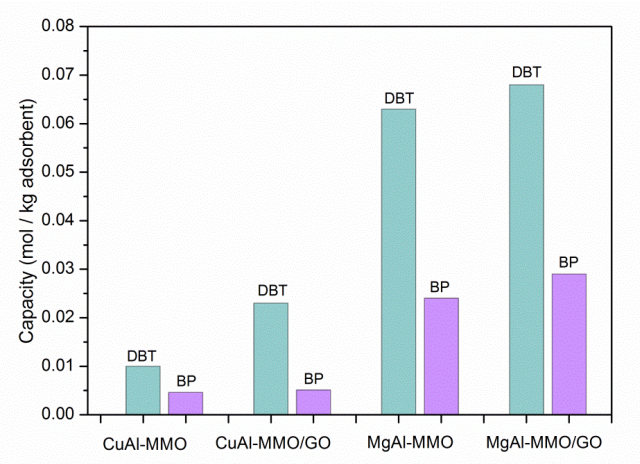

Figure 4. DBT adsorption capacity in the presence of BP: DBT and BP uptakes from dodecane solution, containing 1500ppm DBT and 1500ppm BP, by pure and hybrid CuAl-MMO and MgAl-MMO adsorbents.

Conclusions

The non-reactive adsorption performance of GO-containing inorganic hybrid materials for sulphur-removal from liquid hydrocarbons was studied for the first time, by investigating DBT adsorption from a dodecane solution onto MgAl-, CuAl-, and CoAl-MMO adsorbents. Synthesis of true hybrid MMO/GO adsorbents was achieved through in-situ precipitation of LDH particles onto exfoliated GO sheets, followed by thermal conversion. In these MMO hybrid materials, small quantities of GO likely act as effective spacer between the adsorbent particles, leading to improved accessibility of active adsorption sites, resulting in significantly enhanced organosulfur uptake. These improvements are unaffected by the presence of a typical fuel components (BP), indicating a robust selectivity for sulphur-containing aromatics. Additionally, the cycle stability of the pure MMO was enhanced by the addition of GO, due to robust binding between the charge-complementary hybrid components, inhibiting MMO particle sintering during adsorbent regeneration.

The adsorption capacities per m^2 are highest for the CuAl-MMO/GO system, reflecting the combined benefits of GO incorporation and the enhanced sulfur-affinity of the Cu-substituted MMO system. Further, our adsorption results suggest that GO incorporation into CoAl-MMO and CuAl-MMO leads to a significant change in DBT adsorption mechanism, suggesting that the GO component performs an additional function in transition-metal containing MMO systems. Higher absolute organosulfur capacities (per mass adsorbent) may therefore be accessible through improved understanding and utilization of the adsorption mechanism of sulfur-containing aromatics onto transition-metal MMO/GO adsorbents and by finding methods to synthesize copper-containing MMO adsorbents with higher intrinsic surface areas; for the latter option GO-support might provide additional crucial benefits by stabilising smaller, otherwise labile adsorbent nanoparticles.

Beyond the direct relevance to petroleum purification, the consistent improvements in DBT adsorption across the three hybrid adsorbent systems studied demonstrate the general benefit of using a small proportion of well exfoliated graphene oxide as a two dimensional, charged support for other two dimensional functional materials, representing a broad class of possible future hybrids. Importantly, the study is also an example for the direct utilization of specific GO properties such as facile exfoliation in aqueous base solution, 2D geometry and negative surface charge, rather than considering GO as an aggressive route to imperfect graphene. Further, the findings highlight the need for thorough synthetic approaches to fabricate true hybrid materials for maximum performance enhancement. These outlined principles provide a basis for the development of sulphur-compound adsorbents with higher capacities and are likely to be relevant to a number of other GO-hybrid materials applications

where adsorption from liquid hydrocarbons is a crucial step, such as liquid-liquid separation or fine-chemical synthesis via heterogeneous catalysis.

Supporting Information.

Experimental details, Tables S1-S3, Figure S1.

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References

[1] A.K. Geim, Graphene: Status and Prospects, Science, 324 (2009) 1530-1534.
[2] J.-H. Ahn, B.H. Hong, Graphene for displays that bend, Nat Nano, 9 (2014) 737-738.
[3] C.J. Shearer, A. Cherevan, D. Eder, Application and Future Challenges of Functional Nanocarbon Hybrids, Advanced Materials, 26 (2014) 2295-2318.
[4] A. Celaya-Sanfiz, N. Morales-Vega, M. De Marco, D. Iruretagoyena, M. Mokhtar, S.M. Bawaked, S.N. Basahel, S.A. Al-Thabaiti, A.O. Alyoubi, M.S.P. Shaffer, Self-condensation of acetone over Mg–Al layered double hydroxide supported on multi-walled carbon nanotube catalysts, Journal of Molecular Catalysis A: Chemical, 398 (2015) 50-57.
[5] J. Xu, G. Dong, C. Jin, M. Huang, L. Guan, Sulfur and Nitrogen Co-Doped, Few-Layered Graphene Oxide as a Highly Efficient Electrocatalyst for the Oxygen-Reduction Reaction, ChemSusChem, 6 (2013) 493-499.
[6] Q. Xiang, J. Yu, M. Jaroniec, Graphene-based semiconductor photocatalysts, Chemical Society Reviews, 41 (2012) 782-796.
[7] X. Wang, X. Li, L. Zhang, Y. Yoon, P.K. Weber, H. Wang, J. Guo, H. Dai, N-Doping of Graphene Through Electrothermal Reactions with Ammonia, Science, 324 (2009) 768-771.
[8] A. Garcia-Gallastegui, D. Iruretagoyena, V. Gouvea, M. Mokhtar, A.M. Asiri, S.N. Basahel, S.A. Al-Thabaiti, A.O. Alyoubi, D. Chadwick, M.S.P. Shaffer, Graphene Oxide as Support for Layered Double Hydroxides: Enhancing the CO2Adsorption Capacity, Chemistry of Materials, 24 (2012) 4531-4539.
[9] C.X. Guo, H.B. Yang, Z.M. Sheng, Z.S. Lu, Q.L. Song, C.M. Li, Layered Graphene/Quantum Dots for Photovoltaic Devices, Angewandte Chemie International Edition, 49 (2010) 3014-3017.
[10] G. Zhao, L. Jiang, Y. He, J. Li, H. Dong, X. Wang, W. Hu, Sulfonated Graphene for Persistent Aromatic Pollutant Management, Advanced Materials, 23 (2011) 3959-3963.
[11] H.-X. Wang, Q. Wang, K.-G. Zhou, H.-L. Zhang, Graphene in Light: Design, Synthesis and Applications of Photo-active Graphene and Graphene-Like Materials, Small, 9 (2013) 1266-1283.
[12] Z. Sui, Q. Meng, X. Zhang, R. Ma, B. Cao, Green synthesis of carbon nanotube-graphene hybrid aerogels and their use as versatile agents for water purification, Journal of Materials Chemistry, 22 (2012) 8767-8771.
[13] Z. Dong, C. Jiang, H. Cheng, Y. Zhao, G. Shi, L. Jiang, L. Qu, Facile Fabrication of Light, Flexible and Multifunctional Graphene Fibers, Advanced Materials, 24 (2012) 1856-1861.
[14] H. Bai, C. Li, X. Wang, G. Shi, On the Gelation of Graphene Oxide, The Journal of Physical Chemistry C, 115 (2011) 5545-5551.
[15] J.S. Lee, K.H. You, C.B. Park, Highly Photoactive, Low Bandgap TiO2 Nanoparticles Wrapped by Graphene, Advanced Materials, 24 (2012) 1084-1088.
[16] V. Chandra, J. Park, Y. Chun, J.W. Lee, I.-C. Hwang, K.S. Kim, Water-Dispersible Magnetite-Reduced Graphene Oxide Composites for Arsenic Removal, ACS Nano, 4 (2010) 3979-3986.
[17] X.-L. Wu, L. Wang, C.-L. Chen, A.-W. Xu, X.-K. Wang, Water-dispersible magnetite-graphene-LDH composites for efficient arsenate removal, Journal of Materials Chemistry, 21 (2011) 17353-17359.
[18] Y. Mathieu, L. Tzanis, M. Soulard, J. Patarin, M. Vierling, M. Molière, Adsorption of SOx by oxide materials: A review, Fuel Processing Technology, 114 (2013) 81-100.

[19] V. Chandra Srivastava, An evaluation of desulfurization technologies for sulfur removal from liquid fuels, RSC Advances, 2 (2012) 759-783.
[20] B.C. Gates, H. Topsøe, Reactivities in deep catalytic hydrodesulfurization: challenges, opportunities, and the importance of 4-methyldibenzothiophene and 4,6-dimethyldibenzothiophene, Polyhedron, 16 (1997) 3213-3217.
[21] A.J. Hernández- Maldonado, R.T. Yang, Desulfurization of Transportation Fuels by Adsorption, Catalysis Reviews, 46 (2004) 111-150.
[22] S. Achmann, G. Hagen, M. Hämmerle, I.M. Malkowsky, C. Kiener, R. Moos, Sulfur Removal from Low-Sulfur Gasoline and Diesel Fuel by Metal-Organic Frameworks, Chemical Engineering & Technology, 33 (2010) 275-280.
[23] S. Haji, C. Erkey, Removal of Dibenzothiophene from Model Diesel by Adsorption on Carbon Aerogels for Fuel Cell Applications, Industrial & Engineering Chemistry Research, 42 (2003) 6933-6937.
[24] J. Bu, G. Loh, C.G. Gwie, S. Dewiyanti, M. Tasrif, A. Borgna, Desulfurization of diesel fuels by selective adsorption on activated carbons: Competitive adsorption of polycyclic aromatic sulfur heterocycles and polycyclic aromatic hydrocarbons, Chemical Engineering Journal, 166 (2011) 207-217.
[25] F. Duan, C. Chen, G. Wang, Y. Yang, X. Liu, Y. Qin, Efficient adsorptive removal of dibenzothiophene by graphene oxide-based surface molecularly imprinted polymer, RSC Advances, 4 (2014) 1469-1475.
[26] A. Samokhvalov, B.J. Tatarchuk, Review of Experimental Characterization of Active Sites and Determination of Molecular Mechanisms of Adsorption, Desorption and Regeneration of the Deep and Ultradeep Desulfurization Sorbents for Liquid Fuels, Catalysis Reviews, 52 (2010) 381-410.
[27] Y. Shen, P. Li, X. Xu, H. Liu, Selective adsorption for removing sulfur: a potential ultra-deep desulfurization approach of jet fuels, RSC Advances, 2 (2012) 1700-1711.
[28] Y. Liu, F. Guo, J. Hu, S. Zhao, H. Liu, Y. Hu, Screening of desulfurization adsorbent in metal–organic frameworks: A classical density functional approach, Chemical Engineering Science, 137 (2015) 170-177.
[29] Z. Liu, R. Ma, M. Osada, N. Iyi, Y. Ebina, K. Takada, T. Sasaki, Synthesis, Anion Exchange, and Delamination of Co−Al Layered Double Hydroxide: Assembly of the Exfoliated Nanosheet/Polyanion Composite Films and Magneto-Optical Studies, Journal of the American Chemical Society, 128 (2006) 4872-4880.
[30] D. Iruretagoyena, M.P. Shaffer, D. Chadwick, Adsorption of carbon dioxide on graphene oxide supported layered double oxides, Adsorption, 20 (2014) 321-330.
[31] D. Iruretagoyena, M.S.P. Shaffer, D. Chadwick, Layered Double Oxides Supported on Graphene Oxide for CO_2 Adsorption: Effect of Support and Residual Sodium, Industrial & Engineering Chemistry Research, 54 (2015) 6781-6792.
[32] J.P. Rourke, P.A. Pandey, J.J. Moore, M. Bates, I.A. Kinloch, R.J. Young, N.R. Wilson, The Real Graphene Oxide Revealed: Stripping the Oxidative Debris from the Graphene-like Sheets, Angewandte Chemie International Edition, 50 (2011) 3173-3177.
[33] L. Xiong, F.-X. Chen, X.-M. Yan, P. Mei, The adsorption of dibenzothiophene using activated carbon loaded with cerium, J Porous Mater, 19 (2012) 713-719.