Full Length Article

Graphene oxide/mixed metal oxide hybrid materials for enhanced adsorption desulfurization of liquid hydrocarbon fuels

Robert Menzel [a,c,*,1], Diana Iruretagoyena [b,*,1], Yifan Wang [a], Salem M. Bawaked [d,e], Mohamed Mokhtar [d,e], Shaeel A. Al-Thabaiti [d,e], Sulaiman N. Basahel [d,e], Milo S.P. Shaffer [a]

[a] Department of Chemistry, Imperial College, London SW7 2AZ, UK
[b] Department of Chemical Engineering, Imperial College, London SW7 2AZ, UK
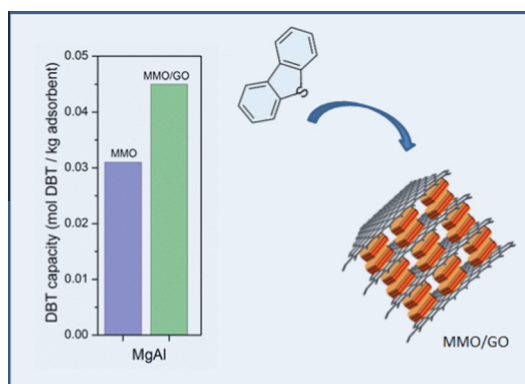[c] Bio Nano Consulting, The Gridiron Building, One Pancras Square, London N1C 4AG, UK
[d] Department of Chemistry, Faculty of Science, King Abdulaziz University, Jeddah, Saudi Arabia
[e] Surface Chemistry and Catalytic Studies Group, King Abdulaziz University, Jeddah, Saudi Arabia

HIGHLIGHTS

- Sulfur uptake using MMOs supported on GO was studied for the first time.
- Sulfur uptake and stability of MMOs is enhanced by the presence of GO.
- GO-MMOs show good selectivity for organosulfur compounds over sulfur-free aromatics.

GRAPHICAL ABSTRACT

ARTICLE INFO

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 5 wt% 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.

* Corresponding authors. Present address: School of Chemistry, University of Leeds, Leeds LS2 9TJ, UK (R. Menzel).
E-mail addresses: R.Menzel@leeds.ac.uk (R. Menzel), d.iruretagoyena09@imperial.ac.uk (D. Iruretagoyena).
[1] These authors contributed equally to the work.

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 TiO_2 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 sulfur-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

2.1. 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 m²/g) and the measured specific surface area of the MgAl-MMO nanoparticles (135 m²/g, Table 1), small quantities of the more expensive GO should be sufficient to promote the formation of true hybrid materials.

2.2. 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 elemental 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.