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Development of Porous Carbon Nanomaterials from Petroleum Waste for CO$_2$ Capture and Mineralization

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Abstract. Development of *in situ* preparation method of porous low-density carbon materials from industrial waste is important. Alkali earth metal doped porous carbon materials can serve as a support for CO$_2$ mineralization in pores to generate the final carbonate enriched porous carbons, MCO$_3$-PC, as a composite for potential applications in CO$_2$ capture and sequestration. Herein we report on developing mineral carbonization technology using porous carbons from vacuum residue to generate products that are best suited economically for CO$_2$ sequestration. Activating of vacuum residue (VR) using activation reagent as Ca(OH)$_2$ and MgO mixed with KOH gives a porous structure and metal particles that can react with CO$_2$. The study of the synthesized material showed the presence of nonporous carbon and alkali earth metal ions.

Introduction

Global warming or the environmental changes caused by the release of increased amounts of greenhouse gases (such as CO2) over the past several decades polluted the atmosphere which resulted in growing needs for the development of alternative and environment benign energy resources. One of the promising solutions to capture CO2 is synthesizing a nanoporous material using petroleum waste. Synthesizing nanoporous material from activating pure asphalt can be achieved by using very high temperature. However, the cost is very high. Therefore, activation agents are used to synthesis these porous material, some of these activation agents are KOH, Ca(OH)$_2$ and MgO. The purpose of this research is to produce very useful material from what is usually considered waste material. Specifically, CO2 capture and utilization.
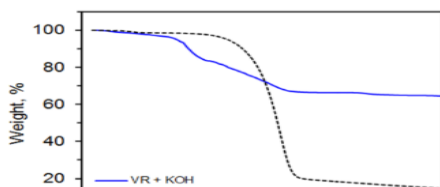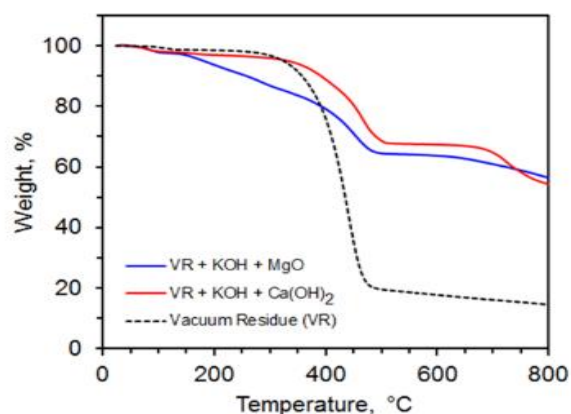
1.   Result and discussion

Figure 1. Thermogravimetric curves of vacuum residue (VR), black broken lines, and a 4/1 mixture of potassium hydroxide (KOH) and VR, blues line, (heating at 5-10 ºC min-1, under N2 atmosphere).

1.1. Thermogravimetric analysis:

Figure 2. Thermogravimetric curves of vacuum residue (VR), black broken lines, and a 1/1 mixtures of Ca(OH)2 + 4/1 mixtures of KOH with VR blue line, and MgO + 4/1 mixtures of KOH red line, (heating at 5-10 ºC min-1, under N2 atmosphere).

As it appears in the figure the vacuum residue (VR) is not losing any weight until it reaches around 350 ºC where it starts to loss its weight in a steady slope. This dramatic loss of weight stops at 450 ºC where most of the volatile compounds within VR are evaporated and it lost 80% of its original weight. After mixing it with KOH it starts to loss weight at 200ºC and it losses 20 % before it is reach 350 ºC which is the activation temperature of VR. Then with a lower rate it losses 10% between 350ºC and 450ºC. In this case the mixture losses 70% of its initial weight and most of it is in lower temperature than VR which indicate an interaction between VR and KOH

It seems that KOH does not affect Ca(OH)2 as it does with MgO where it looks activated at 400ºC where it losses 20% in a constant rate from 150 to 400 ºC. After that the rate increases to loss another 20% in the range between 400ºC and 500ºC giving us a total loss of 40%. The interaction before 400 could be result of an activation but further characterization is needed. When Ca(OH)2 is mixed with KOH it showed more stability and that can be seen in the constant weight before it reached 400ºC and the following losing. Furthermore, calcium mixture losses 30% of its

weight in the range of 400 to 500ºC which indicate its been activated
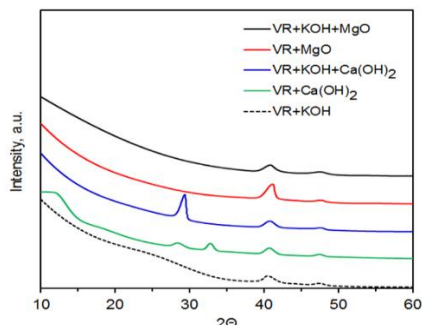
1.2. X-ray diffraction analysis

Figure 3. Powder X-ray diffraction (PXRD) pattern of the five carbon materials made from vacuum residue using different methods.

It seems that all of the mixtures have the same peak at 48 while they differ on the other peaks. Calcium compounds have peaks between 30 and 35 where the KOH CaOH2 mixture have an intense one at $30^{°}$ which found to be identical for calcite CaCO3 peak indicating its existence(1). On the other hand, from the fronting peak at 2θ 42 on MgO mixture that it stays there with lower concentration and didn't form MgCO3 ether with added KOH or pure since it does not have a peak at 2θ=30 (2) (3). For Ca(OH)2 with VR there are 2 peaks around 2θ = 30 where they indicate the presence of some unreacted Ca(OH)2 (4) . Finally, peaks at 40 are characteristic for activated carbon particle which is a proof for activation (5)(6).
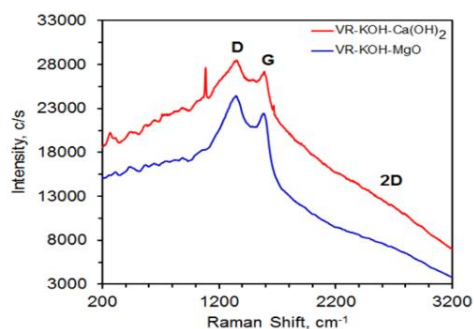
1.3. Raman analysis

Figure 4. Raman spectrum of the carbon materials made from vacuum residue using KOH, Ca(OH)2 and MgO as an activating agent.

Vacuum residue (VR) is mostly composed of carbon and hence its spectrum is similar to that of carbon. The above figure displays a typical Raman spectrum that consists of calcite and VR activated with KOH. Additional to the G band and D band, at 1100 cm-1 we can see the calcite band which is very intense which means that we have Calcite in

higher concentration than CaOH, which captured the volatile compounds in the reaction. To this end, there is not a special spectrum of VR, as in the case for different forms of amorphous carbon. Raman analysis will not be helpful with Magnesium Carbonate due to its inactivity.

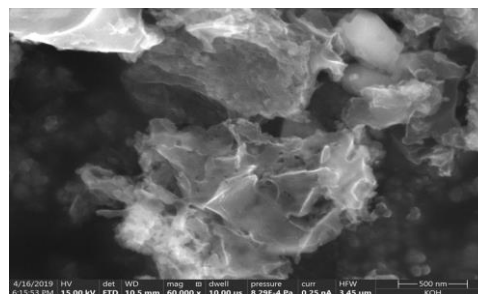## 1.4. Scanning Electron Microscope analysis

Figure 5. A picture of the (VR)+KOH at magnification of 60000 times using by Scanning Electron Microscope (SEM).

As it is clear from the morphology of the material it is rough and not uniformed at all. This lack of uniformity indicates high surface area that can accommodate more CO2. Furthermore, by zooming and focusing the porous would be clearer where it can absorb small molecules as CO2.

Conclusion

Promising preliminary results indicates a change in the vacuum residue and increase the yield of producing the porous material. These data clearly showed the forming of nonporous carbon that have metals also. The expectation for the surface area is to exceed 1000 m2/g but due to time limitation, BET analysis was not performed yet.

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