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The different poisoning behaviors of various alkali metal containing compounds on SCR catalyst

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ABSTRACT

Alkali metals are poisonous to the metal oxide catalyst for NO removal. The chemical configuration of alkali containing substance and interacting temperature can affect the poisoning profile. A computational method based on Frontier Molecular Orbital analysis was proposed to determine the reacting behavior of various alkali-containing substances with SCR catalyst. The results reveal that the poisoning reactivities of various substances can be ranked as: E (MOH) > E (M_2SO_4) > E(MCl) > E(MNO_3) > E($MHSO_4$). The experimental activity tests of the catalysts calcined at stepped temperatures show that NaOH can react with the catalyst below 200 °C. NaCl and $NaNO_3$ start to react with the catalyst at a temperature between 300 and 400 °C. Unlike MOH, MCl and MNO_3, which can produce volatile or decomposable species for the anions after reacting with the catalyst, M_2SO_4 and $MHSO_4$ will leave both cations and anions on the catalyst surface. The sulfate ions left on the catalyst can generate active acid sites for NH_3 adsorption. The experimental results also show that Na_2SO_4 and $NaHSO_4$ will not lower the NO conversion. The after-reaction influences of various alkali metals were studied using theoretical and experimental methods. The theoretical results show that the acidity decreases with doping of alkali metal. Experiments show a consistent result that the NO conversion decreases as undoped >LiCl > NaCl > KCl.

1. Introduction

Nitric oxides (NO_x), mostly nitric monoxide (NO), emitted from stationary and mobile sources is thought to be one of the major pollutants in atmosphere. Selective catalytic reduction (SCR) is the most efficient and commonly used technologies to remove gas phase NO from flue gas. Catalyst systems consisting of vanadia supported on titania (TiO_2) and promoted with tungsten oxide (WO_3) or molybdenum oxide (MoO_3) have been proven to be highly active and been commercially applied for decades [1]. However, several issues have emerged regarding the deactivation of the SCR catalyst during operation. One of the important issues is its chemical poisoning by substances in the reaction mixture. Alkali metals have been reported to be severely poisonous to vanadia based SCR catalyst. After Shikada et al. [2] found the poisoning effect of potassium on supported vanadia catalyst, numerous papers [3–13] have been published on the influence of alkali metal and its mechanism. Most of the literature suggests that the poisoning strength of the alkali metal is associated with the basicity [3,12], that is Cs >Rb >K >Na > Li. Neutralization of active acid sites was found to be the main reason for catalyst deactivation, as proved by NH_3 adsorption characterizations and NO reduction tests [4,5,8]. Researchers also found that doping of alkali metal on the catalyst surface would weaken the strength of V=O bond and thus lower the oxidizing ability of catalyst [6,14], which is also a reason for catalyst deactivation. Although lots of work has been done on the poisoning of SCR catalyst by alkali metals, there are still issues waiting to be studied. For instance, researchers have mostly conducted characterizations on the 'poisoned catalyst', which is prepared by impregnation method and calcined in the end. The reactions between various alkali species and the catalysts were ignored. Furthermore, most studies were focusing on one specific alkali metal or compound. Jensen et al. [15] have built a pilot platform for catalyst deactivation using aerosol deposit. They conducted a serial of experimental studies on the deactivation of catalyst by polyphosphoric acid [15], potassium phosphate [16], KCl and K_2SO_4 [17]. They have focused on the distribution of poisons and the final physical and chemical influences on the catalyst. Their studies also indicate that alkali

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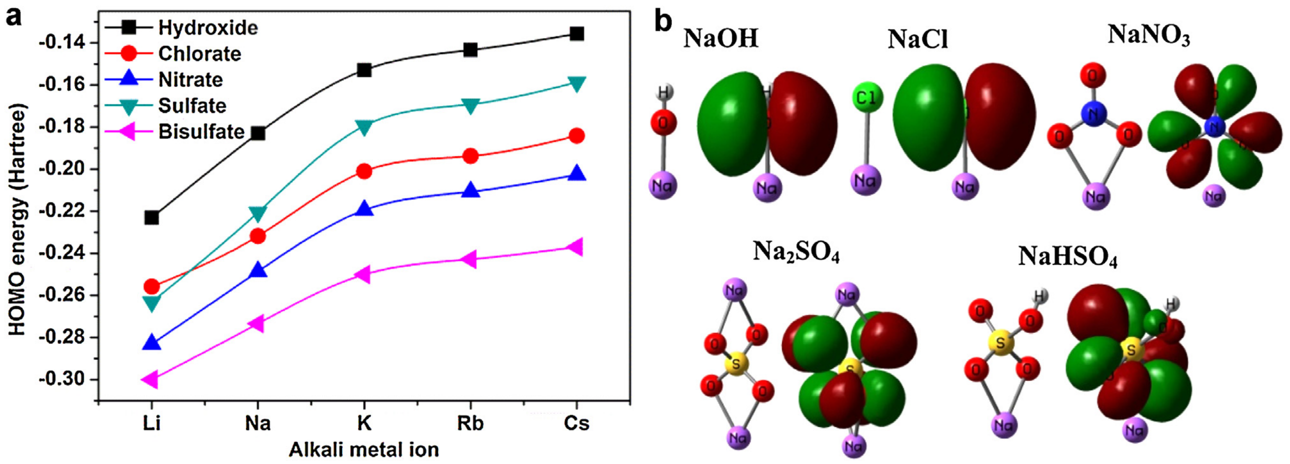

Fig. 1. The HOMO energies of various alkali species (a) and HOMO snapshots of Na-containing molecules (b).

metals can exist in various compounds under different situations. Potassium is usually contained in biomass-firing flue gas [17] and sodium is rich in coals from some regions, such as Zhundong region in northern area of Xinjiang Province of China [18]. The alkali containing species in the flue gas of municipal solid waste combustion [19] can be more complicated due to the broad origins of waste. Other types of flue gas from glass furnaces, steel sintering furnaces, diesel engines and other combustion units also contain alkali metals in various forms. One another important factor is the temperature of the area where alkali species interacts with the catalyst, which has not been reported. In general, a study on the poisoning of SCR catalyst by alkali species concerning the poisoning strength of various species, interaction profiles and reaction temperature is still needed.

Our study screened the poisoning reactivities of alkali metal hydroxide, chlorate, nitrate, sulfate and bisulfate using Density Functional Theory (DFT) calculations. Reactions between sodium compounds and the VO_x-WO_x/TiO_2 catalyst at various temperatures were conducted to study the reacting kinetics of poisons with the catalyst. The 'after poisoning' effects of various alkali metals were also studied by both DFT calculations and experiments.

2. Experimental and theoretical

All DFT calculations were performed using the gradient corrected Becke's [20,21] three-parameter hybrid exchange functional in conjunction with the correlation functional of Lee, Yang, and Parr [22] (B3LYP). Throughout the theoretical study, V, K, Rb and Cs were treated by the Los Alamos set of double-zeta type basis set (LANL2DZ). For other atoms related in this study, 6-311 + (d,p) basis set was employed. Each stationary structure has been confirmed as a minimum-energy structure from the calculated vibrational frequencies. The Gaussian 03 [23] package was applied in the theoretical part.

A commercial SCR catalyst composed by V_2O_5 and WO_3 supported on anatase TiO_2 was used in this study. The loading rate of V_2O_5 and WO_3 are 0.8% and 3.5% based on TiO_2 respectively. The catalyst was doped with various Na-containing compounds including NaOH, NaCl, $NaNO_3$, Na_2SO_4 and $NaHSO_4$. These Na-containing species were added onto the catalyst surface by the impregnation method using the respective aqueous solution. The impregnation procedure is shown as follows: impregnated with respective aqueous solution, dried at 105 °C for 12 h, and calcined at 500 °C in air for 5 h or at stepped temperatures (200, 300, 400, 500 °C) in simulated air (20% O_2 and 80% N_2). Different alkali loadings were used in Figs. 4 and 6 to better present the differences of the data in their own figure.

The catalytic activity tests for the reduction of NO by NH_3 were carried out in a fixed bed micro-reactor with catalyst samples of 0.2 g. The simulated gas for these tests contained 1000 ppm NO, 5 vol% O_2, and 1000 ppm NH_3 in N_2. The catalytic reactions were carried out at temperatures from 150 to 450 °C under atmosphere pressure, with a total flow rate of 0.8 L min^{-1} and GHSV = 2.4×10^5 mL/(g*h). The NO concentrations before and after reaction were determined using an ECOM-J2KN gas analyzer manufactured in Germany.

Brunauer-Emmett-Teller (BET) surface area was measured by N_2 adsorption at 77 K using a Quantachrome Autosorb-1 instrument.

3. Results and discussion

3.1. Initial screening of the poisons

Frontier molecular orbital (FMO) theory was firstly used to screen the reactivities of various poisons with the catalyst. As discussed in our previous studies [24,25], energy of the lowest unoccupied molecular orbital (LUMO) can be used to evaluate the acidity of catalyst site, which is crucial for the adsorption of NH_3. Lower LUMO energy indicates the easier to accept electrons from other molecules and also the stronger acidity. Alkali metals are well known for easily neutralizing the acidity of catalyst. In this study, energies of highest occupied molecular orbitals (HOMO) of the alkali-containing molecules were computed to analyze their abilities to donate electrons. The higher the HOMO energy is, the easier it is to donate its electrons to the unoccupied orbital of the acid sites of a catalyst. In another word, HOMO energy indicates the reactivity of a poison with the catalyst. In this study, the main active site, vanadia, was modeled and used to react with the poisons. The vanadia site was represented by the mono VO_4H_3 cluster, which has been proven to well simulate the electronic and structural profiles of vanadia site. The structure validity has been discussed in the Supplementary material. One thing should be noticed is that LUMO energy was chosen as the electronic parameter for model validity discussion since LUMO energy is the crucial indicator to screen the poisoning strength of various substances. The calculation results show that the LUMO energy of VO_4H_3 is −0.121 Hartree. Various alkali metal containing molecules in after-combustion flue gas including hydroxide, chlorate, nitrate, sulfate and bisulfate were studied. All the molecular structures and snapshots of HOMOs are shown in Supplementary material. Fig. 1 shows the HOMO energies of these molecules and HOMO snapshots of the Na-containing