Magnetic composites based on metallic nickel and molybdenum carbide: A potential material for pollutants removal

Raquel V. Mambrini^a, Thales L. Fonseca^a, Anderson Dias^b, Luiz C.A. Oliveira^a, Maria Helena Araujo^a, Flávia C.C. Moura^{a,*}

^a Departamento de Química, Universidade Federal de Minas Gerais, Belo Horizonte, MG 31270-901, Brazil

^b Departamento de Química, Universidade Federal de Ouro Preto, Ouro Preto, MG 35400-000, Brazil

HIGHLIGHTS

- New magnetic molybdenum carbide composites can be prepared by CVD from ethanol.
- Magnetic molybdenum carbide shows promising results for pollutants removal.
- The carbide composites can be easily recovered magnetically and reused.

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ABSTRACT

New magnetic composites based on metallic nickel and molybdenum carbide, Ni/Mo₂C, have been produced via catalytic chemical vapor deposition from ethanol. Scanning electron microscopy, thermal analysis, Raman spectroscopy and X-ray diffraction studies suggest that the CVD process occurs in a single step. This process involves the reduction of NiMo oxides at different temperatures (700, 800 and 900 °C) with catalytic deposition of carbon from ethanol producing molybdenum carbide on Ni surface. In the absence of molybdenum the formation of Ni/C was observed. The magnetic molybdenum carbide was successfully used as pollutants removal by adsorption of sulfur and nitrogen compounds from liquid fuels and model dyes such as methylene blue and indigo carmine. The dibenzothiofene adsorption process over Ni/Mo₂C reached approximately 20 mg g⁻¹, notably higher than other materials described in the literature and also removed almost all methylene blue dye. The great advantage of these carbide composites is that they may be easily recovered magnetically and reused.

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1. Introduction

Transition metal carbides have been widely investigated in recent years because of their good catalytic activity and selectivity for hydrogenation, hydrodesulfurization and hydrodenitrogenation reactions in petroleum refining [1]. Among them molybdenum carbide has been extensively studied due to its unique physical and chemical properties including mechanical hardness, thermal stability, superconductivity and surface reactivity. Also, it has been reported that it possesses catalytic behavior comparable to noble metals [2–4]. The synthesis of Mo₂C is typically carried out using Temperature Programmed Reaction (TPRe) where molybdenum oxide is heated under an atmosphere of hydrogen/hydrocarbon (e.g. CH₄, C₂H₆, C₂H₂, etc.) [5–7]. Herein we report the preparation of the

magnetic composite Ni/Mo₂C via chemical vapor deposition (CVD) using ethanol as the carbon source.

Magnetic particles have many potential technological applications, e.g. support for catalysts [8,9], magnetic resonance imaging [10,11], drug delivery [12], adsorption processes [13,14] and environmental remediation [8,15–17]. Magnetic particles can be coated with a protective layer of different materials to improve their stability and to introduce new surface properties and functionalities. Some of these coating materials are silica [18], alumina [19], gold [20], and polymers, such as polystyrene [21], polyaniline [22], polymethyl methacrylate [23] and polyacrylamide [24]. Carbon is a versatile coating material due to its chemical stability, biocompatibility, possibility of surface modification and pore creation [25], and have been used as efficient adsorbent in different applications.

The use of commercial fuels and the emissions from refineries are of great environmental impact and are among the main targets of the new environmental standards that suggests the reduction of sulfur and nitrogen in fuels like gasoline and oil diesel. The removal of these compounds is a major operation in petroleum refining and

* Corresponding author. Tel.: +55 31 34097556; fax: +55 31 34095700.

E-mail address: flaviamoura@ufmg.br (F.C.C. Moura).

is achieved by catalytic processes operated at high pressures and temperatures [24,25]. The developed of new materials capable of lowering these reaction conditions have been intensively investigated [26].

In this work we describe the preparation and characterization of new magnetic composites based on metallic nickel and molybdenum carbide covered with carbon and their use as adsorbent of sulfur and nitrogen compounds using as model molecules dibenzothiophene and quinoline. The adsorption of organic dyes has also been investigated.

Transition metal carbides are considered as the new promising catalysts and have been widely investigated in recent years because of their good catalytic activity and selectivity in hydrogenation, hydrodesulfurization, and hydrodenitrogenation in petroleum refining [1].

Molybdenum carbide has been extensively studied due to its unique physical and chemical properties including mechanical hardness, thermal stability, superconductivity, and surface reactivity. Also, it is reported that molybdenum carbide possesses catalytic behavior comparable to the noble metals [2–4].

The synthesis of molybdenum carbide is typically carried out using Temperature Programmed Reaction (TPRe) where a given amount of the molybdenum oxide is heated while it is exposed to a mixture of hydrogen with a hydrocarbon like CH_4 , C_2H_6 , C_2H_2 , etc. [5–7]. Herein we report the production of molybdenum carbide covering the surface of Ni^0 metallic. The magnetic composite $\text{Ni}/\text{Mo}_2\text{C}$ was obtained by chemical vapor deposition (CVD) using ethanol as carbon source. Magnetic particles have many potential technological applications in different areas, such as in catalysis as support [8,9], in biomedicine as magnetic resonance imaging [10,11] in drug delivery, in adsorption process [13,14] and in environmental remediation [8,15–17]. Magnetic particles can be coated with a protective layer of different materials to improve their stability and to introduce new surface properties and functionalities. Some of these coating materials are silica [18], alumina [19], gold [20], and polymers, such as polystyrene [21], polyaniline [22], polymethyl methacrylate [23] and polyacrylamide [24]. Carbon is a versatile coating material due to its chemical stability, biocompatibility, possibility of surface modification and pore creation [25], and have been used as efficient adsorbent in different applications.

The use of commercial fuels and the emissions from refineries are of great environmental impact and are among the main targets of the new environmental standards that suggest the reduction of sulfur and nitrogen in fuels like gasoline and oil diesel. The removal of these compounds is a major operation in petroleum refining and is achieved by catalytic processes operated at high pressures and temperatures [26,27]. Therefore research has been developed for new material capable of lowering the conditions reactions to removal of sulfur compounds and nitrogen compounds [28].

The study of magnetic particles coated with carbon for sulfur and nitrogen removal is of great interest. In this work the produced magnetic molybdenum carbide was used as an adsorbent of sulfur and nitrogen compounds using model molecules dibenzothiophene and quinoline and also has been used as organic dyes adsorbent.

2. Experimental

Commercially available solvents and reagents of high purity were used as received. Nickel oxide, NiO , was obtained by heating 2 g of nickel chloride, NiCl_2 , (*Synth*) in air $10^\circ\text{C min}^{-1}$ up to 450°C during 4 h. NiO was impregnated with $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$ (Rio-Lab) at different Ni:Mo molar ratios to produce NiMo oxides. For the preparation of Ni/C or $\text{Ni}/\text{Mo}_2\text{C}$ a chemical vapor deposition (CVD) reaction using ethanol (*Synth*) as carbon source was investigated. About 500 mg of NiO or Ni/Mo oxides in a quartz tube of 30 mm

diameter was placed in the central part of the oven and heated at $10^\circ\text{C min}^{-1}$ up to 700, 800 and 900°C , and then a CVD process was carried out using ethanol (80 mL min^{-1}) in N_2 for 1 h, after which time the system was allowed to cool to room temperature under argon flow.

Raman spectroscopy was carried out using a Horiba/Jobin-Yvon LABRAM-HR spectrometer with the 632.8 nm line of a helium–neon laser (effective power of 6 mW at the sample surface) as excitation source, diffraction gratings of 600 and 1800 grooves/mm, Peltier-cooled CCD detector, confocal Olympus microscope ($100\times$ magnification), and experimental resolution of typically 1 cm^{-1} for 10 accumulations of 30 s.

The powder XRD data were obtained in a Rigaku model Geigerflex equipment using $\text{CuK}\alpha$ radiation and scanning from 2° to 75° (2θ) at a scan rate of 4 min^{-1} . Magnetization measurements were carried out in a magnetometer LakeShore 7404 VSM System. The surface area was determined by nitrogen adsorption using the BET method with 22 nitrogen adsorption/desorption cycles in an Autosorb 1 Quantachrome instrument. Scanning electron microscopy (SEM) analyses were carried out in a Jeol JSM 840A and a Quanta 200 ESEM-FEG from FEI. Adsorption experiments were carried out with 30 mg of the magnetic composites and 5 mL of quinoline, dibenzothiophene or dye (methylene blue or indigo carmine) solutions (50 mg L^{-1}). All systems were kept for 24 h at room temperature. The concentrations of the dyes were measured by UV/Vis spectrophotometry using an UV mini-1240 Shimadzu. The consumption of quinoline and dibenzothiophene were monitored by gas chromatography (Shimadzu, GC17A model equipped with a FID detector) using an Equity-5 column and argon as carrier gas. Zeta potential at different pH's were measurement using a Dispersion Technoly, Inc., model: DT1200 SN:447.

3. Results and discussion

3.1. Preparation and characterization of magnetic composites

The magnetic composites were prepared by chemical vapor deposition reaction with ethanol as the carbon source at 700, 800 and 900°C , using NiO and NiMo oxides, which are not magnetic, as starting materials. All the materials became strongly magnetic after the ethanol/CVD process and presented very low specific area *ca.* $15\text{ m}^2/\text{g}$, which is expected considering the preparation method.

Diffraction patterns of the materials (Fig. 1a) showed that the ethanol reduced Ni^{2+} (NiO) to form Ni/C composites. Metallic nickel was formed at 700°C and a small amount of carbon was produced on its surface (Fig. 1a in detail). When molybdenum is introduced (NiMo oxides) the formation of carbon is preferentially observed at 700°C . However, at higher temperatures (800 – 900°C) the carbon amount decreases to form higher quantities of molybdenum carbide, Mo_2C . The presence of metallic nickel in all samples can explain the magnetic behavior of the materials due to its high saturation magnetization presented by Ni^0 . This magnetic property is very useful to the adsorption applications that allow the materials to be easily removed from de reactions system by application of a magnetic field.

Regarding the removal of the magnetic particles from a catalytic reaction by means of the application of a magnetic force, this magnetic force will be proportional to the field gradient applied and to the magnetic moment of the particles. Hence, the magnetic force acting in the particle will be proportional to its magnetization. In consequence if the field applied is sufficient to saturate the particle then the magnetic force will be proportional to the saturation magnetization of the particle. The magnetic properties of these materials are strategic and very important for the intended application. Being magnetic, the materials can be removed easily from a

Fig. 1. XRD for the Ni/C (a) and Ni/Mo₂C (b), after ethanol/CVD process at different temperatures.

reaction system after application of a magnetic field gradient and be pulled into the strongest magnetic field region facilitating their removal [29].

The room-temperature magnetization curve (Fig. 2) shows a saturation magnetization value of 49.9 and 13.2 emu g⁻¹, for Ni/C 800 and Ni/Mo₂C 800, respectively. These saturation magnetization values are coherent once the sample Ni/C presents higher amount of Ni compared to Ni/Mo₂C.

Scanning electron micrographs of Ni and NiMo oxides after ethanol/CVD process are shown in Figs. 3 and 4, respectively. Ni particles were partially coated with filamentous carbon as can be seen in the SEM images of all NiO samples after CVD (Fig. 3). In some cases it is possible to observe carbon filaments, approximately 1 μm long and diameters of a few nanometers and also some Ni particles completely coated by carbon. In contrast, when Mo is introduced in the sample the morphology completely changes (Fig. 4). The ethanol/CVD process of NiMo oxides produces higher amounts of coated materials probably by the formation of molybdenum carbide as suggested by XRD.

Further information regarding the carbon structures was obtained by Raman spectroscopy (Fig. 5). In the Raman spectra of the NiO after CVD it is possible to see two intense bands attributed to D and G-bands of carbon materials, suggesting the formation of the Ni/C composites. The G-band, related to the vibration of sp² hybridized carbon in the two-dimensional graphite for ordered carbon species, can be observed at 1578 cm⁻¹. The D-band is highly

sensitive to amorphous carbon or defects in the carbon materials and appears at 1331 cm⁻¹ and can be ascribed to the defects in the fibrous carbon structure. The intensity of the D-band in comparison with the graphitic carbon G-band suggests that defective carbon is more abundant in the sample after ethanol/CVD at 700 °C. The more intense and narrow G-band with I_G/I_D ratio of 4.3, observed as the ethanol/CVD process temperature increases, reflects the more organized and crystalline carbon structures. This organized carbon was also observed in the XRD patterns with reflection peaks with 2θ at approximately 26°.

The Raman spectra of the Ni/Mo₂C material after the ethanol/CVD process shows characteristic bands of molybdenum carbide, Mo₂C [30], as the main product, in agreement of XRD patterns. Also some peaks can be observed related to G and D band for carbon.

The amounts of carbon deposited on the materials were estimated by thermal analysis TG/DTG (Fig. 6). For all Ni/C composites, it is possible to observe a weight loss between 500 and 620 °C related to carbon oxidation according to Eq. (1), and a weight gain related to Ni oxidation (Eq. (2)) at higher temperatures (Fig. 6a and b).

Therefore, the results clearly show that the temperature of the ethanol/CVD process directly affects the amount of carbon deposited on the surface of the materials with 14, 16 and 19%, for the samples treated at 700, 800 and 900 °C, respectively. Also, it is interesting to observe from DTG curves (Fig. 6b) that the velocity of carbon decomposition is different for the materials prepared at 700, 800 and 900 °C. For the sample Ni/C 700 the carbon decomposes in a maximum of velocity at 512 °C and for the materials Ni/C 800 this temperatures is much higher of 616 °C. These results suggest that the carbon deposited during the CVD process at 800 °C is more stable and crystalline than the carbon deposited at 700 °C. These results are in agreement with the ones obtained by XRD with a slight increase in the intensity of the peak attributed to the carbon as well as by Raman spectroscopy that presents a pronounced increase in the intensity of the G band, related to better graphitized carbon, and specially in I_G/I_D ratio with the increase in the temperature of CVD process.

The thermal behavior of the material completely changes with the addition of molybdenum. It is possible to observe an initial weight gain after 350 °C related to the Ni oxidation (Eq. (2)). At higher temperatures (ca. 800 °C) it is possible to observe a weight loss that can be related to decomposition of the very stable

Fig. 2. Magnetic hysteresis curves for the Ni/C800 and NiMo/C800 materials and in detail magnetic separation of the materials after utilization.

Fig. 3. SEM images of Ni/C obtained by ethanol/CVD process at 700 °C (Ni/C700), 800 °C (Ni/C800), and 900 °C (Ni/C900).

molybdenum carbide, forming molybdenum oxide (Eq. (3)), confirmed by the XRD results obtained for the TG residue.

Also, a strong increase in the amount (50%) of carbon deposited as carbide on the materials is observed for the Ni/Mo₂C materials (Fig. 6c and d) at 900 °C.

TG results strongly indicate that the carbonaceous materials in Ni/Mo₂C materials are completely different from those without Mo. The first one decomposes at 700 °C and for the latter the decomposition starts at 480 °C. We believe that these results are related to the decomposition of very stable and highly crystalline molybdenum carbide formed during the CVD process, as observed by XRD. On the other hand, the oxidation of carbon at 480 °C is related to the formation of a less crystalline carbon, such as graphite or carbon filaments. It is easy to observe that the temperature of nickel oxidation increase with the temperature of CVD. Probably the

highest the temperature of CVD the higher the coating of Ni particles by Mo₂C, making the Ni more difficult to oxidize.

From the results presented above we proposed that the ethanol decomposition mechanism to form the carbonaceous phases in the solid phase seems to be different in the molybdenum presence. Metallic nickel showed activity for ethanol decomposition, especially at high temperatures, to form graphitic or amorphous carbon. However, in the presence of molybdenum, initially the reaction with ethanol takes place with the activation of ethanol to form atomic carbon on the surface of the particles with chemical reduction of Ni and Mo. In a second step, the reduced molybdenum is able to react with the carbon to form highly crystalline and stable molybdenum carbide. In this step, the surface of nickel remains in the metallic form (Ni/Mo₂C). It is interesting to note that the presence of molybdenum inhibits the formation of graphitic carbon on the nickel surface (Fig. 7), which avoids the poisoning of surface nickel with carbon deposits.

Fig. 4. SEM images of Ni/Mo₂C obtained by ethanol/CVD process at 700 °C, 800, and 900 °C.

The formation of the Ni/Mo₂C composite was studied with different amounts of molybdenum. The CVD process was carried out with Ni oxide impregnated with different Ni:Mo molar ratio (NiMo, NiMo_{0.5} and NiMo_{0.25}).

The XRD (Fig. 8) and Raman (Fig. 9) analyses of the materials show that the molybdenum carbide amount increases with the molybdenum impregnation. This increase happens concomitantly with a decrease of carbon formation. These results are in agreement with the proposal in Fig. 7 that molybdenum favors the activation of ethanol compared to the carbon formation on the nickel surface.

3.2. Adsorption studies

The magnetic Ni/C and Ni/Mo₂C materials obtained by CVD at different temperatures were used as adsorbents for different contaminants, *i.e.* dibenzothiophene, quinoline, and organic dyes methylene blue (MB) and indigo carmine (IC). The obtained results are shown in Figs. 10 and 11.

The adsorption of IC dye in the Ni/C composites is low, 32, 22 and 22% for the materials treated at 700, 800 and 900 °C,

respectively. The adsorption of MB was lower (less than 10%) for all Ni/C materials (Fig. 10a).

After addition of Mo, Ni/Mo₂C, it is possible to observe that the adsorption capacity strongly increases (Fig. 10b). This is likely due to interactions of the molybdenum carbide coating with the dye molecules. Moreover, it is worth noting that the treatment temperature led to a completely different behavior of the adsorption properties of the materials.

Adsorption of IC dye on composites treated at 700 and 800 °C are relatively low, *i.e.*, 43 and 31%, respectively. However, the adsorption of methylene blue is very high, reaching almost 100% after 20 min. A different behavior was observed for the composite treated at 900 °C with adsorption capacities of 34% for methylene blue and 99% for indigo carmine. These results suggest that, beyond the hydrophobic interaction, the electronic characteristics of the dyes are also an important factor in the adsorption properties on the materials surface.

In order to understand these electrostatic interactions between the dyes and the adsorbent materials, zeta potential measurements at different pH were carried out (Fig. 12). The zeta potential at different pH curves allows the determination of the point of zero charge

Fig. 5. Raman spectra of the composite Ni/C (a) and Ni/Mo₂C (b), obtained after ethanol/CVD process at different temperatures.

Fig. 6. TG and DTG curves of the Ni/C (a and b) and Ni/Mo₂C (c and d), obtained after ethanol/CVD process at different temperatures, in air.

Fig. 7. Representation of the reaction of Ni and NiMo oxides with ethanol during the CVD process to form the magnetic composites.

Fig. 8. XRD analyses of the Ni/Mo₂C with different amounts of molybdenum, obtained by CVD of ethanol at 800 °C.

Fig. 9. Raman spectra of the Ni/Mo₂C with different amounts of molybdenum, obtained by CVD of ethanol at 800 °C.

(PZC) of the materials and an evaluation of the surface charge of the particles under study.

Fig. 12 shows a point of zero charge (PZC) at pH 2.6 and 3.0 for the Ni/Mo₂C 700 and Ni/Mo₂C 800 materials, respectively. Since the initial pH of the dye solutions was 4.0, those results indicated that the surface of the materials is negatively charged and therefore preferentially adsorb positively charged molecules such as methylene blue dye. On the other hand, the Ni/Mo₂C 900 material,

with PZC at pH 5.1, would have a positively charged surface at pH 4.0 and therefore would absorb more anionic dyes such as indigo carmine.

The type of carbon produced by the CVD process, in the presence of Mo, may explain the higher adsorption properties of the Ni/Mo₂C composites, once the specific area are very similar for all the materials. Moreover, chemical groups such as phenolic, carboxylic acid

Fig. 10. Structure of methylene blue (a), indigo carmine (b), dibenzothiophene (c), and quinoline (d).

Fig. 11. Indigo Carmine and methylene blue adsorption for the Ni/C (a), and Ni/Mo₂C (b) materials, obtained after the ethanol/CVD process at different temperatures (pH = 4, natural pH of the dye solution).

Fig. 12. Zeta potential measurements for Ni/Mo₂C materials obtained after ethanol/CVD process at 700, 800 and 900 °C.

can be formed on the carbon, which can influence the adsorption process.

Another group of pollutants (nitrogen and sulfur compounds) was tested in the adsorption process. The preliminary results

are displayed in Fig. 13. In general, the molybdenum carbide presents a slightly better adsorption capacity compared to the material without Mo. The best adsorbent was the Ni/Mo₂C 700 with an adsorption capacity of approximately 20 mg g^{-1} , which is higher in comparison with other materials described in the literature.

The magnetic properties can be useful for the separation of the adsorbent from the reaction mixture, which may be recovered after been used in the adsorption process. The material with adsorbed pollutants was separated by a magnetic field, from the mixture. Then, the material was washed with ethanol to release the pollutants, dried at 60 °C, and the regenerated materials were used as adsorbent in a new solution. After 4 cycles of adsorption/desorption the sample still showed almost the same adsorption capacity (Supplementary material).

Analyses of the liquid mixtures after the adsorption experiments by atomic absorption spectrometry did not show any significant concentration of Ni or Mo ions in solution. Moreover, kinetic experiments showed that the adsorption stopped when the material was magnetically removed from the medium. These results strongly suggest the occurrence of the adsorption in heterogeneous phase.

These results and promising catalytic activity accredited them to be used in catalytic processes that use catalysts to replace noble metals as an active phase.

Fig. 13. Adsorption of dibenzothiophene and quinoline on Ni/C (a), and Ni/Mo₂C (b) obtained after ethanol/CVD process at different temperatures.

4. Conclusion

The CVD reaction of Ni and NiMo oxides with ethanol at temperatures ranging from 700–900 °C produces magnetic composites based on Ni magnetic particle with carbonaceous material deposits Ni/C and Ni/Mo₂C.

Preliminary studies in the use of the magnetic composites as adsorbent of model dyes and especially for dibenzothiophene and quinoline, important contaminants in the liquid fuels present great potential to be used in technological applications. The great advantage of these composites is that they could be easily recovered magnetically and reused.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.jhazmat.2012.09.002>.

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