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RESEARCH PAPER

Experimental study on ammonia adsorption by coal ashes

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Abstract: Unreacted ammonia in Selective Catalytic Reduction (SCR) and Selective Non-catalytic Reduction (SNCR) technology may be adsorbed by fly ash and lead to ash blocking in the air preheater or hindering the secondary utilization of ash. Ammonia adsorption by fly ash may have a close relationship to the concentration of ammonia in flue gas. Regarding Ximeng lignite and Yangquan anthracite as the subjects investigated, NH_3 temperature-programmed desorption (NH_3-TPD) was utilized to study the relationship between ammonia chemical adsorption and mineral composition of the ash, the atmosphere of ash production, cooling rate of ash as well as the amount of residual carbon in the ash. The results show that rapid cooling and reduction atmosphere could increase the amount of amorphous phase in the ash and facilitate ammonia adsorption. On the other hand, ash with residual carbon could adsorb more ammonia than mineral ash as a result of acidic functional group on the surface of residual carbon.

Key words: coal ash; ammonia; adsorption; SCR; SNCR; NO_x control

Selective Catalytic Reduction (SCR) and Selective Non-catalytic Reduction (SNCR) technology have been widely used in the denitration projects in coal-fired power plants[1,2]. Aqua ammonia or other reductant (such as urea) is injected into furnace or flue to convert NO_x to N_2. Unreacted ammonia would react with SO_3 or steam in the flue gas to form ammonium sulfate and ammonium hydrogen sulfate, which would result in fly ash fouling[3–5]. The operating experience in European power plants showed, 80% of ammonia slip would be adsorbed by fly ash. When ammonia slip concentration in flue gas was 2 mL/m^3, fly ash would adsorb 100 mg ammonia per 1 kg ash[6]. Fly ash is widely used in cement manufacturing, the adsorbed ammonium salt would turn into ammonia in alkaline environment of concrete. The ammonia spreading into the air would have an offensive smell and may harm human health, which has held back market access of some fly ash[7]. The blocking in the preheater caused by ammonia slip has been studied a lot[8,9], but lack of deep study on ammonia adsorption by fly ash. This work focuses on the ammonia adsorption of coal ashes in order to provide basic theoretical knowledge for flue gas $DeNO_x$ technology.

1 Experimental

1.1 Coal ashes production

Ximeng (XM) lignite and Yangquan (YQ) anthracite were used to prepare ash samples. The proximate analysis and ash fusion temperature are shown in Table 1. Chemical composition of coal ashes are displayed in Table 2.

Coal ashes were obtained according to the standard GB/T 1574—2007 in muffle furnace at 815°C. The produced ashes were put into alundum tube within a horizontal tube furnace heated to 900, 1000 and 1100°C at 15°C/min, and burned in air flow or mixed gas (φ_{CO}:φ_{CO_2}=4:6) at 1 L/min. After being heated to the required temperature for 60 min, the ashes were gotten out and cooled freely in air. In this way, the oxidized or reduced coal ashes at three temperatures were produced. If putting the ashes burned in the air flow into liquid nitrogen (LN), oxidized ashes were cooled rapidly. The produced coal ashes were marked in Table 3.

Putting the crucibles containing pulverized coal into muffle furnace at 850°C and controlling the burning time, the ashes containing different contents of residual carbon were produced. The residual carbon of XM ashes was 0%, 8.1% and 28.6% respectively, and that of YQ ashes was 0%, 8.3% and 25.0% respectively. They were used to study the effect of residual carbon content on the ammonia adsorption.

1.2 Experimental methods

Coal ashes were analyzed by X-ray diffraction with the X'Pert PRO of Panalytical. The surface area of ashes

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containing residual carbon was measured by BET with ASAP 2020 MICROPORE Analyzer. The morphological characteristics of residual carbon in ashes were observed by SEM with Hitachi SU-70.

All the coal ashes were analyzed by NH_3-TPD with Micromeritic AutoChem II 2920. After accurately weigh 0.1 g of coal ash and put into U-shaped pipe, the ash was heated to 500°C at 15°C/min in helium flow of 60 mL/min and activated for 30 min to remove water and other adsorptive materials, and then cooled to 100°C. The ammonia adsorption did not reach saturation until the TCD signal of chromatograph remained stable for 10 min. The ash was purged by helium flow to remove the ammonia physically adsorbed. After the base line of TCD signal is stable, the ash was heated to 700°C (550°C for ashes containing residual carbon) and the data of NH_3-TPD were gotten.

NH_3-TPD is one of the effective ways to characterize surface acidity of solid matter, some qualitative analysis could be done according to the NH_3-TPD curve: the amount of peaks stands for the number of different intensity acid centers on the surface of solid matter. The corresponding temperature of peaks means the strength of acid sites. The area between curve and horizontal axis reflects the quantity of desorbed ammonia. In theory, the amount of ammonia desorbed from coal ashes equals to the amount of ammonia adsorbed by ashes. Thus, ammonia adsorption characteristic of ashes could be obtained indirectly by analyzing the NH_3-TPD curves.

2 Results and discussion

2.1 XRD phase identification

The XRD patterns of XM and YQ ashes produced under different conditions were shown in Figures 1 and 2, respectively.

There were quartz (SiO_2), anorthite ($CaAl_2Si_2O_8$), anhydrite ($CaSO_4$), hematite (Fe_2O_3) and other mineral crystals in XM ashes burned at 900°C. The kinds of crystals in ashes were fundamentally the same except the reductive ash, because reductive atmosphere would lower decomposition temperature of $CaSO_4$[10], which made the diffraction peak of anhydrite disappear. The diffraction peak of anhydrite disappeared in ashes burned at 1000°C, but augite ($Ca(MgFeAl)SiAl_2O_6$) was observed. Hematite disappeared in ashes burned at 1100°C, and the crystals of ashes were composed primarily of quartz, anorthite and augite.

The YQ ashes burned at 900°C were composed mostly of quartz, aluminum silicate ($Al_2Si_4O_{10}$), anhydrite, hematite, mayenite ($Ca_2Al_{14}O_{33}$). The diffraction peaks of mullite ($Al_6Si_2O_{13}$) and Al_2O_3 appeared in ashes burned at 1000°C, and quartz, anhydrite, hematite existed meanwhile. The ashes burned at 1100°C consisted mainly of quartz and mullite.

2.2 Ammonia adsorption by coal ashes

2.2.1 Effect of ash composition

Figures 3 and 4 show the NH_3-TPD patterns of oxidized XM and YQ ashes cooled in the air, which were burned at 900, 1000 and 1100°C. Three TPD curves of XM ashes corresponding to different burned temperatures interlaced with each other, and the ammonia absorption were not obviously strong or weak. The adsorption amount decreased as the burning temperature increased. The adsorption capacity of ashes burned at 900 and 1000°C were close together, but that of ash burned at 1100°C reduced significantly. Coal ashes are the mixture of mineral crystals and glass phase. The XRD results show that there are large differences in composition of crystals in ashes, and the amount of glass phase would increase as heating temperature increases[11]. As a result, the ammonia adsorption influenced by heating temperature was influenced radically by composition of coal ashes burned at different temperatures.

Table 1 Proximate analysis and ash fusion temperature

Coal	Proximate analysis w_{ad}/%				Ash fusibility t/°C		
	M	A	V	FC	DT	ST	FT
XM	15.22	16.13	30.91	37.74	1151	1161	1239
YQ	3.69	9.88	7.58	78.86	>1500	>1500	>1500

Table 2 Chemical composition of coal ashes

Coal	Chemical composition of coal ashes w/%							
	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	K_2O	Na_2O	SO_3
XM	62.02	12.18	4.57	4.38	6.47	0.79	1.80	7.01
YQ	54.33	34.74	4.42	1.31	1.20	0.54	1.08	1.02