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Removal of volatile odorous organic compounds over NiAl mixed oxides at low temperature

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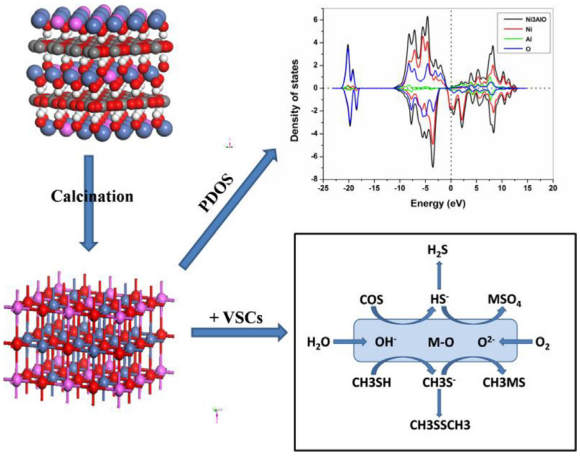
HIGHLIGHTS

- Deep removal of sulfur containing odours over NiAl mixed oxides was studied.
- There is a strong interaction between Ni and Al element on Ni3Al-HTO.
- Interaction between Ni and Al would increase the quantity and activity of the basic sites.
- Origin of plentiful basic sites on HTO was explored by First-principles calculation.

GRAPHICAL ABSTRACT



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ABSTRACT

In this paper, a series of NiAl hydrotalcite-like compounds (HTLCs) were prepared by the urea–decomposition method. Removal of carbonyl sulfide (COS) and methyl mercaptan (CH_4S) over the hydrotalcite–derived oxides (HTO) at low temperature was studied. The Ni3Al-HTO exhibited higher catalytic activities than Ni3Al mixed oxides prepared by physical mixing method (Ni3Al-PM) or impregnation/calcination method (Ni3Al-IC). Based on the characterization, it was found that desulfurization activities are closely tied to the surface acid-base properties of catalysts. CO_2-TPD indicates that the basic characteristic of the Ni3Al-HTO is prominent. XPS results showed that there was a strong interaction between Ni and Al element on Ni3Al-HTO. The first principle calculation based on density function theory was applied with the aim to study the change of basic sites. The results showed that Ni3Al-HTO presents a half-metallic characteristic. Electron transfer from the Al and O atom to the Ni atom was observed, which is helpful for the transfer of electrons from the surface and improves the catalytic activity. Analysis of the DRIFT spectra suggests that sulfate species was formed by the action of surface basic sites, resulting in the formation of H_2O on the surface.

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1. Introduction

Odor pollution is a public pollution with effluvial smell caused by one or more substances. Direct emissions of malodorous gases can not only be harmful to the health of human beings but also pose a serious threat to the surrounding environment [1]. The odoriphore including sulfur and carbonyl could stimulate the olfactory cells, make people feel unpleasant and cause bad effects on people's health and life. Among all types of the odorous gases, sulfur-containing odorous gas is the most typical one, which includes hydrogen sulfide, carbon disulfide, methyl mercaptan, methyl sulfide, dimethyl disulfide [2,3]. There is a wide range of sources of sulfur containing effluvial gases, such as the corruption process of plants and animals in the ecological environment of nature, petroleum processing, various chemical productions and storage process [4–9]. The sulfur-containing effluvial gases can strongly stimulate people's olfactory organ and make people feel short of breath and cause restlessness, nausea, and vomiting, what's more, it would pose a relatively great harm to the human respiratory system, digestive system, nervous system and endocrine system.

Nowadays, major technology for processing odorous gases includes combustion, alkali absorption, catalytic oxidation, adsorption and biological deodorization [10–14]. Combustion leads to direct combustion of Malodorous gas, which is simple and convenient. But it also causes high energy consumption and sulfur oxides emission at the same time, and there are still problems in total control; alkali absorption is mainly used on specific occasions as removing imported high concentration Methyl mercaptan and (or) dealing with large amount of gas, which costs highly in the investment and operation process and leads to high power consumption and intricate operation process; biological deodorization uses reaction of microbial metabolism to degrade the effluvial substance, which requires uncomplicated equipment and produces no secondary pollution, has the advantages of convenient maintenance and management as well. However, in the meanwhile, large area, strong gas resistance, difficulties to domesticate and culture the microorganism are the shortcomings of this technology. Adsorption and catalytic oxidation are the hotspots of the current malodorous gas study, which have many advantages, such as high desulfurization precision, simple operation, low investment cost and so on.

One of the most commonly used adsorbent materials is activated carbon and molecular sieve. The inner pore of activated carbon is developed, the specific surface area is large, the surface area of micropore which controls the adsorption amount occupies more than 95% of the total surface area and the performance of physical adsorbing is very strong, therefore, it can be used to absorb organic compounds like methyl mercaptan. However, the ability of unmodified activated carbon to adsorb methyl mercaptan is limited by the needs to alter its physical and chemical properties in order to enhance its adsorption of methyl mercaptan. It was found that when the activated carbon was immersed in alkali metal solution or metal salt solution, the metal would be attached on the surface of activated carbon and lead to increasing number of the site on the surface of the activated carbon, which is used for mercaptan adsorption, and increase the adsorption content of activated carbon on the mercaptan.

S. Bashkova et al. [15,16] studied deeply on the removal of methyl mercaptan by activated carbon. The results showed that activated carbon has a good effect on the removal of methyl mercaptan. After modifying the activated carbon by using methods as urea impregnation, calcination and loading Fe ion, the results show that the surface properties of activated carbon have important influences on the adsorption capacity of methyl mercaptan and the desulfurization effect of the activated carbon can be further enhanced by using the Fe ion as a modifying method. H. Chiang [17] et al. conducted research on the adsorption characteristics of methyl mercaptan and hydrogen sulfide on the surface of activated carbon. The results showed that methyl mercaptan is more likely to be adsorbed by activated carbon. The possible reason is that methyl mercaptan has polar (-SH) and nonpolar (-CH3) functional groups, and is easier to be hydrolyzed by water. H. Tamai et al. [18] modified the activated carbon by using the methods of HNO_3/H_2SO_4 impregnation, high-temperature calcination and supporting hexadecylamine, and investigated their methyl mercaptan removing ability. The results showed that the ability to adsorb methyl mercaptan of the activated carbon which was modified by HNO_3/H_2SO_4 impregnation had enhanced. Although the activated carbon desulfurization agent has great adsorption capacity and faster adsorbing rate, but the high use-cost and the secondary pollution and resources wasting problems caused by abandoned activated carbon greatly limited the application of the activated carbon in the field of odor gas purification, therefore, it is very necessary to actualize renewing and recycling and long-term operating stability when methyl mercaptan material is removed by activated carbon.

Molecular sieve is a synthetic zeolite, it has long been widely used in adsorption, catalysis and separation and other fields for its large specific surface area. In order to further improve the efficiency of desulfurization, metal ions are often pulled into the molecular sieve to modify it. Through the physical adsorption and effects between the solitary electrons of the metal and sulfur atoms, the modified molecular sieves can form a strong M-S bond to achieve the purpose of removing the mercaptan [19]. However, the regeneration temperature which is high makes the operating cost of the molecular sieve regeneration process greatly increased, thus limited its use.

Metal oxide is another ideal catalyst or adsorbent for volatile organic compounds. Noble metal doped materials have been investigated. Additional catalysts like cobalt oxides[20,21], rare earth oxides[22,23], copper oxides[24,25] and nickel oxides[26] have also been employed. To obtain effective catalysts, various methods can be used to prepare nanostructured metal oxides for catalytic applications, including co-precipitation, sol-gel techniques, solvothermal processes, micro-emulsion methods, combustion procedures, and so on [27]. The composite metal oxide solid solution, which was prepared by calcination of hydrotalcite-like compounds (HTLCs) as the precursors in the process, has the similar basicity as MgO, high specific surface area, and high thermal stability, and it's now regarded as a new type of solid alkali material with broad application prospect[28]. Z.Y. Sun et al. [29,30] used in-situ growth method and obtained the hydrotalcite composite metal oxide films. After attaching cobalt phthalocyanine, the thin films have high catalytic conversion rate (85.7%) on mercaptan. I. Chatti et al. [31] have prepared three Mg–Al hydrotalcites containing cobalt(II) phthalocyanine by direct synthesis, anion exchange, and structure reconstruction. The results of the mercaptan oxidation reaction were compared to those obtained with an industrial non-basic impregnated active charcoal. An important activity difference in favor of the prepared catalysts was obtained, confirming that the adequate tuning of basic and oxidant properties lead to a promising catalyst.

In the present work, a series of NiAl HTLCs were synthesized utilizing urea method. The removal of carbonyl sulfide (COS) and methyl mercaptan (CH_4S) over hydrotalcite-derived mixed oxides was investigated. The catalyst was systematically optimized with respect to the Ni/Al mole ratio, Urea/Metal mole ratio, and calcination temperature. The catalysts were characterized by various techniques such as XRD, N_2 adsorption/desorption, SEM, CO_2-TPD, and XPS. Density functional theory (DFT) is increasingly used to fill gaps in mechanisms of environmental catalysis. So, theoretical calculations based on DFT were used for analyzing the electronic