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The effect of cations (NH_4^+ , Na^+ , K^+ , and Ca^{2+}) on chemical deactivation of commercial SCR catalyst by bromides

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ABSTRACT

Alkali and alkaline-earth metals from fly ash have a significant deactivation effect on catalysts used for selective catalytic reduction of NO_x by NH_3 (NH_3 -SCR). Bromides are considered effective additives to improve Hg^0 oxidation on SCR catalysts. In this work, the effects of different bromides (NH_4Br , NaBr , KBr , and CaBr_2) on a commercial $\text{V}_2\text{O}_5\text{-WO}_3/\text{TiO}_2$ catalyst were studied. NO_x conversion decreased significantly over the KBr -poisoned catalyst (denoted as L-KBr), while that over NaBr - and CaBr_2 -poisoned catalysts (denoted as L-NaBr and L-CaBr, respectively) decreased to a lesser extent compared with the fresh sample. Poor N_2 selectivity was observed over L-NaBr, L-KBr and L-CaBr catalysts. The decrease in the ratio of chemisorbed oxygen to total surface oxygen ($\text{O}_a/(\text{O}_a + \text{O}_b + \text{O}_w)$), reducibility and surface acidity might contribute to the poor activity and N_2 selectivity over L-KBr catalyst. The increased O_a ratio was conducive to the enhanced reducibility of L-CaBr. Combined with enhanced surface acidity, this might offset the negative effect of the loss of active sites by CaBr_2 covering. The overoxidation of NH_3 and poor N_2 selectivity in NH_3 oxidation should retard the SCR activity at high temperatures over L-CaBr catalyst. The increased basicity might contribute to increased NO_x adsorption on L-KBr and L-CaBr catalysts. A correlation between the acid-basic and redox properties of bromide-poisoned catalysts and their catalytic properties is established.

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1. Introduction

An important issue in selective catalytic reduction of NO_x by NH_3 (NH_3 -SCR) is the deactivation effects of alkali metals, alkaline-earth metals, and halogens on SCR catalysts [1–5]. Commercial SCR catalysts can be significantly deactivated by alkali and alkaline-earth salts obtained from fly ash. The effects of

alkali and alkaline-earth metals on $\text{V}_2\text{O}_5\text{-WO}_3/\text{TiO}_2$ catalysts have been studied extensively [3, 6–9]. It was believed that the surface acidity of SCR catalysts decreased significantly upon K, Na, and Ca poisoning [4,8,10]. Other researchers proposed that suppression of reducibility was more important in the deactivation of $\text{V}_2\text{O}_5/\text{TiO}_2$ catalysts by Na^+ and Ca^{2+} ions [11]. It was revealed that the strength of the $\text{V}=\text{O}$ bond was reduced and

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the oxidizing capability of the V-based catalyst was weakened by loading of alkali metal on the catalyst surface [12]. Du *et al.* [13] investigated the effect of alkali metal species on SCR catalysts using theoretical and experimental methods, and found that the poisoning effect of Na^+ depended on the type of anion used. The SCR catalyst could be also deactivated due to pore blocking by alkali and calcium sulfate deposition [14].

Although the poisoning of SCR catalysts by alkali metals has been extensively researched, there are still many issues to be studied. For instance, the deactivation mechanism of Ca on SCR catalyst is controversial. Yang *et al.* [15] studied the adsorption of NH_3 on CaO and sulfated CaO and found that NH_3 could be dissociated to produce NH_2 on both the CaO and sulfated CaO catalysts. The intermediate NH_2 could then react with surface oxygen to form NO on CaO, and possibly reduce NO over the CaSO_4 catalyst. It was reported that the reducibility of vanadium species and the intensity of surface acidity was weakened by CaO and CaCO_3 , whereas the concentrations of the surface-active oxygen and the Brønsted acid sites were improved by loading of CaSO_4 on the SCR catalyst [9]. Furthermore, it should be emphasized that calcium salts have the strongest Lewis acidity among the alkaline-earth metals [16].

Halogens (especially Cl and Br) play important roles in the removal of NO_x and Hg^0 by SCR catalysts [17]. The addition of calcium bromide to the fuel is believed to be an effective means for oxidizing Hg^0 in coal-fired boilers [18]. CaBr_2 injection is widely applied to improve Hg^0 oxidation and capture in power plants [19–21]. Bromides are thought to donate the most electron density to metals. An increase in electron density at the metal center facilitates oxidative processes [22,23]. Although the emergence of quantitative acid sites (which are very important in the NH_3 -SCR reaction) could be observed upon Cl addition, the deactivation effects of Cl on SCR catalysts are serious and irreversible [2,24]. In spite of these observations, the correlation between bromides and SCR catalysts has been ignored. The effects of bromides on the catalytic performance and structure of SCR catalysts is not clear.

In this study, the commercial $\text{V}_2\text{O}_5\text{-WO}_3/\text{TiO}_2$ catalyst was poisoned by different bromides (NH_4Br , NaBr, KBr and CaBr_2). The fresh and poisoned catalysts were studied by means of Brunauer-Emmett-Teller (BET) surface area analysis, X-ray photoelectron spectroscopy (XPS), hydrogen temperature-programmed reduction (H_2 -TPR), oxygen temperature-programmed oxidation (O_2 -TPO), and carbon dioxide temperature-programmed desorption (CO_2 -TPD), aiming at a better understanding of the effects of bromide-poisoning on the structure and NH_3 -SCR activity of the commercial SCR system.

2. Experimental

2.1. Catalyst poisoning

The commercial $\text{V}_2\text{O}_5\text{-WO}_3/\text{TiO}_2$ catalyst (hereafter denoted as L catalyst) was obtained from China Guodian Corporation. The bromide-poisoned catalysts were prepared by impregnating the L catalyst with aqueous solutions of NH_4Br , NaBr, KBr and CaBr_2 (the mass of loaded bromides was equal). Then the

samples were dried at 110 °C and calcined at 450 °C for 4 h (except for the NH_4Br -poisoned sample, because the decomposition temperature of NH_4Br is less than 450 °C). The poisoned samples were denoted as L- NH_4Br , L-NaBr, L-KBr and L- CaBr_2 , respectively.

2.2. Catalytic performance

The steady-state NH_3 -SCR performance and NH_3 oxidation over the catalysts were evaluated in a fixed-bed quartz reactor. The reaction conditions were as follows: 0.15 g catalyst, 500 ppm NO , 500 ppm NH_3 , 5% O_2 , and N_2 balance with a total gas flow rate of 200 mL/min, gas hourly space velocity (GHSV) = $7.0 \times 10^4 \text{ h}^{-1}$ (STP). The temperature-programmed desorption of NH_3 (NH_3 -TPD) and NO_x ($\text{NO} + \text{O}_2$ -TPD) were also carried out on the same system.

2.3. Catalyst characterization

The BET specific surface area was estimated by N_2 physisorption at -196 °C using a Quantachrome Nova Automated Gas Sorption System. The XPS spectra were obtained using a PHI-5300/ESCA system. The H_2 -TPR, O_2 -TPO and CO_2 -TPD experiments were accomplished by means of a Micromeritics AutoChem II 2920 device. In a typical O_2 -TPO experiment, about 50 mg of catalyst was used. The catalyst was first pre-treated with helium (30 mL/min) at 300 °C for 1 h, and then exposed to 500 ppm NH_3 at the same temperature for 1 h. After cooling down to room temperature in helium (30 mL/min), the sample was purged by O_2 until the baseline was stable. Finally, the sample was heated to 1000 °C at a rate of 10 °C/mL/min in a specific O_2 content. The procedures for NH_3 -TPD, H_2 -TPR and CO_2 -TPD were similar to those used in our previous work [2].

3. Results and discussion

3.1. SCR activities over bromide-poisoned catalysts

In order to study the effect of bromides on the SCR catalyst, the commercial L catalyst was sampled and impregnated by four kinds of Br-containing salts (NH_4Br , NaBr, KBr, and CaBr_2). The effects of bromides on SCR activity are shown in Fig. 1.

The addition of NH_4Br had a negligible effect on SCR activity over the L catalyst. At 400–450 °C, the NO_x conversion over L-NaBr and L- CaBr_2 decreased to a certain extent compared with the fresh sample. However, the NO_x conversion decreased significantly over L-KBr catalyst in the test temperature range (especially at high temperature). At 450 °C, only 24% of NO_x conversion could be obtained over the L-KBr catalyst. No change in N_2 selectivity was observed over the NH_4Br -poisoned catalyst compared to the L catalyst (see Fig. 1(b)). The N_2 selectivity at high temperatures decreased over L-NaBr, L-KBr and L- CaBr_2 catalysts. In the case of the L-KBr catalyst, the N_2 selectivity was much lower than that of the fresh sample at 450 °C. This indicated that the poisoning effects of Br-containing salts on the SCR activity were very different due to the various kinds of cations. The results demonstrated that the counter-anions

Fig. 1. NO_x conversion (a) and N₂ selectivity (b) vs temperature over fresh and bromide-poisoned commercial SCR catalysts. Reaction conditions: 0.15 g catalysts, 500 ppm NO, 500 ppm NH₃, 5% O₂, N₂ balance, GHSV = 7.0 × 10⁴ h⁻¹.

played a crucial role in determining the activity of bromide-poisoned catalysts. For discussing the poisoning effect of bromides on structure and activity, the fresh and poisoned L catalysts were characterized by means of BET, XPS, TPR, and TPD.

3.2. Characterization of physicochemical properties

3.2.1. BET and XPS characterization

The addition of bromides influences the surface physicochemical properties and consequently affects the catalytic activity. The specific BET surface area was tested and the results are shown in Table 1. It is shown that the addition of Br-containing salts had a negligible effect on the specific surface area. The biggest change was found in the L-NHBr sample, where the BET surface area increased to 47.9 m²/g (from 46.0 m²/g of the L catalyst).

Surface-chemisorbed oxygen was believed to be the most active oxygen species, which contributes to excellent SCR activity [3]. XPS analysis was carried out and the results of O 1s analysis of bromide-poisoned samples are shown in Table 1 and Fig. 2. Generally, the O 1s peaks could be fitted into three bands. The sub-band at ~533.2 eV was assigned to H₂O on the catalyst surface (hereafter, denoted as O_w) [25]. The sub-band at 531.5–532 eV was attributed to the surface-chemisorbed oxygen (such as O₂²⁻ pertaining to defect-oxide or hydroxyl oxygen, hereafter, denoted as O_α). The sub-band at ~530.4 eV was attributed to the lattice oxygen O₂²⁻ (hereafter, denoted as O_β) [26]. Three kinds of oxygen existed on the fresh L catalyst.

Table 1

The BET specific surface area, surface atomic concentrations and acidity of bromide-poisoned SCR catalysts.

Sample	BET surface area (m ² /g)	V ⁴⁺ /(V ⁴⁺ + V ⁵⁺) ^a	O _α /(O _α + O _β + O _w) ^a	Surface acidity (μmol/g) ^b
L	46.0	59.2%	29.1%	70.6
L-NHBr	47.9	52.3%	27.0%	44.0
L-NaBr	46.3	67.0%	22.6%	35.5
L-KBr	45.1	57.8%	22.8%	27.4
L-CaBr	46.3	70.7%	31.6%	104.2

^a Calculated from XPS results. ^b Calculated from NH₃-TPD results.

Compared with the fresh sample, the O_α/(O_α + O_β + O_w) ratio increased over the L-CaBr catalyst. The increasing ratio of O_α indicated the formation of new surface-chemisorbed oxygen due to the addition of CaBr₂. On the contrary, the ratio decreased over other catalysts, especially the L-NaBr (22.6%) and L-KBr (22.8%) catalysts. The decrease of surface-chemisorbed oxygen might be ascribable to the overlay of active sites by Br-containing salts. The lower ratio of O_α/(O_α + O_β + O_w) is likely to contribute to poor reducibility and ultimately affect the SCR activity. In the literature, the decrease in the ratio of O_α after impregnation of alkali metals was attributed to the formation of strong bonds between surface oxygen and the doped metal [3]. The order of O_α/(O_α + O_β + O_w) ratios was as follows: L-CaBr > L > L-NHBr > L-KBr > L-NaBr, and the trend was almost consistent with that of SCR activity. The low concentration of O_α might result in a less reactive oxidation procedure, which would diminish the SCR activity [3].

The oxidation state of vanadium was also acquired and the V 2p XPS spectra for different catalysts are presented in Fig. 3. The presence of two oxidation states (V⁵⁺, V⁴⁺) for fresh and poisoned catalysts was established by peaks at 517.1–517.6 and 516.4–516.7 eV. V⁴⁺ and V⁵⁺ appeared on all of catalysts

Fig. 2. O 1s XPS spectra of fresh and bromide-poisoned L catalysts.

and the main contribution corresponded to V^{4+} species. The ratios of $V^{4+} / (V^{4+} + V^{5+})$ are listed in Table 1. It is noteworthy that the $V^{4+} / (V^{4+} + V^{5+})$ ratio of the L-CaBr and L-NaBr catalysts increased dramatically compared to that of the L catalyst. This revealed that the addition of CaBr and NaBr might alter the electronic density distribution around V. According to literature, the increased amount of V^{4+} would favor the SCR reaction due to the redox cycle of V^{5+}/V^{4+} [27]. It was also reported that the formation of V^{4+} was promoted by fluorine doping due to charge compensation, which enhanced the amount of surface superoxide ions correspondingly [28].

3.2.2. Redox properties

In order to investigate the effect of bromides on the reducibility of L catalyst, H_2 -TPR was carried out with different catalysts and the resultant profiles are shown in Fig. 4. For the fresh L catalyst, two main broad peaks were found at 586 and 857 °C, which could be attributed to the reduction of $V^{5+} \rightarrow V^{3+}$ and $W^{6+} \rightarrow W^0$, respectively [3,7]. The impregnation of NH_4Br and $CaBr_2$ enhanced the reducibility of L catalyst and both peaks shifted to lower temperatures, especially for the L-CaBr catalyst, where the two peaks were found at 538 and 773 °C. The relatively low reduction temperature on L-CaBr is possibly due to the strong interaction between $CaBr_2$ and the catalyst surface. The superior reducibility might be correlated with the high ratio of O_α and V^{4+} on $CaBr_2$ -poisoned catalysts. An improvement in the reducibility on Ca-doped catalyst due to enhanced oxygen mobility was reported by other researchers [29]. It was also re-

Fig. 4. H_2 -TPR curves of fresh and bromide-poisoned L catalysts.

ported that the addition of Ca could improve the reducibility of Pt oxides supported on Al_2O_3 by reducing the Pt-Al interaction [30]. However, it was confirmed that the addition of $CaSO_4$ resulted in more N_2O production in the SCR reaction due to its excellent reducibility [9].

For the L-NaBr and L-KBr catalysts, the peaks ascribed to the reduction of $V^{5+} \rightarrow V^{3+}$ and $W^{6+} \rightarrow W^0$ also appeared but the intensity of all peaks decreased. More importantly, the peaks corresponding to V^{5+} reduction shifted to higher temperatures, and the peaks ascribed to W^{6+} reduction shifted to lower temperatures, for both catalysts. Similar changes were also observed after addition of Na and K to V-W/Ti catalysts. Chen *et al.* [3] attributed this to the diminution in the reduction degree of V species and the influence of the chemical environment around W species by Na, K doping. The TPR results displayed that the reducibility of surface species decreased over L-KBr and L-NaBr catalysts.

According to the literature, regeneration of the $V^{5+}=O$ species could be achieved through two steps, which involve the generation of V^{4+} and oxidation of the reduced species by gaseous O_2 [31]. For the purpose of investigating the redox properties of bromide-poisoned L catalysts, the samples were pre-treated in NH_3 and followed by the O_2 -TPO experiment.

As shown in Fig. 5, a small peak at 393 °C and a strong peak at 752 °C were found on the L catalyst. The low-temperature peak could be attributed to reoxidation of surface V (such as V^{4+}) after NH_3 reduction. The peaks shifted to lower temperatures after poisoning by KBr. On the L-CaBr catalyst, a small peak was found at 450 °C. The reoxidation temperature shifts to a higher value than the corresponding temperature on L catalyst. Thus, the reoxidation of active sites was retarded by $CaBr_2$ addition, which meant that the stability of active sites was improved upon modification. Combining the H_2 -TPR and O_2 -TPO data, it could be concluded that the redox properties were affected by addition of bromides. The reducibility of surface V species decreased over L-KBr and L-NaBr catalysts, while the reoxidation ability was retarded on the L-CaBr catalyst. For commercial V-W/Ti catalyst, the redox cycle of V^{5+} and V^{4+} ($V^{5+} \leftrightarrow V^{4+}$) plays an important role in the NH_3 -SCR reaction. Not only the reducibility, but also the ability of re-oxidation, is important for NH_3 -SCR. The results indicated that the active sites (such as V^{5+}) might be reduced easily; however, the

Fig. 3. V 2p XPS spectra of fresh and bromide-poisoned L catalysts.

Fig. 5. O₂-TPO curves of fresh and bromide-poisoned catalysts after pretreatment by NH₃.

re-oxidation of V⁴⁺ was difficult after CaBr₂ addition. This may be an important reason for the lower activity of these catalysts.

3.3. NH₃ and NO adsorption

One of the most significant steps in the NH₃-SCR reaction is the NH₃ adsorption on the surface acid sites of the catalysts. The surface acidity of bromide-poisoned catalysts was characterized by NH₃-TPD. As shown in Fig. 6, all curves present a wide NH₃ desorption peak at 150–350 °C. After poisoning by CaBr₂, the peak shifted to a higher temperature and the amount of desorbed NH₃ increased significantly compared to that of fresh L sample. This indicated the appearance of new acid sites and enhancement of the surface acidity of L-CaBr catalyst. The amounts of desorbed NH₃ were calculated from NH₃-TPD and the results are displayed in Table 1. The capacity of L-CaBr for NH₃ adsorption was about 1.5-times that of the fresh L sample. For the L-NHBr and L-NaBr-loaded catalysts, the amount of desorbed NH₃ decreased at different degrees compared to that of the fresh L catalyst. It is worth noting that the amount of desorbed NH₃ was much lower over L-KBr catalyst (~39% of acidity of L catalyst), and the peak shifted to lower temperatures, which demonstrated that the surface acidity was weakened by KBr [3]. In the literature, alkali poisoning was studied by a density functional theory-based approach and the results indicated that the decrease in surface acidity is due to electron

Fig. 6. NH₃-TPD curves of fresh and bromide-poisoned L catalysts.

transfer from the K atom to the terminal O atom [7]. These results reveal that the adsorption of NH₃ on SCR catalyst is facilitated after CaBr₂ poisoning, while the NH₃ adsorption is restrained on other catalysts. However, strong acidity might affect selective catalytic oxidation of NH₃ over L-CaBr catalyst. This will be discussed later.

Meanwhile, the NO adsorption capacity of bromide-poisoned catalysts was characterized by NO + O₂-TPD and the results are also displayed in Table 2 and Fig. 7. It is shown that small amounts of NO and NO₂ were desorbed on the L catalyst (2.00 μmol/g of NO, 3.24 μmol/g of NO₂). For the L-CaBr catalyst, both NO and NO₂ could be found and the amount of NO₂ increased to 4.60 μmol/g. However, for the L-KBr catalyst, NO₂ could hardly be detected in the test temperature range. The formation of NO₂ was related to the surface oxidized species after NO adsorption. As indicated in H₂-TPR, the reducibility of surface species decreased over L-KBr catalyst. The oxidation of NO adsorbed species would be affected by this catalyst.

3.4. NH₃ oxidation performance

The quantity of adsorbed NH₃ on the surface is related to the surface acidity, and the H-abstraction degree of NH₃(ads) is related to the redox properties of SCR catalysts [32]. The catalytic oxidation of NH₃ plays an important role in the NH₃-SCR reaction. In order to discuss the effect of bromide-poisoning on SCR performance, the NH₃ oxidation performance was tested over these catalysts and the results are displayed in Fig. 8. The fresh and bromide-poisoned catalysts exhibited nearly no NH₃ conversion at temperatures lower than 300 °C. On the fresh L catalyst, the NH₃ conversion rapidly increased to 48% as the

Table 2

NO_x adsorption capacities of Br-poisoned SCR catalysts from NO + O₂-TPD.

Sample	NO (μmol/g)	NO ₂ (μmol/g)
L	2.00	3.24
L-CaBr	2.23	4.60
L-KBr	3.42	0.00

Fig. 7. NO + O₂-TPD curves of fresh, and KBr- and CaBr₂-poisoned L catalysts (NO concentration not shown here).

Fig. 8. NH₃ conversion (a) and N₂ selectivity (b) vs temperature over fresh and bromide-poisoned catalysts in NH₃ oxidation test. Reaction conditions: 0.15 g catalyst samples, 500 ppm NH₃, 5% O₂, N₂ balance, GHSV = 7.0×10^4 h⁻¹.

temperature increasing to 450 °C. The NH₃ oxidation performance was improved over L-CaBr catalyst and the NH₃ conversion increased to 58% at 450 °C. The addition of NH₄Br showed positive effects on NH₃ oxidation and the NH₃ conversion increased at high temperatures over L-NHBr catalyst, whereas the oxidation of NH₃ was restrained over L-KBr catalyst, which was in agreement with the SCR activity at high temperatures.

With respect to the selectivity toward N₂, KBr and CaBr₂ poisoning showed negative effects on the NH₃ oxidation reaction (see Fig. 8(b)). For L-CaBr catalyst, the strong interaction between NH₃ and surface acid sites might affect the selective catalytic oxidation of NH₃. The adsorbed NH₃ species, either in the protonated NH₄⁺ form or in the coordinated NH₃ form, would be partly oxidized by the adsorption sites first [32]. The decrease in N₂ selectivity was possible owing to overoxidation of NH₃ at high temperatures, which is believed to be one important reason for the decline of activity in NH₃-SCR.

3.5. Surface basicity

CO₂-TPD was performed to characterize the surface basicity of fresh and bromide-poisoned L catalysts. The intensity and distribution of surface basic sites could be characterized by the desorption temperature and the amount of CO₂. The CO₂-TPD

profiles are shown in Fig. 9.

The peaks at lower temperature (located in the range of 450–600 °C) are assigned to –OH basic sites on the catalysts [2]. The peaks at higher temperature (located in the range of 650–850 °C) could be assigned to basic O²⁻ attached to metal ions, which exhibited a strong interaction with CO₂ [2]. The fresh L catalyst exhibited two desorption peaks in the test temperature range. The peaks could be assigned to –OH basic sites (at 463 °C) and strong basic sites O²⁻ (at 745 °C). The strength of the basic sites could be reflected by the desorption temperatures of CO₂ [33]. After bromide poisoning, the peaks assigned to –OH basic sites shifted to higher temperatures, suggesting that the intensity of –OH basic sites increased. The halogens are the most electronegative elements. The bromides are supposed to donate the most electron density to the metal [22]. Besides, the Na⁺, K⁺, and Ca²⁺ cations might enhance the electron donation effects on the surface. This might be an important reason for the enhancement of surface basicity of bromide-poisoned catalysts. For the L-KBr catalyst, a new peak appeared at 588 °C, which implied that an additional basic site might be produced after loading of KBr. It was reported that the surface basicity could be proved by the binding energy (BE) of O 1s in the XPS spectra [34]. In this work, the BE value of O 1s decreased to 530.3 on L-NaBr catalyst, indicating that the surface basicity was improved.

The enhancement of surface basicity might affect the adsorption of NH₃ over L-KBr and L-NaBr catalysts. This was in agreement with NH₃-TPD results. The enhancement of basicity should also affect the interaction between NO adsorbed species (such as NO₂⁻ and NO₃⁻) and the catalyst surface. From NO + O₂-TPD, it could be seen that the desorption temperatures of NO increased on the L-KBr catalyst. This demonstrated that the stability of NO adsorbed species was improved. Meanwhile, the amount of adsorbed NO on L-KBr catalyst, and the amount of adsorbed NO₂ on L-CaBr catalyst both increased. The strengthening of basicity by KBr and CaBr₂ was an important factor. On the other hand, the redox property was suppressed significantly on L-KBr catalyst. Thus, the NH₃-SCR catalytic activity decreased, even though more NO could be adsorbed on this catalyst.

Fig. 9. CO₂-TPD curves of fresh and bromide-poisoned L catalysts.

4. Conclusions

In summary, the SCR activity of a commercial catalyst was affected significantly by bromide poisoning. The counter-anions played a crucial role in determining the activity of bromide-poisoned catalysts. The decrease in the ratio of surface chemisorbed oxygen, reducibility, surface acidity, and amount of adsorbed NO_x contributed to the poor activity and N_2 selectivity over the KBr-poisoned catalyst. The inhibition of reoxidation ability, overoxidation of NH_3 and poor N_2 selectivity in NH_3 oxidation retards the SCR activity at high temperature over L-CaBr catalyst. Additional *in situ* work to investigate the structure-activity relationships over bromide-poisoned catalysts is being carried out in our lab.

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Graphical Abstract

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The effect of cations (NH_4^+ , Na^+ , K^+ , and Ca^{2+}) on chemical deactivation of commercial SCR catalyst by bromides

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The decrease in the ratio of chemisorbed oxygen (O_a), reducibility and surface acidity contribute to the KBr-poisoned catalyst, and the overoxidation of NH_3 is attributed to the deactivation effect of CaBr_2 on the SCR catalyst.

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不同阳离子 (NH_4^+ , Na^+ , K^+ , Ca^{2+}) 溴化物对商用 SCR 催化剂 化学中毒影响机制研究

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摘要: 燃煤飞灰中的碱金属和碱土金属对 NH_3 -SCR 催化剂的活性有显著的影响。近年来, 研究者针对碱金属/碱土金属氧化物对 SCR 催化剂中毒作用开展了大量研究。另一方面, 研究普遍认为, 含溴化合物对提高 SCR 催化剂汞氧化性能具有明显促进作用。目前为止, 针对碱金属/碱土金属溴化物对 SCR 催化剂影响的系统研究较少。我们课题组系统研究了不同阳离子的溴化物 (NH_4Br , NaBr , KBr 和 CaBr_2) 对商用 V_2O_5 - WO_3 / TiO_2 催化剂性能的影响。

与未中毒样品相比, KBr 中毒后的催化剂 (记为 L-KBr) 上 NO_x 转化率明显下降, 而 NaBr 和 CaBr_2 中毒的催化剂 (分别记为 L-NaBr 和 L-CaBr) 上的 SCR 活性也有一定程度的降低。另外 L-NaBr , L-KBr 和 L-CaBr 催化剂的 N_2 选择性较差。XPS 结果显示, KBr 中毒后化学吸附氧 (O_a) 比例减小; 同时, KBr 中毒后还原性和表面酸度降低, 这些可能是导致 L-KBr 催化剂的活性和 N_2 选择性变差的主要原因。对于 L-CaBr 催化剂, 中毒后化学吸附氧 O_a 比例有所增加, 这与 H_2 -TPR 结果显示可还原性增强一致。O₂-TPO 结果显示, L-CaBr 催化剂可氧化性降低, 说明 CaBr_2 中毒还是影响到催化剂表面的氧化还原循环。催化剂 CaBr_2 中毒后表面被覆盖减少了反应活性位数量, 但表面酸性的增强可能会抵消活性位点损失带来的负面影响。NH₃ 氧化结果显示, NH₃ 在 L-CaBr 催化剂表面发生过氧化反应, 特别是高温下生成较多 N_2O , 降低 N_2 选择性, 这可能是高温下 L-CaBr 催化剂 SCR 活性和 N_2 选择性下降的重要原因。CO₂-TPD 结果表明, L-KBr 和 L-CaBr 催化剂表面碱性强度增加, 可能有助于增加 NO_x 物种的吸附量。基于以上活性评价和表征分析结果, 我们尝试建立了不同溴化物中毒的催化剂表面酸碱性、氧化还原和催化性能之间的关系。

关键词: 溴化物; 阳离子; 催化剂失活; SCR 催化剂; N_2 选择性; 表面酸性

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