



Ion-exchange synthesis of Cr (III), Co(II) and Hg(I) doped dolomite for H₂S capture

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Abstract In the present work, Cr (III), Co(II) and Hg(I) doped dolomite are employed as H₂S capture agents. The X-ray diffractions pattern shows that nor the doping process neither the H₂S capture have affected the nanostructure of dolomite. The gravimetric obtained results for hydrogen sulfide capture are: 2.4 mg/g (DOL-Cr), 8.8 mg/g (DOL-Co), and 2.4 mg/g(DOL-Hg). The un-doped dolomite exhibits a H₂S capture capacity of only 0.4 mg/g. The FTIR results suggest that the higher H₂S capture capacity of the cobalt-doped sample, could be related with the presence of pre-adsorbed water molecules.

Keywords Hydrogen sulfide, Dolomite, Clay, Metal doping

Introduction

As it is well known today, Hydrogen sulfide is a major air pollutant entering the atmosphere, and can contaminate water and soil. So, it is very important to develop methodologies able to promote its withdraw from air, water or soil.

Taking into account that they are present all around the world, as well as its non toxic (except from inhalation) nature and cheap prices, clays are very good potential matrices for solid-gas adsorption, as well as for solid-solution compounds as shown for crude oil adsorption on vermiculite [1,2].

In the present work, Co(II) and Hg(I) doped dolomite are employed as H₂S capture agents.

Experimental

Chromium (III), cobalt (II) and mercury (II) doped dolomite were prepared as follows: 10g of dolomite was suspended in 100 mL of a 0.5 mol/L aqueous solution of COCl₂ (or 100 mL of a 0.05 mol/L aqueous solution of Hg₂Cl₂ or a 0.05 mol/L aqueous solution of Cr(NO₃)₃) for 24 h and mechanically stirred (300 pm). Then, the prepared matrix was filtered off and washed with distilled water and dried under vacuum at room temperature (28 °C). The doped matrices will be named, hereafter, as DOL-Cr, DOL-Co and DOL-Hg.



The hydrogen sulfide (H_2S) employed to adsorption on the modified matrices were prepared by reacting FeS with concentrated HCl . The adsorption processes were performed as follows: about 2.4 cm^3 of the modified matrix was confined in a glass reactor through which a H_2S flux ($10 \text{ cm}^3/\text{min}$) was passed by 30 minutes. The total mass of employed modified matrices was measured in an analytical balance before and after the H_2S . So, the total amount of adsorbed H_2S per gram of modified matrix was determined gravimetrically.

The X-ray diffraction patterns were obtained in a Rigaku diffractometer model Miniflex II, with a scan rate of $5^\circ/\text{min}$, applied voltage of 15 kV and current 15 mA , using $\text{Cu K}\alpha$ radiation and a Ni filter.

The infrared spectra were ($4000\text{-}400 \text{ cm}^{-1}$) were obtained in KBr pellets, by using a Perkin-Elmer FTIR (model spectrum 65) apparatus.

X-ray fluorescence analysis were performed in a EDX-720 Shimadzu apparatus.

Results and Discussion

The gravimetric obtained results for hydrogen sulfide capture are: 2.4 mg/g (DOL-Cr), 8.8 mg/g (DOL-Co) and 2.4 mg/g (DOL-Hg). The un-doped dolomite exhibits a H_2S capture capacity of only 0.4 mg/g .

It is worth noting that such adsorption capacities are well above those verified for 13X and 5A zeolites [3] and for pillarized montmorillonite [4] and about 20% higher than that exhibited by rhodamine B recovered kaolinite [5].

The obtained X-ray diffraction pattern obtained for the un-doped matrix is shown in Figure 1. It was verified that the employed dolomite exhibits a little contamination with quartz.

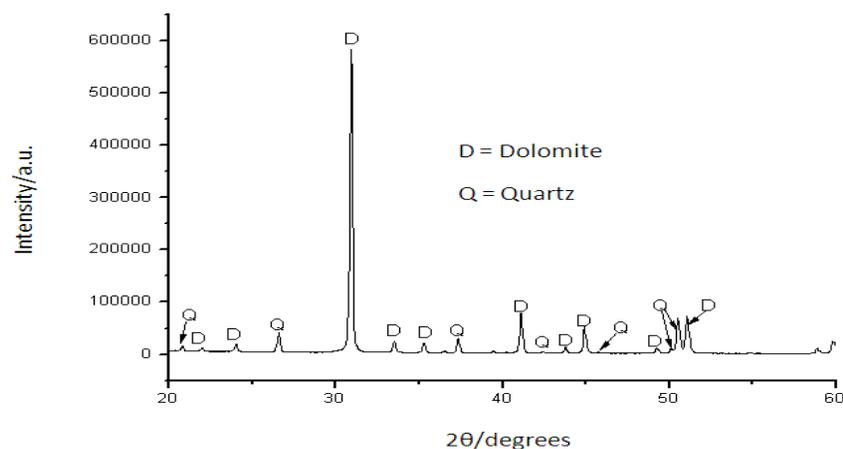


Figure 1: X-ray diffraction patterns for the un-doped dolomite sample

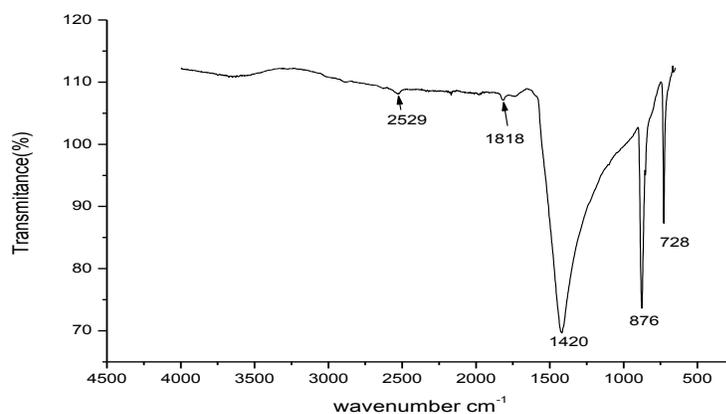


Figure 2: FTIR spectrum for un-doped dolomite



The X-ray diffraction patterns for DOL-Cr, DOL-Co and DOL-Hg, as well as the H₂S reacted matrices (not shown) exhibits the same diffraction peaks of the un-doped dolomite. Hence, can be concluded that nor the doping process neither the H₂S capture have affected the nanostructure of dolomite.

The FTIR spectrum for the un-doped dolomite sample is shown in Figure 2. As can be verified, only the characteristic peaks of dolomite are observed, such as out of plane deformations (876 cm⁻¹), symmetric stretching (1420 cm⁻¹), in plane deformations (713 cm⁻¹), as well as combination band at 1818 and 2529 cm⁻¹, characteristics of carbonate.

None Si-O-Si (very intense peak in 1051 cm⁻¹, in SiO₂, for example). Hence, can be concluded that the quartz contamination detected by X-ray diffractometry is a minor one.

The FTIR spectrum of the H₂S reacted un-doped sample (not shown) do not exhibits any modification, IF compared with Figure 1 spectrum.

The FTIR spectra for DOL-Co and DOL-Hg, before and afeter reaction with H₂S are shown in Figure 3. As can be verified, Co(II) doped samples exhibits the characteristic OH stretching band around 3300 cm⁻¹. On the contrary, Hg(I) doped samples do not exhibits such bands.

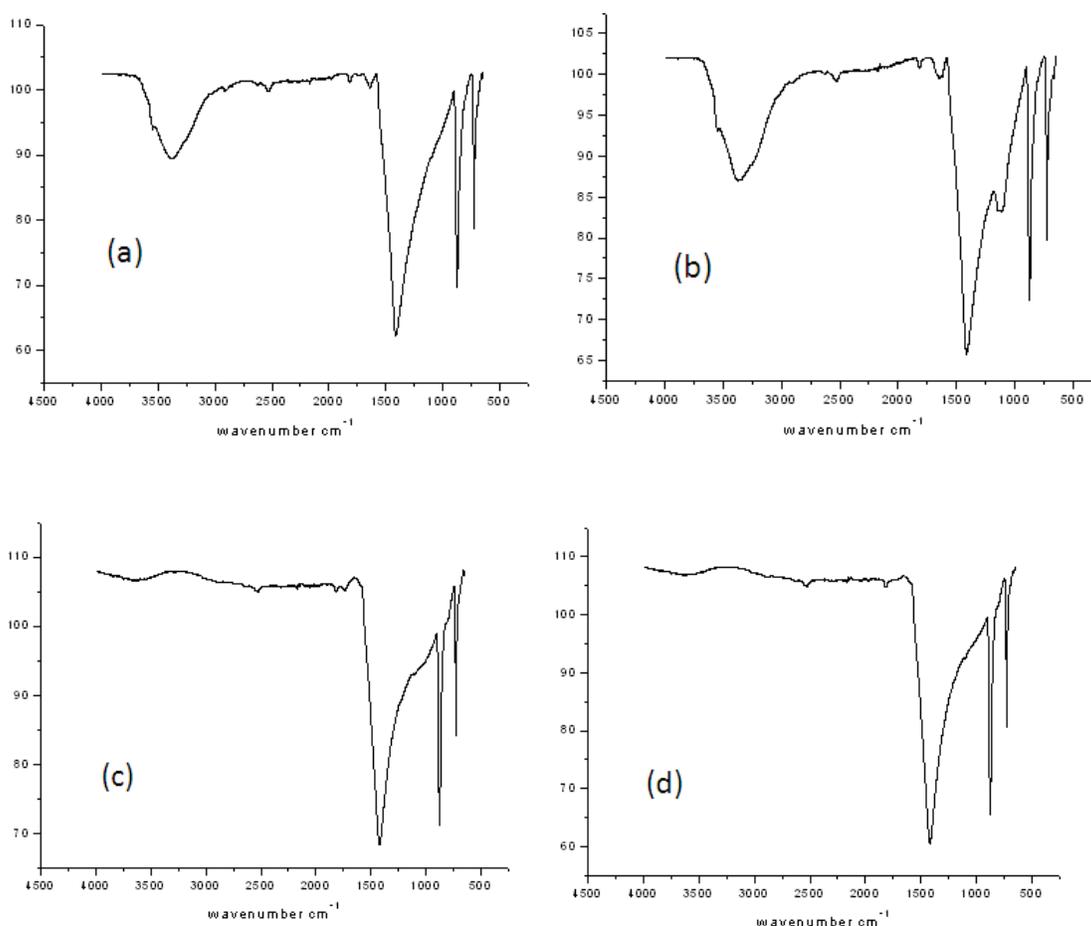


Figure 3: FTIR spectra for DOL-Co (a), DOL-Co-H₂S (b), DOL-Hg (c) and DOL-Hg-H₂S (d)

Such fact can be related with the higher H₂S capture capacity of the cobalt-doped sample, since, as verified for activated carbons, the presence of a sufficient amount of water pre-adsorbed on the carbon surface can plays an important role in the process of H₂S adsorption [6].

Furthermore, taking into account that the coordination number for Co(II) is six (octahedral geometry), whereas for Hg(I) it is four (tetrahedral geometry), it is possible to suppose that there are a higher number of H₂S molecules coordinated to each metal cation when the matrix is cobalt-doped.



Additionally, it is important to consider the hard and soft acid and bases model [7]: Co^{2+} is a borderline acid, whereas Hg^+ (in reality, Hg_2^{2+} since it is a dimer), is a soft one. Sulfur can be considered, depending on its chemical neighborhood, a soft or a borderline basic site. In H_2S is a borderline one. So, there is a higher affinity between the pair $\text{Co}^{2+}\text{-SH}_2$ than the $\text{Hg}^+\text{-SH}_2$ pair.

The elemental analysis results (as mass %) based on X-ray fluorescence data for DOL-Co and DOL-Hg matrices are: $\text{Co}_2\text{O}_3 = 11.3\%$ and $\text{HgO} = 35.3\%$. In the H_2S reacted samples, the SO_3 percentages are: 14.7% for DOL-Co and 10.2% for DOL-Hg. So, the X-ray fluorescence data shows that the cation exchange efficiency are practically identical for Co(II) and Hg (I): 0.18 mol of Co and 0.16 mol Hg are inserted per 100g of the respective matrices.

As previously presented, the total amount of adsorbed H_2S , based on gravimetric data, are 8.8 mg/g (DOL-Co) and 2.4 mg/g (DOL-Hg). Considering a sample of 100 g, the total amount of adsorbed H_2S (mol) are 0.028 and 0.008, respectively. Hence, the Co(II) doped matrix has a higher H_2S removal capacity by $0.028/0.008 = 3.5$ in comparison with Hg(I) matrix. A distorted octahedral environment around Co(II) can be supposed.

Comparing X-ray fluorescence (for metal cation exchange) data with gravimetric (for H_2S capture) data it is possible to conclude that for both matrices a minor amount of the metal cation sites are been employed. Such fact probably are related with the lower H_2S pressure (1 atm) employed in the experiments.

It is worth noting that the Dol-Co sample exhibits a higher H_2S capture capacity (8.8 mg/g) than a kaolinite-Co doped sample (4.7 mg/g) [8].

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