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N-doped CNT nanocatalyst prepared from camphor and urea for gas phase desulfurization: Experimental and DFT study

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ABSTRACT

In the present work, mesoporous nitrogen-doped carbon nanotubes (N-CNTs) were synthesized by using a low-cost and unique set of precursors (camphor and urea). The CVD method at 1000 °C was used with different camphor/urea ratios, and Co-Mo/MgO nanocatalyst was utilized as growth catalyst. Application of mesoporous N-CNTs in selective oxidation of H_2S was studied experimentally and N-CNTs interactions with H_2S was also investigated using DFT calculations. The as-synthesized N-CNTs were characterized using FTIR, FE-SEM, elemental analysis, X-ray diffraction (XRD), XPS and nitrogen adsorption/desorption. The N-CNT2 sample with urea to camphor ratio (U/C) of 1 showed the highest sulfur yield at the three temperatures studied for which selectivity and conversion of 89% and 97% were obtained at 190 °C. Considering experimental results, the relatively higher amount of pyridinic nitrogen (*i.e.* pyridinic and pyridinic oxide) was suggested as the reason for such high catalytic activity which was proved by quantum mechanical calculations. Further, DFT calculations were performed for elucidating the reaction and finding the most active nitrogen atoms in which the pyridinic oxide was found to be the most active followed by pyridinic. According to experiment and DFT results, the pyridinic species were determined as the most active phases of N-CNT toward H_2S oxidation.

1. Introduction

Hydrogen sulfide (H_2S) is a toxic and malodorous pollutant that can be emitted from different industrial processes [1-7]. It is highly corrosive and causes severe problems in animals and human beings [2] and there are strict rules for limiting its emission [8]. The most important process used for removing H_2S is Claus process [9] and it can remove up to 98% of it [2]. To further purify the Claus tail gas different processes such as H_2S adsorption [4] or H_2S catalytic removal [2] can be used. Among them, selective oxidation of H_2S to elemental sulfur is well-suited as a tail gas treatment process [2]. Catalysts used for removing H_2S can be classified into two major categories; Metal-based and carbon-based catalysts [2]. Iron oxide and vanadium oxide are among the most active metal based-catalysts in H_2S selective oxidation [2,8,10-12]. H_2S selective oxidation would be continuous when operating at a temperature higher than the sulfur dew point (~180 °C), whereas it would be discontinuous below its dew point. In the latter case, the catalyst needs to be regenerated over short periods of time [2]. At relatively high temperatures, metal-based catalysts perform better and carbon-based catalysts are preferred for discontinued process at lower temperatures. The main drawback of using carbon-based catalysts at temperatures higher than 180 °C is their poor selectivity [2,13,14].

Carbon based metal-free catalysts have variety of applications in catalytic [13,14] or adsorptive [15-18] processes. The tuning potential of carbon-based materials that can be achieved through tailor-designed pore and surface properties has introduced them as attractive materials in catalytic applications [19]. Carbonaceous materials in the form of activated and porous carbons (APCs) [20,21], nitrogen containing porous carbon [14], carbon nanotube (CNT) [17,22], nitrogen-doped carbon nanotube (N-CNT) [13], carbon nanofiber [23], graphene [18] have been used in H_2S removal processes.

APCs are the most studied structure of carbon used for removing H_2S selective oxidation. They are typically suitable at lower temperatures, but their selectivity decreases at higher temperatures [14,20,21]. It is claimed that in the presence of activated

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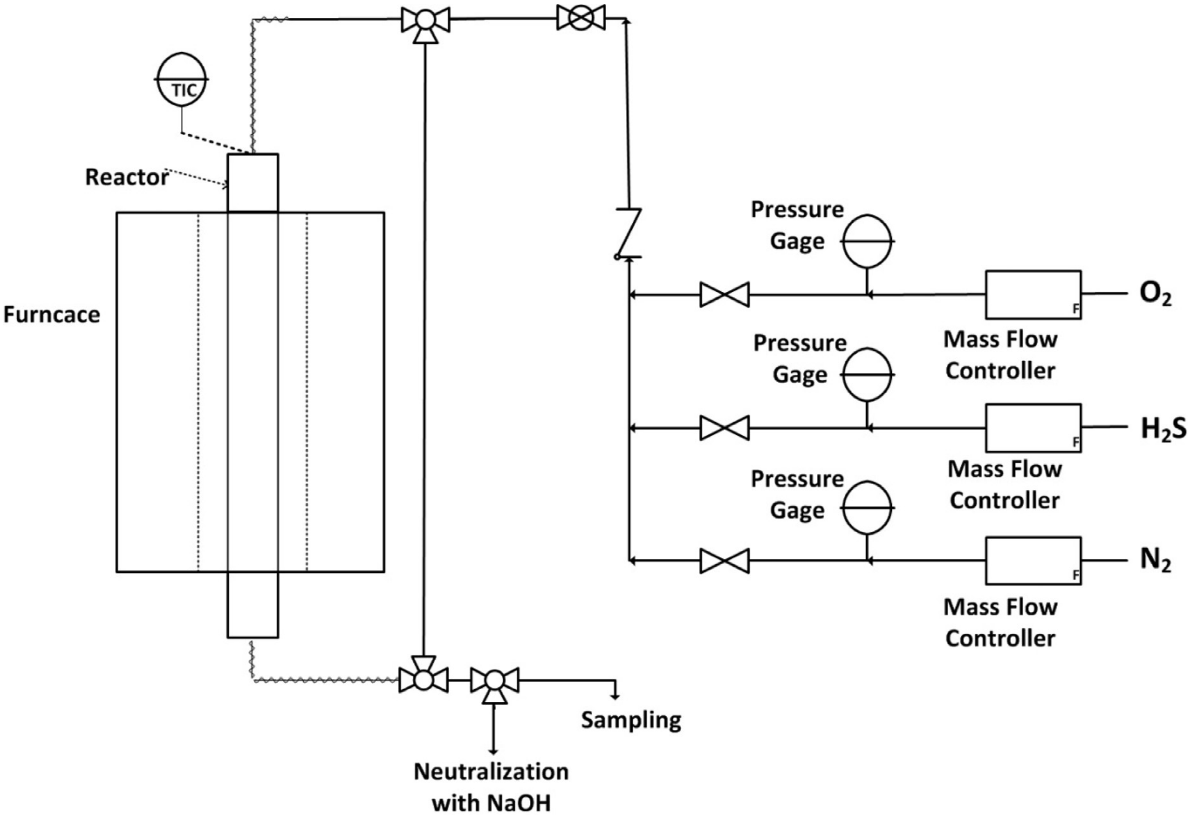

Fig 1. Schematic illustration of reaction setup used in this research (TIC is abbreviation of Temperature Indicator Controller).

carbon, H_2S reacts with oxygen to yield elemental sulfur, however, some side reactions can also occur simultaneously leading to the production of undesired products, such as SO_2 [24]. Several methods have been used to enhance the catalytic activity and sulfur capacity of APCs [14,20,21]. For example, in the work by Fang et al. [20], loading metal-oxide on APCs at 180 °C significantly enhanced their sulfur capacity such that sulfur loading of 142 mg $_{\text{Sulfur}}$/g $_{\text{catalyst}}$ in Mn/APC was achieved. In another work by Sun et al. [14], millimeter sized mesoporous carbon spheres (MCS) were synthesized and impregnated by using different alkaline salts. Sulfur capacity of 2.46 g H_2S/g catalyst was obtained for the MCS-15%MgO sample [21]. Incorporating nitrogen in the structure of APCs has also been reported as an efficient method of increasing sulfur interactions with carbon-based materials which can significantly improve catalytic activity [14]. A high sulfur loading of 2.77 g S/g catalyst has been obtained using nitrogen-rich APCs, mainly due to the formation of pyridinic-type nitrogen. These nitrogen species are suggested to act as highly active sites in the H_2S oxidation reaction [14].

CNTs are also used for selective oxidation of H_2S, however, CNT by itself is not active enough in this reaction [13]. To overcome this problem, Mohammadalizadeh et al. [22] decorated CNT by tungsten sulfide and enhanced its catalytic activity. For the first time, application of N-CNT as a metal-free catalyst for selective oxidation of H_2S was studied by Chizari et al. [13] where they could achieve 91% conversion and 75% selectivity to elemental sulfur at 190 °C. N-CNT supported on SiC was then used for this purpose and results better than those obtained with iron-based metallic catalyst were reported [25]. These results showed the potential application of nitrogen-doped CNTs as suitable catalysts for H_2S selective oxidation.

Doping processes on carbon materials can lead to a mixture of different nitrogen species. Nitrogen doping on CNTs can be accomplished either in-situ or by performing post treatment on pristine CNTs. Each method tends to yield higher contribution of specific type of nitrogen species. It has been reported that in-situ doping leads to formation of more pyridinic and/or pyrrolic nitrogen atoms, whereas post treatment of CNTs results in higher contribution of graphitic nitrogen atoms [26]. Synthesizing N-CNT by post treatment of CNTs using ammonium hydroxide [27], CNT and deionized water and by CVD method using various gaseous [28], liquid [29] and solid sources [30] have been reported. However, the high cost associated with such preparation methods has been a burden toward commercial application of carbon-based catalysts which needs to be addressed.

Density functional theory (DFT) calculations are useful for studying various catalysts and adsorbents evaluating interactions between different catalytic sites and H_2S in selective oxidation reaction [31-34]. Recently, Fellah has shown that H_2S adsorption can be considered as initial step in catalytic partial oxidation of H_2S [31]. DFT studies could also provide insights on the interactions between H_2S and different nitrogen sites, thereby elucidating the role of various nitrogen species on the catalyst activity toward H_2S selective oxidation.

In the present work, we propose the application of camphor and urea as abundant and low-cost solid precursors for the N-CNT catalyst synthesis for the first time. The nature of different nitrogen species as active sites for H_2S selective oxidation is investigated through experimental characterization and DFT study. DFT calculations were performed to determine the most active nitrogen atoms of N-CNTs toward H_2S selective oxidation and to provide mechanistic insights about this reaction over N-CNTs. Steady state reactor tests were run to evaluate catalytic activity and selectivity of the prepared samples. The experimental reactor results were compared with the DFT results and the nature of active sites were investigated. The effects of specific surface area (SSA), pore size

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