Experimental research of technology activating catalysts for SCR DeNOx in boiler

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Abstract. In order to improve activity of the catalysts used in SCR DeNOx system of flue gas, a series of catalysts activated by different activating liquids under varied conditions in boiler directly were conducted. Then these catalysts were characterized by SEM, FT-IR and BET technology. And NO conversions of the activated catalysts were studied and compared with that of inactivated catalyst. The above experiment shows that NO conversion of the activated catalyst can be up to 99%, which 30% higher than that of inactivated catalyst, so activity of catalysts were improved greatly. Furthermore, optimal activating liquid labeled L2 and effective technology parameters were gained in the experiment.

1. Introduction
Currently, DeNOx of flue gas by Selective Catalytic Reduction (SCR) is widely used in China because of its simplicity and higher denitrification efficiency, and the catalysts are usually arranged in the high-dust zone, in which catalysts can be easily clogged and inactivated through physical and chemical reaction with fly ash and flue gas, and thus activity of these catalysts will be decreased gradually. Once activity of the catalyst decreases, the denitrification efficiency of flue gas will accordingly decrease, so, activity of the catalysts must be kept at a higher level so as to maintain a higher denitrification efficiency during boiler operation [1-3]. In order to solve the above problem, many methods were taken in the past, one of them is that the catalysts are taken out from SCR DeNOx reactors and transported to a special factory to be activated through special activating liquids and processes and then transported back and installed in the SCR DeNOx reactors [4-7]. Obviously, this method means time-consuming and expensive costs. Thus, an activation method that catalysts are directly activated in the SCR DeNOx reactors was proposed. For the above activation method, many key technologies will be encountered and must be solved. Among the key technologies, activating liquid and efficient loading methods are included. To find out an efficient technology activating in boiler, sixteen kinds of activating liquids were prepared by means of single factor variable design experiments according to the main ingredients of SCR DeNOx catalysts which are widely used in coal-fired power plants currently, then experimental investigations of catalysts activation were conducted under the conditions of different process parameters. Then experiments of flue gas denitrification in the bench were done, and NO conversion of the activated catalysts were studied and
compared with that of the inactivated catalysts. In addition, analysis of micro-structure of the activated catalysts by SEM, FT-IR were also conducted.

2. Experimental

2.1. Catalysts preparation

The basic principle of technology activating catalysts in boiler is increasing effective activating ingredients on inactivated catalysts to restore or increase some activity. “in boiler” means the activating carried out in the SCR DeNOx reactor directly when the boiler is in the period of stopping or overhaul. The whole activating process will be taken on as Fig 1.

![Figure 1. Diagram of the on-line activating process](image)

**Table 1. Components of activating liquids**

| number   | ammonium vanadate (%) | ammonium molybdate (%) | ammonium tungstate (%) | Oxalate (%) | notes                                    |
|----------|------------------------|-------------------------|------------------------|-------------|------------------------------------------|
| L0-L4    |                        |                         |                        |             |                                          |
| L0       | 0.8                    |                         |                        |             |                                          |
| L1       | 0.9                    |                         |                        |             |                                          |
| L2       | 1.0                    |                         |                        |             |                                          |
| L3       | 1.1                    |                         |                        |             |                                          |
| L4       | 1.2                    |                         |                        |             |                                          |
| L5-L8, LiF | content of vanadate as in liquid LiF | L5 7 | L6 8 | L7 10 | L8 11 | LiF 9 | LiF is the number of the optimal liquid in L0-L4 |
| L9-L12, LiW | content of vanadate and molybdate as in liquid LiW | L9 7 | L10 8 | L11 4 | L12 5 | LiW 6 | LiW is the number of the optimal liquid in L5-L8, LiF |
| L13-L16, LiM | content of vanadate, molybdate and tungstate as in liquid LiM | L13 6 | L14 7 | L15 8 | L16 9 | LiM 7.6 | LiM is the number of the optimal liquid in L9-L12, LiW |

2.1.1. Washing and activating of catalysts. In the experiment, washing and activating of catalysts were carried on through soaking with activating liquids. First, the test catalysts were grinded into fine powder, which diameter is 0.178mm, then activating liquids with different content of ammonium vanadate, ammonium molybdate, ammonium tungstate and oxalate were prepared as shown in Table 1 [8-11]. And the activated catalysts were labeled as Ln (n≥1) respectively on the basis of activating...
liquids. After that, the inactivated catalysts were soaked in beaker by the prepared liquids at temperature of 40 °C for 30min. At last, drain the soaked catalysts in air for 1h.

2.1.2. Drying of catalysts. While drying condition parameter is regarded as an invariant factor, the drained catalysts were dried at 105 °C for 30min in the drying oven. In the experiment, the influence of drying condition was taken in account. Thus, drying condition parameters were set as shown in Table 2 when drying condition seems as variable and catalysts was labeled as C1 and L2.

| catalysts | drying condition | C1 | L2 |
|-----------|------------------|----|----|
|           | drying at 80°C for 15min; then drying at 105°C for 15min |    |    |
|           | drying at 105°C for 30min |    |    |

2.1.3. Baking of catalysts. The baking of catalysts was conducted in muffle furnace followed by drying. When baking condition is regarded as constant, the baking temperature was kept at 500°C and baking time was 10min. But while studying the influence of baking condition on the activity and characterization of activated catalysts, the baking condition parameter, baking temperature and time included was set as shown in Table 3, and the corresponding catalysts were labeled as Cn (n≥2).

| catalysts | baking temperature 400°C | 500°C | 600°C | 650°C | 700°C |
|-----------|--------------------------|-------|-------|-------|-------|
|           | C2 | L2 | C3 | C4 | C5 |
|           | baking time 5min | 10min | 30min |
|           | C6 | L2 | C7 |

2.2. Catalytic activity measurements
Activity of the catalysts was measured in a fixed-bed reactor, which operating under atmospheric pressure and its inner diameter is 16mm. The inlet gas composition was set as follows: 1000 ppm NO, 1000 ppm NH₃, 1200 ppm SO₂, 5 vol.%O₂, and N₂ as the balance gas. The total flow rate of 600ml/min was maintained for all the test runs with a space velocity of 6000h⁻¹. And NOx concentrations at outlet of the reactor were continuously measured by the gas analyzer (Testo 350) produced in Germany. During the whole test, the temperature was maintained at 300-400°C. Then NO conversion can be calculated by the following equation: NO conversion= (NOin-NOout) ×100%/NOin.

3. Results and discussion

3.1. Characterization of catalysts
3.1.1. SEM analysis of catalysts. The surface microscopic images of inactivated catalyst C0, catalysts L2, L5 and L11 activated by different activating liquids, catalysts C2 and C5 activated at different baking temperature, catalysts C6 and C7 activated for different baking time are shown in Fig. 2. For inactivated catalyst C1, it can be seen from Fig.2 (a) that, the surface is covered with fine particles and the space among particles are clogged by fine particles, so the specific surface area is reduced greatly, thus the denitrification activity of catalyst C0 is much lower than that of fresh catalyst[12-14]. For the activated catalysts as shown in Fig.2 (b)-(h), it is obvious that, the surface is also covered with fine particles, but owing to the washing and activating by activating liquid, space among particles is larger than that of the inactivated catalyst C0. Fig.2 (b)-(d) showed the surface microscopic images of catalysts activated by different liquids, it can be seen that space among particles of activated catalysts L2, L5 and L11 is almost the same, the result shows that influence of activating liquids on the
distribution of particles on catalytic surface is small. On the other hand, it is obvious from Fig. 2 (b), (e), (f) that with the increasing of baking temperature, space among particles increases at first, when the temperature is 700 °C, the space of catalyst decreases obviously. For catalyst C6, L2 and C7, which activated by baking in air for 5min, 10min and 30min, it is known from Fig.2 (b), (g) and (h) that, the surface is also covered by small particles, and the surface of catalyst, which baking for too long time during the on-line activation, is decreased but still larger than that of the inactivated catalyst C0.

3.1.2. FT-IR analysis of catalysts.

Fig.3 shows the FT-IR patterns of the inactivated catalyst C0 and catalysts L2, L4, L10 and L11, activated by different activating liquids. For the whole tested catalysts, a broad band in the range 500-680 cm\(^{-1}\), which attributes to the vibration of the titanium dioxide, is found. What’s more, the activated catalysts in Fig.3 showed other absorption peaks as well, such as 1080.30, 1180.95, 2332.31 and 2360.49 cm\(^{-1}\).

Fig.4 shows the FT-IR patterns of activated catalysts C2, L2 and C5 baked at the temperature of 400 °C, 500 °C and 700 °C for 10min and C6, C7 baked at 500 °C for 5min and 30min respectively. It can be seen from Fig.4 that FT-IR spectra of the tested catalysts showed similar bands at 671.07, 1398.34 and 2360.49 cm\(^{-1}\), on the other hand, the spectra of the activated catalyst at 1398.34 cm\(^{-1}\) is stronger than that of other catalysts. The result shows that the symmetry of vanadium species is higher than that of the other catalysts. The result shows that the symmetry of vanadium species is higher than that of the other tested catalysts.

The bands in the range 1080.30-1180.95 cm\(^{-1}\) are close to the vibration frequency of V=O, which was associated with V\(_2\)O\(_5\), and the peak at 2332.31 and 2360.49 cm\(^{-1}\) are assigned to V\(^{4+}\)-OH, which is the intermediate of catalyst. Thus, it can be gained that the active ingredient on surface of the activated catalysts increased greatly, for the above results, the activity of activated catalyst may be increased effectively. For the activated catalyst L2, the band at 1396.76 cm\(^{-1}\), which attributed to the asymmetric bending vibration of NH\(^{4+}\) adsorbed on Brønsted acid sites, was found. And the band on the FT-IR result of catalyst L2 contributes to the SCR DeNOx reaction.
3.2. Influence of technical parameters on catalytic activity

3.2.1. Influence of activating liquids. Obviously in Fig. 5, NO conversion of activated catalyst is much higher than that of the inactivated catalyst C0. And NO conversion of catalyst L2 is up to 99% in the temperature range 300-400 °C, but that of inactivated catalyst C0 is only 66%, the difference between them is up to 30%. It is obvious that NO conversion of the catalyst L2 activated by activating liquid L2 was greatly enhanced, the result shows that activating liquid L2 contributes to the increase of NO conversion.
conversion of the activated catalyst. At the same time, in the test, with the increasing of content of ammonium vanadate, ammonium tungstate, ammonium molybdate and oxalate in activating liquid, NO conversion of the activated catalyst increased at first, but when the content is up to the optimal value, with the content increased, NO conversion decreased, and still higher than that of inactivated catalyst C0. Therefore, based on the SEM and FT-IR results, it can be obtained that, the activating liquid L2 is the optimal liquid, so the optimal content of ammonium vanadate is 1%, ammonium molybdate is 9%, ammonium tungstate is 6% and oxalate is 7.6%.

3.2.2. Influence of drying condition. The parameters of catalysts dried in different condition are shown in Table 5. It can be seen from the Table 4 that the surface area of catalyst C1 is larger than that of catalyst L2, and the support TiO2 is still rutile, at the same time, NO conversion of activated catalyst C1 is higher than that of catalyst L2. The result shows that the drying condition with catalyst dried at 80 °C for 15min, then dried at 105°C for 15min is optimal.

| Table 4. Characteristics of the catalysts activated in different drying conditions |
|-----------------|-----------------|-----------------|
| drying condition | activated catalyst C1 | activated catalyst L2 |
| surface area (m²/g) | 51.24 | 47.55 |
| TiO2 crystal phase | anatase titanium | anatase titanium |
| the largest NO conversion (%) | 99.12 | 99 |

Figure 6. NO conversion of the activated catalysts baked at different temperature

3.2.3. Influence of baking temperature. Fig. 6 shows the activity of catalysts baked at different temperatures. It can be known that with increasing baking temperature, activity of the activated catalysts increased at first, but when the baking temperature is higher than 600°C, the activity of catalysts decreased. As the result obtained by SEM, when baking temperature is too high, particles on the surface of catalyst were parts of aggregation and form a platy structure, so activity of the catalyst decreased. As shown in Fig. 6, the activated catalyst baked at the temperature of 500°C and 600°C showed the highest activity. Therefore, taking the cost of activating into account, the catalyst activated by baking at 500 °C is the best.

3.2.4. Influence of baking time. The NO conversion of activated catalysts baked at 500°C for 5min, 10min and 30 min was showed in Fig.7. It is known from Fig.7 that the influence of baking time on catalytic activity is little, the NO conversion of the three kinds of activated catalysts were up to 80%,
and when the catalyst activated by baking 500 ℃ for 10min, the activity is the highest, which is up to 99%.

4. Conclusion
Through experimental investigations and structural characterization of SCR De-NOx catalyst activation, the following can be concluded:

(1) Compared with inactivated catalyst, activated catalysts have higher contact area with flue gas and larger specific surface area, furthermore, the vibration frequency of V=O, NH4+ adsorbed on Brønsted acid sites and V4+-OH were found, thus the activity of activated catalysts were increased effectively.

(2) The NO conversion of inactivated catalyst C0 is only 66%, but after being activated by activating liquids in boiler, the NO conversion of activated catalysts are higher than that of inactivated catalyst C0. Furthermore, NO conversion of activated catalyst L2 is up to 99%, which is 33% higher than that of inactivated catalyst C0. It is obvious that the activity of catalyst L2 was enhanced greatly. Thus activating liquid labeled L2 is the ideal liquid.

(3) While inactivated catalyst activated by activating liquid L2 at 40 ℃, then dried in air at 80 ℃ for 15min and at 105 ℃ for 15min, and baked at the temperature of 500 ℃ for 10min, the activity of catalyst was enhanced greatly. Thus the technology activating catalyst in boiler is efficient and promising in engineering application.

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