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Carbon supported vanadia for multi-pollutants removal from flue gas

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ABSTRACT

Coal combustion generates flue gas that contains many types of pollutants including sulfur dioxide (SO_2), nitrogen oxides (mainly NO) and heavy metals (Hg, Pb, As, etc.). Abatement of these pollutants has been an important task for sustainable development of the world, especially of the countries heavily relying on coal as the main primary energy. The dominant flue gas cleaning technologies used worldwide today are effective only for a single pollutant removal at conditions significantly different from each other and from that of flue gas emission. This inevitably leads to high cost for multi-pollutants removal. Research in past decades showed that carbon supported catalysts have superior properties for abatement of many flue gas pollutants, individually or simultaneously, at temperatures of flue gas emission. Among them, activated coke supported vanadia (V_2O_5/AC) attracted more attention due to its high activities in adsorption and oxidation, which are key properties needed for abatement of these pollutants. This article, as a plenary lecture of the 8th International Symposium on Gas Cleaning at High Temperatures (GCHT-8), is mainly a feature report that summarizes the main research on V_2O_5/AC catalyst for SO_2, NO and Hg removal, especially the contributions made by Chinese researchers. It concentrates on in-depth understanding on surface science and catalysis, including the role of V_2O_5 in adsorption and oxidation of the pollutants; effects of SO_2 and moisture on formation and consumption of poisonous sulfates; the role of AC in adsorption and oxidation of the pollutants and in decomposition of poisonous sulfates; the forms of intermediates and their transformation mechanism; and effects of alkali species in flue gas on activities of SO_2 and NO removal.

1. Introduction

Coal is a main fossil energy in the world mainly for power and heat generation through combustion. In China, for example, coal constitutes about 70% primary energy consumption in recent years, about 3 billion tons in 2009 and 80% for combustion. This made coal combustion the largest source of atmospheric pollution in China. The major pollutants include sulfur dioxide (SO_2, 23.2 Mt/y in 2008 in China [1]), nitrogen oxides (mainly NO, 12.5 Mt/y in 2008 in China [2]) and heavy metals such as mercury (Hg, about 200 t/y in 2000 in China [3]). The severe environmental problems caused by these pollutants are not expected to be solved satisfactorily in the near future due to technical and economic reasons. Their abatement is and will continually be an important task for sustainable development of China and the world.

Many technologies have been developed to abate SO_2, NO and Hg, such as Ca-based SO_2 capture processes, low NO_x combustion techniques and selective catalytic reduction (SCR) of NO, and carbon-based Hg capture processes. Each of these technologies, however, is effective only for removal of a single pollutant at conditions usually quite different from each other and from that of flue gas emission (usually 120–200 °C for power plants and industrial boilers, referred as stack temperatures hereafter). These certainly lead to a high cost if all of these pollutants are to be controlled. Furthermore, some of these technologies even produce secondary pollutants, such as the popular Ca-based SO_2 removal technologies, which produce low quality gypsum that is difficult to be used or disposed of. Sustainable development calls for technology breakthroughs that are economically attractive and robust for simultaneous multi-pollutant removal and also for sulfur recovery.

Much research showed that carbon-based materials (including activated carbon, activated coke and activated carbon fibers) are capable to remove SO_2, NO and Hg from flue gas individually and simultaneously [4–9]. The MET-Mitsui-BF process is an excellent example of simultaneous removal of these pollutants at about 150 °C using coal-derived activated coke (AC in short) and has been practiced on industrial scales for more than two decades [10]. To make the process more efficient, research has been carried out to increase the AC's ability for SO_2, NO and Hg removal, such as different techniques for preparation and modification of AC and supporting various metal oxides onto AC. Among numerous

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methods reported, activated coke supported V_2O_5 (V_2O_5/AC) stood out and was studied extensively in past decade. The advantages of V_2O_5/AC are its abilities to capture SO_2 and Hg, and to catalyze SCR of NO with NH_3 at stack temperatures at rates and capacities much higher than that of AC, which lead to savings in equipment, operation and retrofitting, as well as in sulfur recovery.

This article summarizes main research and developments in V_2O_5/AC for SO_2, NO and Hg removal in scientific point of view, especially the contributions made by Chinese researchers. A fraction of the work can be found in a review article published in 2008 in Chinese [11].

2. Key requirements for multi-pollutants removal from flue gas over a single sorbent/catalyst

The multi-pollutants removal from flue gas refers to simultaneous SO_2, NO and Hg removal under the same conditions in a single process. This can be realized in theory at a broad temperature range, but the stack temperatures are mostly preferred and practical due to minimal energy requirements. Since most forms of sulfur and Hg should not be disposed of freely, adsorption processes, physical or chemical, are of choice particularly those under dry conditions. The dry methods eliminate the use and separation of water and lower the cost of sulfur recovery. The stack temperature operation also favors adsorption, a crucial step for most abatement processes, because it is the lowest temperature in combustion systems. These requirements make activated coke based materials (sorbents/catalysts) more advantageous than others because of their high adsorption capability for many pollutants. This is attributable to their structural properties, such as high surface area and large pore volume, and chemical properties, such as various types of surface functional groups.

SO_2, NO and Hg are generated at combustion temperatures under oxidative conditions (with O_2 contents of 3–5 vol.% in most flue gases) but are not at the highest oxidation states of S, N and Hg, respectively. This makes abatements of them difficult due to their low solubility in water and low adsorption capacity on most sorbents. Oxidation, therefore, is an important step for their abatements, as has been evidenced by known facts, such as higher adsorption capacity of SO_3 than SO_2, higher adsorption capacity of NO_2 than NO, partial oxidation of NH_3 for reduction of NO, and higher adsorption capacity of Hg^{2+} than Hg^0. The key and common feature of a sorbent/catalyst for simultaneous removal of these pollutants, therefore, is proper oxidation activity under flue gas conditions, especially at the stack temperatures. In this regard, any sorbent effective for abatement of these pollutants is actually a catalyst with proper oxidation activities. This is the main reason for supporting V_2O_5 or other metal oxides on activated carbons.

Flue gases always contain water because all fossil fuels contain hydrogen that is fully oxidized into water during combustion. In addition, coal and air used in combustion contain moisture and injection of heavy oils into boilers needs steam. The water in flue gases usually has a great effect on activity and stability of many sorbent/catalysts, especially at stack temperatures. Although this effect has been recognized in the literature on adsorption of SO_2, NO and Hg, the effect on stability of sorbent/catalyst was usually overlooked especially for those containing metal oxides. In multi-pollutants removal, most of metal oxides transform into water-soluble sulfates upon SO_2 adsorption in the presence of O_2. These sulfates could be stripped off gradually from the catalyst surface by moisture in flue gas. A stable sorbent/catalyst, therefore, should contain a metal oxide that does not react with sulfuric acid or SO_3 easily or the sulfate formed can be readily converted back to oxide at conditions of flue gases.

3. SO_2 removal

It is generally recognized that various types of activated carbon or coke (AC) are capable to capture SO_2 from flue gas at temperatures lower than stack temperatures, less than 50 °C in particular. The overall process includes a number of steps: adsorption of SO_2 on the carbon surface, oxidation of the adsorbed SO_2 to SO_3 by the oxygen-containing functions groups on the AC, and reaction of SO_3 with H_2O in flue gas to form H_2SO_4 that stores in the pores of the AC or is washed off [8,9,12]. This process is favored at lower temperatures due to higher SO_2 adsorption capacity and oxidation activities of surface functional groups on AC. At stack temperatures, however, the SO_2 adsorption capacity decreases and surface functional groups on AC may change, which lead to lower SO_2 removal rates. Supporting metal oxides onto AC was found to be effective to overcome this problem and much research has been done on the subject including those containing CuO, Fe_2O_3, MnO_x, V_2O_5 and others [13–16]. Unfortunately, most of these metal oxides react with SO_2 and O_2 to form water soluble sulfates such as $CuSO_4$, $Fe_2(SO_4)_3$ and $MnSO_4$ that could be stripped off gradually by H_2O in flue gas. In contrast, V_2O_5/AC is more stable because the only sulfate it could form is vanadyl sulfate ($VOSO_4$) and its water solubility is very low.

Fig. 1 shows SO_2 removal (termed conversion) behaviors of an AC and V_2O_5/AC of various V_2O_5 loadings at 200 °C and a space velocity of 6450 L/kg h [16]. Clearly, AC itself has a very low activity on SO_2 capture at the conditions but supporting V_2O_5 results in higher activities. Since data showed that the progressive increases in V_2O_5 loading lead to progressive decreases in the catalyst's surface area, the promotion effect of V_2O_5 on SO_2 capture capability may be attributed to increased usability of the AC's surface. This indicates that a large portion of the AC surface is not usable for SO_2 capture unless it is modified by V_2O_5. The little effect of water and the strong promotion effect of O_2 and O_2 + water on SO_2 capture over V_2O_5/AC shown in Fig. 2 further indicate that the primary role of V_2O_5 is to increase oxidation ability of the AC or provide oxidation sites for SO_2. This is supported by the data in Fig. 3, which show a higher promoting effect of V_2O_5 on SO_2 capture at lower V_2O_5 loadings, i.e. one V atom is responsible for capturing 8 SO_2 molecules at a V_2O_5 loading of 0.5 wt.%. Clearly it is not possible for a V atom to adsorb 8 SO_2 molecules due to steric hindrance, the main role of V_2O_5 could only be catalytic oxidation of SO_2 to SO_3. Furthermore the SO_3 formed should be mobile and tend to migrate or spillover to the AC surface to allow the V atom to oxidize

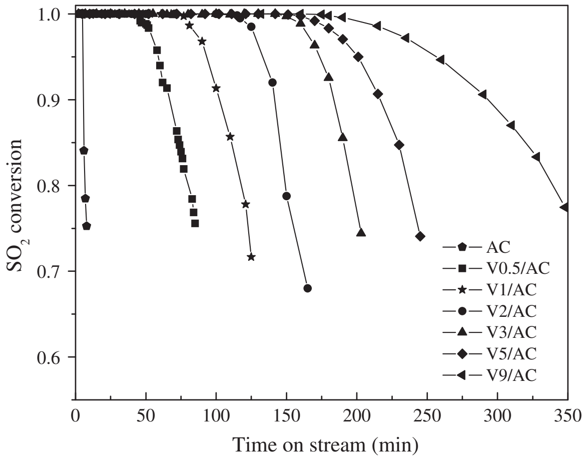

Fig. 1. SO_2 removal behaviors of V_2O_5/AC [16]. The values of *n* in Vn/AC indicate V_2O_5 contents in wt.% in V_2O_5/AC. Conditions: 1500 ppm SO_2, 3.4% O_2, 3.5% H_2O, 6450 L/(kg h), 200 °C.