

ACTIVATED CARBONS AS CATALYST FOR SELECTIVE PARTIAL OXIDATION OF HYDROGEN SULFIDE

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Introduction

Sulfur removal from gas streams is a key process in producing high purity H₂ from fossil fuel for PEM fuel cells. Since only a small amount of H₂S is present in the fuel gas streams, the most effective and promising desulfurization approach is the direct oxidation of H₂S to sulfur by using highly selective oxidation catalysts. The reaction, $H_2S + \frac{1}{2}O_2 \rightarrow \frac{1}{n}S_n + H_2O$, is considered irreversible and limited by kinetics. Thermodynamically, this reaction has the potential to remove H₂S to the parts-per-billion level at low temperature [1]. Several porous solid materials have been found to be capable of catalyzing this H₂S oxidation [2], but their activity (conversion of H₂S) and selectivity (to elemental sulfur) depend on their chemical composition, their porous structure, and other factors [3]. A comparative study of several catalyst materials showed that activated carbon combines a high activity with a good selectivity and is one of the most suitable catalysts for practical use in an H₂S removal process [2]. Activated carbons have been used as catalysts/absorbents in removing H₂S from air, natural gas and other gas streams. Their use in catalytic partial oxidation of H₂S has also been identified as a highly promising approach for removing sulfur content in fuel cell feedstocks [4].

In the past, activated carbons derived from various precursors have been studied and different performances have been observed. The results reported by various investigators are often diverse and contradictory, especially concerning kinetics and reaction pathways. The key mechanisms for H₂S removal and the critical features in an activated carbon catalyst are still not well understood. Experiments have shown that carbon itself is the effective catalyst for H₂S oxidation, even though impurities present in some commercial active carbons are also catalysts [5]. Therefore, a careful evaluation on the roles of pore microstructure and surface chemistry of activated carbons is necessary. In this work, the catalytic activity and selectivity of several commercially available and lab-developed activated carbons from different precursors and different activation processes have been investigated. The microstructures (surface area, pore volume and pore size) of these carbons and their influences on the performance of carbon catalysts have been evaluated.

Experimental

Three commercial activated carbons were used for this study: Centaur (Calgon Carbon, bituminous coal-based, physical activation), WV-B (Westvaco, wood-based, chemical activation), VA-507 (PICA, coconut shell-based, physical activation). In addition, ORNL synthesized carbons from cellulosic materials (from NPPHARM and Matchless United

Company). They were carbonized in a Kiln furnace at 850°C (6 h dwell) in the presence of 9.4 L/min N₂ flow. About 13 g carbonized samples were then activated in a Lindberg tube furnace (model 59754-A) at 875-975°C with a CO₂ flow of 0.5 L/min. Helium was used during heating to the designed temperature and cooling down to room temperature. The activation level was controlled by varying sample holding time at the activation temperature. The samples produced at ORNL were designated as ORNLA or ORNLB followed by a numerical designation for the holding time at the activation temperature.

The nitrogen adsorption/desorption isotherms of these samples were determined at 77 K using an AUTOSORB-1 (Quantichrome Corporation). The outgas temperature was 300°C. Characteristic data derived from the isotherms are listed in Table 1. The commercial samples and the lab-made samples were also characterized by X-ray diffraction (Scintag PAD V X-ray diffractometer; Table 1). The position of the (002) peak is found using Split Pearson VII with K α 2 correction and without weighting factors for curve-fitting.

Table 1. Properties of Activated Carbon Samples

Sample	Holding time (h) /Burn-off (%)	d_{002} (Å)	BET surface area (m ² /g)	V_t (cm ³ /g)	D-R micropore volume (cm ³ /g)	D-A avg. pore diameter (Å)
Centaur		3.574	817	0.465	0.344	15.6
WV-B		-	1840	1.49	0.957	19.2
VA-507		3.767	1022	0.545	0.414	15.6
Lab-made samples						
ORNLA-0	0	3.836	425	-	-	-
ORNLA-1	1.0/16.3		1570	0.712	0.618	13.6
ORNLA-2	2.5/35.6		2010	0.890	0.761	15.0
ORNLA-3	3.5/46.1		2230	0.982	0.816	15.6
ORNLA-4	4.5/58.4		4650	2.11	1.59	17.0
ORNLB-0	0	3.828	544	-	-	-
ORNLB-1	1.0/23.8		799	0.423	0.294	11.4
ORNLB-3	3.0/57.8		2230	1.148	0.833	15.6

Catalytic experiments were conducted in a laboratory scale, fix-bed reactor system. The gas flow rates were controlled by a mass flow controller system (Omega, Model FMA-700 series controllers coupled with FMA-78P4 readout/power supply). The glass reactor tube used was 49.5 cm long with an I.D. of 1.25 cm. It is vertically positioned in an ATS single zone split tube furnace (Series 3210) in the down flow mode. Approximately 7.8 cm carbon sample is loaded in its center region. The reaction temperature is controlled by a K-type thermocouple in the furnace and monitored by another K-type thermocouple axially centered in the reactor tube. The concentrations of the exhaust gases from the reactor are monitored by a Gas Chromatography (GC) and a FTIR Spectrometer (MIDAC). The GC (Model 910, Buck Scientific, Inc.) has a 30 meter metal column (Q-Plot, Restek Corporation) and a FPD detector which can detect sulfur compounds like H₂S or SO₂ down to about 200 ppb.

Results and Discussion

The ability of activated carbons to selectively oxidize H₂S to elemental sulfur was tested by using a H₂/H₂S mixture. The experiments were conducted at 150 °C at atmospheric pressure with a space velocity of 3100 h⁻¹ (GHSV). The input H₂S concentration was 1000 ppm. Air was introduced at the inlet according to an O₂:H₂S ratio of 2:1. The selection of reaction temperature, O₂/H₂S ratio and space velocity was based on a series of tests using the commercial samples. The effects of these parameters on the catalyst performances will be presented elsewhere. In the experiments, hydrogen co-oxidation did not take place under these conditions, and no COS was detected. Figure 1 shows the H₂S conversion and SO₂ evolution of three commercial samples. It was observed that different carbon samples exhibited different catalytic activity and selectivity. The Centaur sample, which had relatively low specific surface area, pore volume and contained about 5% ash, displayed the highest catalytic activity. A 100% conversion of H₂S was observed over a 10 hour test, however sulfur over-oxidation to SO₂ started after being on stream for 2 hours. The VA-507 sample, a high purity carbon (less than 2% ash) with middle surface area and pore volume among three commercial samples, showed the lowest activity and an average selectivity. The WV-B sample with the highest surface area and micro-pore volume was seen to convert all H₂S to elemental sulfur at the beginning, but H₂S was detected at the reactor exit after being on stream for about 4 hours, and SO₂ was measured after more than 6 hours.

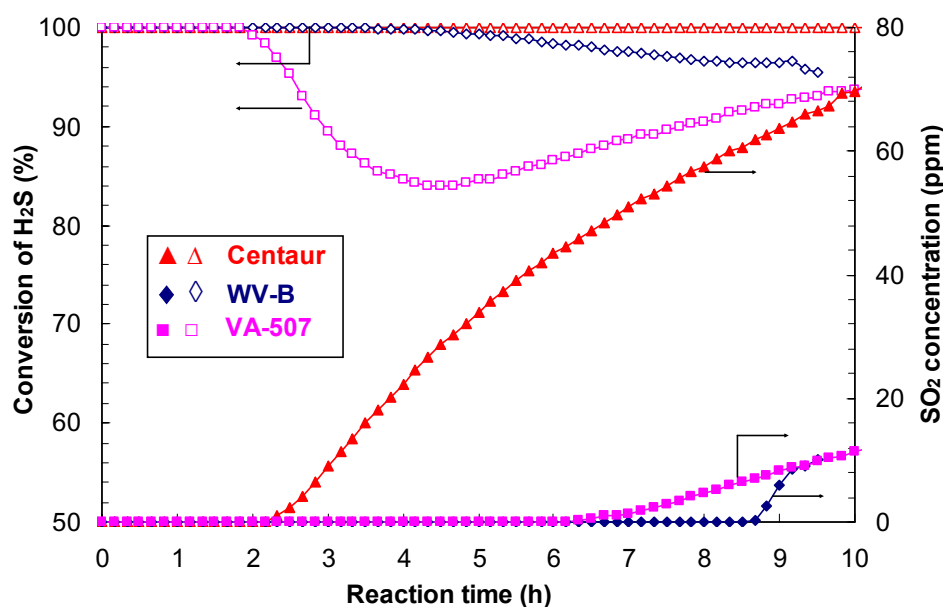


Figure 1. The catalytic behaviors of three commercial activated carbons at 150 °C.

The above results prompt old, but never fully answered questions: What is the role of carbon microstructure in H₂S catalytic oxidation? What kinds of pore structure and size distribution are desired for a good catalyst? To search for answers to these questions, two cellulosic materials, one with high purity (heavy metals ≤ 10 ppm) and one full of natural impurities, were selected as the precursors for making activated carbons. The catalytic performances of these Lab-made samples are shown in Figures 2 and 3. For ORNLA series samples, no SO₂ was detected during a 3 hour test. But emission of H₂S was detected immediately after the introduction of H₂S and air.

Obviously, these carbons displayed a very low activity, even though they all had relatively high surface area and pore volume. As listed in Table 1, an increase in burn-off level increased the specific surface area and pore volume of the ORNLA samples. This increase, however, did not result in any increase in the catalytic activity. The activity decreased with increasing surface area (Figure 2). While this observation still needs careful scrutiny, it indicates additional studies are necessary to ascertain the relationships between microstructures and catalytic behavior.

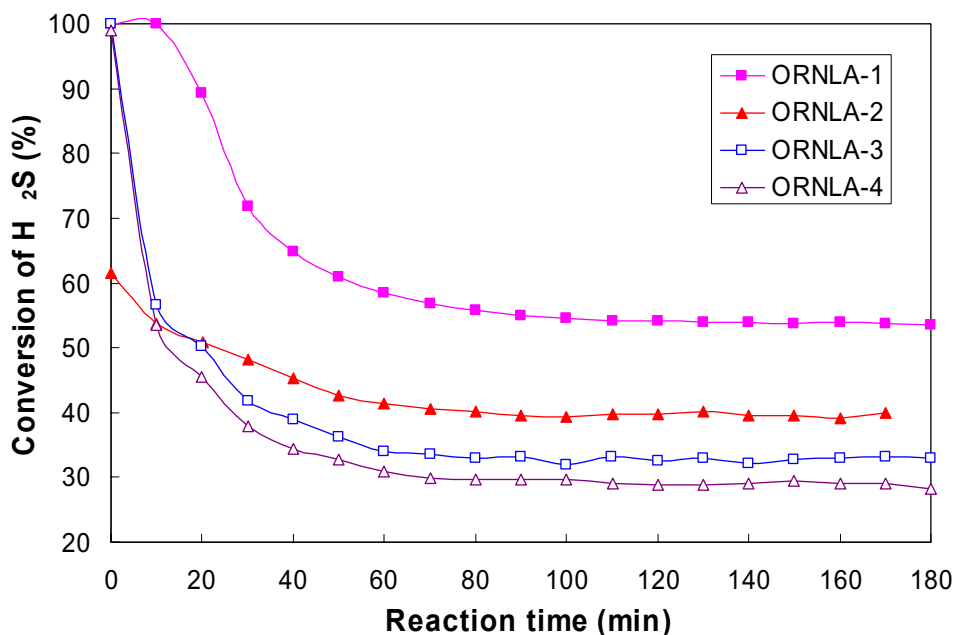


Figure 2. The catalytic behaviors of ORNLA- activated carbons at 150 °C.

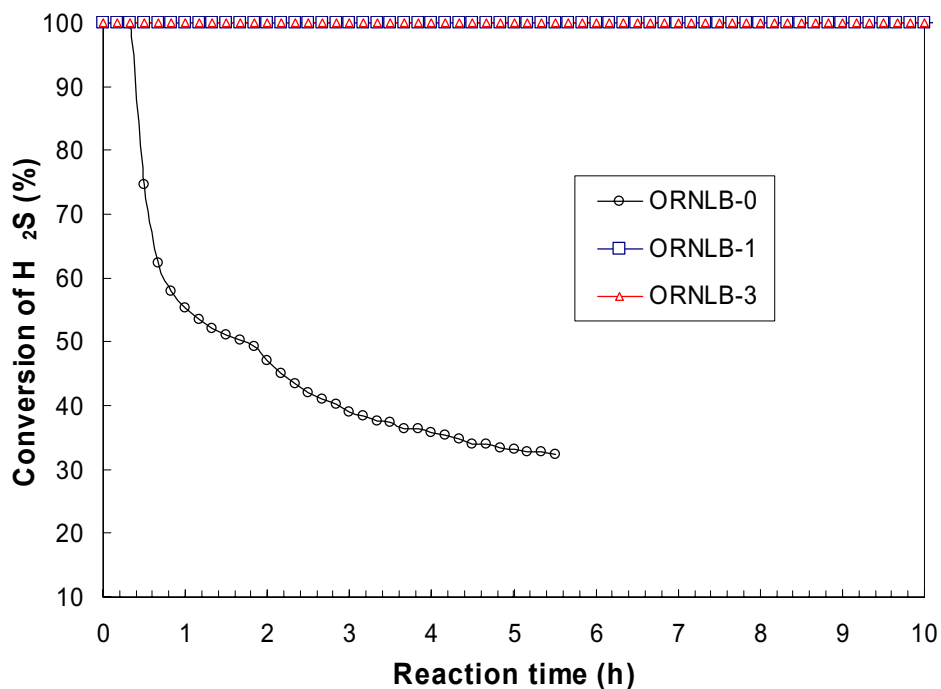


Figure 3. The catalytic behaviors of ORNLB- activated carbons at 150 °C.

As shown in Figure 3, excellent activity and selectivity were observed when activated ORNLB samples (ORNLB-1 and ORNLB-3) were used. Neither SO₂ nor H₂S was detected after they were on stream for more than 10 hours. For comparison, the carbonized sample without activation (ORNLB-0) was also tested. It showed a low catalytic activity. This observation indicates that the development of a microstructure during the activation process is an important factor for achieving high catalytic activity. In addition, the above experimental investigation reveals that impurities may also play a role in a good carbon-based catalyst. More analysis and testing, however, are required to determine the interplay. Continued research seeks to determine which impurity (or impurities) is responsible for the catalytic effects, and why it is active only in a porous structure. Our on-going works on the characterization of carbon samples and ash analysis will attempt to answer these questions.

Conclusions

Different catalytic behaviors have been observed for commercial activated carbons. At this time, no clear correlation has been found between their behaviors and their varying microstructures and impurity concentrations. Our lab-synthesized activated carbons have demonstrated good activity and high selectivity towards H₂S oxidation. On-going research will attempt to define the role of impurities and microstructure on catalytic oxidation of H₂S.

Acknowledgements

This research was sponsored by the U.S. Department of Energy, Office of Hydrogen, Fuel Cells and Infrastructure Technologies under contract DE-AC05-00OR22725 with UT-Battelle, LLC, at Oak Ridge National Laboratory. The research was supported in part by an appointment to the Oak Ridge National Laboratory Postdoctoral Research Associates Program administered jointly by the Oak Ridge Institute for Science and Education and Oak Ridge National Laboratory. Mrs. Ashli Clark is acknowledged for performing nitrogen adsorption measurements.

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