Reduction of NO$_x$ and SO$_2$ in a non-thermal plasma reactor combined with catalyst and methanol

This content has been downloaded from IOPscience. Please scroll down to see the full text.
(http://iopscience.iop.org/0022-3727/41/20/205213)
View the table of contents for this issue, or go to the journal homepage for more

Download details:
IP Address: 115.156.147.6
This content was downloaded on 25/08/2016 at 13:25

Please note that terms and conditions apply.

You may also be interested in:
Removal of SO2 and NOx by pulsed DBD
A Khacef and J M Cormier

Electron beam treatment of exhaust gas with high NOx concentration
Janusz Licki, Andrzej G Chmielewski, Andrzej Pawelec et al.

Industrial applications of atmospheric non-thermal plasma in environmental remediation
Akira Mizuno

NOx remediation in oxygen-rich exhaust gas
A Khacef, J M Cormier and J M Pouvesle

Low-temperature NOx reduction processes
H H Kim, K Takashima, S Katsura et al.

SO2 removal from air with dielectric barrier discharges
A B Saveliev, G J Pietsch, A R Murtazin et al.

Multiparametric investigation on NOx removal
E A Filimonova, Yong ho Kim, Sang Hee Hong et al.
Reduction of NO\(_x\) and SO\(_2\) in a non-thermal plasma reactor combined with catalyst and methanol

Han Jun\(^1\), Heejoon Kim\(^2,3\), Yuhei Sakaguchi\(^2\) and Yao Hong\(^4\)

\(^1\) Hubei Key Laboratory of Coal Conversion and New Materials, Wuhan University of Science and Technology, Wuhan 430081, People’s Republic of China
\(^2\) Department of Ecological Engineering, Toyohashi University of Technology, Tempaku-cho, Toyohashi 441-8580, Japan
\(^3\) Graduate School of Energy and Environment Seoul National Univ. of Technology, Gongneungdong 172, Seoul 139-743, Korea
\(^4\) State Key Laboratory of Coal Combustion, Huazhong University of Science and Technology, Wuhan 430074, People’s Republic of China

E-mail: kim@eco.tut.ac.jp

Received 1 June 2008, in final form 6 August 2008
Published 1 October 2008
Online at stacks.iop.org/JPhysD/41/205213

Abstract

Non-thermal plasma technology has attracted considerable attention due to simultaneous removal of nitrogen oxide (NO\(_x\)) and sulfur oxide (SO\(_2\)) from flue gas. In this study, the synergistic effect of methanol and catalyst on NO, NO\(_x\) and SO\(_2\) removal efficiency in a plasma reactor is investigated. The results show that the removal efficiency of NO\(_x\) is dramatically enhanced by adding 0.4% methanol. Nevertheless, methanol has no significant beneficial effect on the oxidation of SO\(_2\). Based on the experimental results, the optimum content of methanol should be 0.4% and the preferable operating temperature is suggested to be 250 °C for removing NO\(_x\) and SO\(_2\) in a non-thermal plasma-catalyst reactor. Moreover, V\(_2\)O\(_5\)/TiO\(_2\) is found to be more effective than TiO\(_2\) for oxidizing NO, whereas V\(_2\)O\(_5\)/TiO\(_2\) is not better than TiO\(_2\) for SO\(_2\) oxidization unless the discharge power is above 11 W.

1. Introduction

Nitrogen oxides and sulfur oxides are the primary gaseous pollutants from coal-fired power plants, which are the main cause of acid rain, urban smog and greenhouse effect [1]. Up to now, a number of technologies have been developed to treat flue gas. Among the technologies, non-thermal plasma technology has attracted considerable attention due to simultaneous and effective removal of NO\(_x\) (including NO and NO\(_2\)) and SO\(_2\) at relatively low energy costs. Plasma can produce a large number of active radicals such as OH, HO\(_2\) and O, which play an important role in oxidizing NO and SO\(_2\) [2–5]. For example, these radicals first oxidize NO and SO\(_2\) into NO\(_2\) and SO\(_3\), then NO\(_2\) and SO\(_3\) react with water and form acid molecules consisting of HNO\(_3\) and H\(_2\)SO\(_4\). Khacef and Cormier [6] reported that dielectric barrier discharge (DBD) had the potential of removing SO\(_2\) and NO\(_x\) from gas streams. 100% SO\(_2\) and 36% NO\(_x\) were removed at a gas temperature of 100 °C with an energy cost of about 45 eV molecule\(^{-1}\) removed in a gas stream of 163 ppm of SO\(_2\), 523 ppm NO\(_x\), 49 ppm NO, 16% H\(_2\)O, 8% O\(_2\) and N\(_2\) as balance. Lin and Gao [7] also investigated the removal of NO\(_x\) from flue gas by radical injection combined with plasma and NaOH solution scrubbing; the experimental results indicated that the overall de-NO\(_x\) efficiency was as high as 81.2%. Young [8] reported that the direct and indirect applications of DBD were found to remarkably improve the catalytic NO\(_x\) reduction, especially under low temperatures. Kim et al [9] developed a new plasma system assisted with catalyst for removing NO\(_x\) and SO\(_2\). In their system, above 90% NO\(_x\) and 30% SO\(_2\) can be removed under 100 °C. Meanwhile, NH\(_3\) can slightly improve the NO, NO\(_x\), and SO\(_2\) oxidization rate in the case of no water.

Selective catalytic reduction (SCR) is a means of converting nitrogen oxides into diatomic nitrogen and water with the aid of a catalyst. Meanwhile, a gaseous reductant (anhydrous ammonia, aqueous ammonia or urea) is also added
to a stream of flue or exhaust gas. SCR of NOx using ammonia as the reducing agent was patented in the United States by the Engelhard Corporation [10]. In recent years, another research wave concerning the reduction of NOx is SCR by adding a small amount of hydrocarbons. Pophal et al [11] reported the SCR of N2O over Fe-MFI in the presence of C3H6. Hamada et al [12] studied H-form zeolite used as a catalyst and propane used as a reducing agent in an oxygen-rich atmosphere for NOx reduction. They found that the catalyst and additive were effective in improving NOx removal efficiency in the temperature range 473–873 K. Misono and Kondo [13] also investigated the NO reduction using propane as a reducing agent in the presence of rare earth (La, Ce, Pr, Sm, Tb) ion-exchanged ZSM-5 (Zeolite Socony Mobil-five) catalyst. In their experiments, 80–90% NO oxidation fraction can be achieved. The experiments of Mok [14] and Sathiamoorthy [15] demonstrated that hydrocarbon played an important role in enhancing the NO oxidation efficiency. Kung and co-workers [16] also investigated the NOx reduction combined with propane and Cu-ZSM-5 catalysts. The reaction mechanism postulated by the authors was that hydrocarbon was activated by reacting with the adsorbed NO2, then formed adsorbed oxidized N-containing hydrocarbon intermediates, while the reaction between hydrocarbon intermediates and NO was the principal route to producing N2 under lean condition.

The synergistic influence of plasma and hydrocarbon additive on NOx removal has been studied by Filimonova et al [17]. Experiments and calculation showed that C2H4 and C3H6 enhanced NO decomposition and decreased the consumption energy. Shang et al [18] also claimed that C3H6 could increase the NO removal rate by 7–24% in a corona radial reactor.

The experimental study in this work is to study the synergistic effects of methanol, catalyst and plasma on the removal efficiencies of NOx and SO2 under different temperatures and powers.

2. Experimental setup and conditions

2.1. Square wave high voltage supply

A rotating spark gap switch is used to generate fast rising square wave voltages; the schematic representation of the apparatus is shown in figure 1. In this study, commercial ac (100 V; 60 Hz) is input and transformed up to 12.5 kV by a transformer. A high voltage diode, a ballast resistor of 50 kΩ and a capacitor (1200 pF) are lined along the transformer. The high voltage electrode of the reactor is periodically connected and disconnected to the dc high voltage supply as the spark gap switch is rotating at a constant speed. Thus, a +12.5 kV pulsed high voltage is generated. A pulsed high voltage with a rise-time of about 20 ns and a duration of 2.5 ms was applied at around 300–350 pulses s−1 throughout this study.

2.2. Plasma reactor

The schematic of the catalyst-plasma reactor is shown in figure 2, which consists of the mass flow control part, the reaction part with temperature controller and the exhaust gas analysis part. The reactor is composed of a cylindrical quartz tube (inner diameter: 15 mm, length: 1000 mm). The model exhaust gases are generated by using compressed gases (SO2, NO, N2 and dry air) and the flow rates are regulated by mass flow controllers. A metal tube (diameter: 1 mm) as a positive electrode is located inside the quartz reactor, and the negative electrode is located on the outside of the quartz reactor. Moreover, the metal tube is also used to supply additives such as methanol and H2O. The catalysts used in the study are spherical in shape and 2–3 mm in size, which are directly placed in the quartz reactor at a distance of 30–100 mm (changeable) away from the metal tube. The exhaust gas coming out of the reactor is guided to the H2O bath to eliminate SO42− and NO3−. Concentrations of NO and NOx are monitored with an infrared gas analyzer (Shimadzu SOA-7000). The SO42− and NO3− concentrations in the solution are analysed using ion chromatography (Dionex DX-120). Before the experiment, the reactor is heated to a predetermined temperature by an electric heater. Experimental conditions are summarized in table 1.

3. Experimental results and discussion

3.1. Effect of methanol on oxidation of NOx and SO2

SO3 and NO2 are easily soluble in H2O as the following:

\[
\text{SO}_3 + \text{H}_2\text{O} \rightarrow \text{HSO}_3 \rightarrow \text{H}^+ + \text{SO}_4^{2-} + \text{H}^+ + \text{NO}_3. \tag{2}
\]

Hence, the concentrations of SO42− and NO3− in the H2O bath increase with the oxidation rate of NO and SO2 in this study.
concentrations of SO$_2$ and SO$_2$ [19, 20].

It is observed that the plasma can in the presence and absence of methanol under different discharge plasma, which play a crucial role in oxidizing NO and reacted as a reductant, which led to NO$_x$ removal via the reduction pathway.

Figure 3 shows that the concentration NO$_3$ is increased from 0.27 to 0.54 ppm at 300 °C with the addition of about 1.0% (volume) methanol. The main reason for this increment is that the addition of hydrocarbon can produce CH$_3$O and HO$_2$ radicals, which can oxidize NO into NO$_3$. The main reactions between hydrocarbon and NO are assumed to be as follows [19]:

\[
\text{CH}_3\text{OH} + \text{OH} \rightarrow \text{CH}_3\text{O} + \text{H}_2\text{O} \quad k = 1.66 \times 10^{-11} \exp(-854/RT) \text{ cm}^3 \text{s}^{-1}, \quad (3)
\]

\[
\text{CH}_3\text{O} + \text{O}_2 \rightarrow \text{HO}_2 + \text{HCHO} \quad k = 1.1 \times 10^{-13} \exp(-1310/RT) \text{ cm}^3 \text{s}^{-1}, \quad (4)
\]

\[
\text{HCHO} + \text{O} \rightarrow \text{HCO} + \text{OH} \quad k = 2.99 \times 10^{-11} \exp(-185/RT) \text{ cm}^3 \text{s}^{-1}, \quad (5)
\]

\[
\text{HCHO} + \text{OH} \rightarrow \text{HCO} + \text{H}_2\text{O} \quad k = 4.74 \times 10^{-12} T^{1.2} \exp(447/RT) \text{ cm}^3 \text{s}^{-1}, \quad (6)
\]

\[
\text{HCO} + \text{O}_2 \rightarrow \text{HO}_2 + \text{CO} \quad k = 8.5 \times 10^{-11} \exp(-102/RT) \text{ cm}^3 \text{s}^{-1}, \quad (7)
\]

\[
\text{CH}_3 + \text{O}_2 \rightarrow \text{CH}_3\text{O}_2 \quad k = 7.56 \times 10^{-31} T^{-3.64} \text{ cm}^3 \text{s}^{-1}, \quad (8)
\]

\[
\text{CH}_3\text{O} + \text{O}_2 \rightarrow \text{HO}_2 + \text{HCHO} \quad k = 1.1 \times 10^{-13} \exp(-157/RT) \text{ cm}^3 \text{s}^{-1}, \quad (9)
\]

\[
\text{H} + \text{O}_2 \rightarrow \text{HO}_2 \quad k = 5.64 \times 10^{-28} T^{-1.6} \text{ cm}^3 \text{s}^{-1}, \quad (10)
\]

\[
\text{CO} + \text{OH} \rightarrow \text{CO}_2 + \text{H} \quad k = 1.12 \times 10^{-13} \exp(-0.00012/RT) \text{ cm}^3 \text{s}^{-1}, \quad (11)
\]

\[
\text{HO}_2 + \text{NO} \rightarrow \text{NO}_2 + \text{OH} \quad k = 4.2 \times 10^{12} \text{ cm}^3 \text{s}^{-1}, \quad (12)
\]

\[
\text{CH}_3\text{O} + \text{NO} \rightarrow \text{CH}_3 + \text{NO}_2 \quad k = 1.9 \times 10^{-11} \text{ cm}^3 \text{s}^{-1}, \quad (13)
\]

\[
\text{CH}_3\text{O}_2 + \text{NO} \rightarrow \text{CH}_3\text{O} + \text{NO}_2 \quad k = 4.2 \times 10^{-12} \exp(180/RT) \text{ cm}^3 \text{s}^{-1}, \quad (14)
\]

\[
\text{HCHO} + \text{NO}_2 \rightarrow \text{HCO} + \text{HONO} \quad k = 8.29 \times 10^{-16} T^{3.67} \exp(-723/RT) \text{ cm}^3 \text{s}^{-1}, \quad (15)
\]

\[
\text{CH}_3\text{O} + \text{NO}_2 \rightarrow \text{CH}_3\text{ONO}_2 \quad k = 3.3 \times 10^{-13} \exp(180/RT) \text{ cm}^3 \text{s}^{-1}. \quad (16)
\]
It has been well known that OH radicals play an important role in the oxidation reaction of SO2 to SO3. One of the chain reactions by OH radicals can be expressed as follows [22]:

\[
\text{SO}_2 + \text{OH} \rightarrow \text{HOSO}_2 \\
\hspace{1cm} k = 1.19 \times 10^{-11} \exp(-715/RT) \text{ cm}^3 \text{s}^{-1}, \quad (17)
\]

\[
\text{HOSO}_2 + \text{O}_2 \rightarrow \text{HO}_2 + \text{SO}_3 \\
\hspace{1cm} k = 1.3 \times 10^{-12} \exp(-656/RT) \text{ cm}^3 \text{s}^{-1}. \quad (18)
\]

At the same time, OH is also important for reactant in (3) and (6). Hence, SO2 must compete with methanol for OH radicals, which causes the SO2 oxidation rate to decrease with the addition of methanol.

Figure 3 also demonstrates the NOx and SO2 removal rate as a function of the reaction temperature. It can be observed that the conversion rate of NO to NO2 reaches a peak at 300 °C under the synergistic effect of plasma and methanol, and the optimum temperature for oxidizing SO2 to SO3 is about 400 °C. In the case of plasma alone, the peak temperature for oxidizing NO and SO2 is 200 °C.

Figure 4 demonstrates the methanol content dependence of the oxidation fractions of NO, NOx, and SO2. When the content of methanol shifts from 0% to 0.4%, the oxidation fraction of NO increases from 31.6% to 98.8%, while that of NOx is also increased from 14.6% to 41%. Nevertheless, the excess methanol (above 0.4%) has no evident effect on the NO and NOx oxidation fraction. Thus, it can be concluded that the optimum content of methanol for oxidizing NO and NOx is 0.4%. As for SO2, the increase in the methanol content has no positive contribution to the oxidation process; even the SO2 oxidation fraction is slightly decreased with the increase in the methanol content. On the basis of the above experimental results, it is suggested that the optimum methanol content for oxidizing NOx and SO2 is 0.4%.

3.2. Effect of methanol on the activity of catalyst

In recent years, many researchers reported that the catalyst can significantly improve the NOx and SO2 removal efficiency in a plasma reactor [22–26]. Kim et al [20] reported that the oxidation fraction of SO2 to SO3 was up to 70% combined with TiO2, H2O2 and plasma. Toshiaki et al [23] also studied the removal of NOx with a plasma chemical hybrid reactor; the experimental results demonstrated that the removal efficiency of NOx achieved nearly 100% and the operating cost was extremely low. As mentioned above, adding hydrocarbon can effectively improve the oxidation fraction of NOx. The synergistic effects of plasma, methanol and V2O5/TiO2 catalyst on the NOx and SO2 removal efficiency are demonstrated in figure 5.

Despite the addition of about 0.4% methanol, NO removal efficiency in the plasma–V2O5/TiO2 catalyst system are dramatically increased from 31% to 98% under 12 W. Meanwhile, the variation of the NOx removal efficiency also reaches up to 40%. The increase in NOx removal efficiency is due to the chemical reactions between methanol, radical and NOx, and a detailed description of the mechanism is given above.

Although methanol is effective in improving the oxidation of nitrogen oxides, the effect on sulfur oxides is disappointing. The removal efficiency of SO2 decreases with the addition of methanol, which is similar to the result in figure 4. Furthermore, the increase in discharge power seems to have no significant influence on the oxidation process of SO2.
TiO$_2$ catalyst combined with plasma and H$_2$O$_2$ is effective in removing SO$_2$ [20], while the V$_2$O$_5$/TiO$_2$ catalyst is valid for oxidizing NO$_x$ in the same system. Here, the effects of V$_2$O$_5$/TiO$_2$ and TiO$_2$ catalyst on the removal efficiencies of NO$_x$ and SO$_2$ combined with plasma and methanol are compared. In figure 6, once substituting TiO$_2$ for V$_2$O$_5$/TiO$_2$, the removal efficiency of NO and NO$_x$ remarkably decreases. In particular, the discharge power is 11 W; the variations of NO and NO$_x$ removal efficiencies are up to 36% and 18%. Above 12 W, the difference in NO$_x$ removal efficiency versus discharge power between the cases of V$_2$O$_5$/TiO$_2$ and TiO$_2$ still exist. However, the difference is considerably smaller. Figure 6 also shows that the removal efficiency of SO$_2$ with the TiO$_2$ catalyst is higher than that with the V$_2$O$_5$/TiO$_2$ catalyst when the discharge power is below 11 W. In contrast to the variation trend with the V$_2$O$_5$/TiO$_2$ catalyst, the removal efficiency of SO$_2$ will not increase but decrease with the discharge power increment in the case of the TiO$_2$ catalyst. Considering both the operation cost and NO and SO$_2$ removal efficiency, the best catalyst for oxidizing NO and SO$_2$ in a plasma reactor combined with methanol is V$_2$O$_5$/TiO$_2$, and the optimum discharge power is suggested as 12 W.

### 3.3. The effect of temperature

The effect of temperature on the oxidation of NO$_x$ and SO$_2$ in the plasma-V$_2$O$_5$/TiO$_2$ catalyst system combined with 0.4% methanol is discussed to find an optimum reaction temperature, as shown in figure 7. In the experiment, the discharge power of plasma is 11 W and the temperature varies from 200 to 500$^\circ$C. As can be seen in figure 7, in the temperature range 200–250$^\circ$C, the variation of the NO and NO$_x$ removal rate can be neglected. Nevertheless, the removal efficiency is dramatically decreased when the temperature is above 250$^\circ$C. Kim et al reported that the concentration of ozone decreases sharply with the temperature, which results in the decrease in NO$_x$, NO and SO$_2$ oxidation efficiencies [9]. Hence, it is suggested that the optimum temperature for removing nitrogen oxide is 250$^\circ$C.

SO$_2$ removal efficiency decreases with the increase in temperature and reaches the minimum value at 250$^\circ$C. When the temperature is above 250$^\circ$C, the increase in temperature can promote SO$_2$ removal. It might be assumed that the reasons are the following: the ozone concentration will sharply decrease with the increment in temperature, which causes the SO$_2$ removal efficiency to decrease [9]. On the other hand, the increase in temperature can accelerate the kinetic rate of (18) and (19). In the range 200–500$^\circ$C, the minimal and maximal SO$_2$ removal efficiencies are 3% and 20%, respectively.
Figure 7. Removal efficiency of NO, NOx and SO2 versus temperature (H2O content: 2.5%; methanol: 0.4%; catalyst: V2O5/TiO2; discharge power: 11 W).

4. Conclusions

In this paper, we have presented the experimental studies of the effect of methanol on NOx and SO2 removal efficiency in a plasma-catalyst reactor. The comprehensive investigation reported here addresses the effect of the catalyst type, methanol, reaction temperature and power of plasma on NOx and SO2 removal efficiency.

The reaction of OH with methanol results in the formation of CH3O and CH3O2 radicals, and the radicals have a major influence on NO oxidation. In this study, we also demonstrated that methanol can promote NO and NOx removal efficiency, and the optimum operation conditions were 0.4% methanol and 250 °C when the catalyst was V2O5/TiO2. However, methanol has a negative effect on the oxidation of SO2. This fact is considered to be caused by the fact that methanol will compete with SO2 for OH radical. Furthermore, the results also reveal that V2O5/TiO2 is better than TiO2 for oxidizing NO and SO2 in the presence of methanol and plasma.

Acknowledgments

This work was partly supported by the National Natural Science Foundation of China (Grant Nos 50721005 and 5072140649).

References

[4] Han Y and Jiang G 2008 Feasibility analysis of simultaneous DeSO2/DeNOx using plasma and combined photocatalysis 2nd Int. Conf. on Bioinformatics and Biomedical Engineering (Shanghai, China) p 3956