

Article

Low Temperature Performance of Selective Catalytic Reduction of NO with NH₃ under a Concentrated CO₂ Atmosphere

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Abstract: Selective catalytic reduction of NO_x with NH₃ (NH₃-SCR) has been widely investigated to reduce NO_x emissions from combustion processes, which cause environmental challenges. However, most of the current work on NO_x reduction has focused on using feed gas without CO₂ or containing small amounts of CO₂. In the future, oxy-fuel combustion will play an important role for power generation, and this process generates high concentrations of CO₂ in flue gas. Therefore, studies on the SCR process under concentrated CO₂ atmosphere conditions are important for future SCR deployment in oxy-fuel combustion processes. In this work, Mn- and Ce-based catalysts using activated carbon as support were used to investigate the effect of CO₂ on NO conversion. A N₂ atmosphere was used for comparison. Different process conditions such as temperature, SO₂ concentration, H₂O content in the feed gas and space velocity were studied. Under Mn-Ce/AC conditions, the results suggested that Mn metal could reduce the inhibition effect of CO₂ on the NO conversion, while Ce metal increased the inhibition effect of CO₂. High space velocity also resulted in a reduction of CO₂ inhibition on the NO conversion, although the overall performance of SCR was greatly reduced at high space velocity. Future investigations to design novel Mn-based catalysts are suggested to enhance the SCR performance under concentrated CO₂ atmosphere conditions.

Keywords: selective catalytic reduction (SCR); oxy-fuel combustion; low-temperature; Mn; Ce; CO₂

1. Introduction

NO_x emissions are responsible for acid rain and urban smog, and they pose a significant risk to the environment and human health [1]. Selective catalytic reduction of NO_x with NH₃ (NH₃-SCR) has been extensively investigated and also been used commercially for NO_x reduction. The industrial operation is based on V₂O₅-WO₃ (MoO₃)/TiO₂ catalysts, which are reactive within a high temperature window (300–400 °C) [2–4]. However, many pollutants, e.g., sulphur and dusts, are present in this reactive temperature range, causing the deactivation of selective catalytic reduction (SCR) catalyst [5]. Therefore, there is a strong need to develop catalysts for low temperature SCR processes, which can be placed after the electrostatic precipitator and desulfurizer to avoid pollutants such as sulphur and particulates.

Catalysts containing transition metals have been widely researched for low-temperature SCR, due to the effective catalytic ability of transition metals [6–10]. Among them, Mn- and Ce- based catalysts have drawn particular attention due to their abundant oxygen vacancies, which promote the redox cycle during SCR reactions [11–14]. In addition, activated carbon (AC) has been used as catalyst support for SCR, since it has high surface for metal loading and the presence of functional groups on the surface of activated carbon can also promote NO_x conversion [15–19].

Currently, NH₃-SCR is mostly investigated under N₂ atmospheres, to simulate the stationary NO_x sources of power plants. It is realized that oxy-fuel combustion is attracting increasing interest. Using pure oxygen instead of air for combustion generates a flue gas which consists of mainly CO₂ and H₂O, where CO₂ can be easily captured [20–23]. Therefore, more understanding of NH₃-SCR in the presence of an abundance of CO₂ is essential for the future development of SCR technology combined with oxy-fuel combustion processes. However, it is found that there are a few works investigating the influence of CO₂ on SCR [24,25]. For example, Kim *et al.* [24] studied the effect of CO₂ on SCR using a small pore zeolite copper catalyst; and reported that CuSSZ13 catalyst can be deactivated by 10% CO₂ at low temperatures (<300 °C). Magnusson *et al.* [25] studied the influence of 6% CO₂ during SCR, and found no significant influences. To our best knowledge, there is very limited work about the investigation of low-temperature SCR under high concentrations of CO₂, simulating the flue gas from oxy-fuel combustion processes.

Furthermore, it is known that SCR performance is significantly affected by the process conditions such as temperature, space velocity [26–28], concentrations of H₂O [25,29–31], and the presence of SO₂ [6,11,25,30,32,33]. For example, Magnusson *et al.* [25] investigated SCR using a marine based catalyst; they reported that higher space velocity (18,300 h⁻¹) resulted in a continuous decrease in catalytic activity, compared with space velocities of 6100 and 12,200 h⁻¹; in addition, they also reported that at temperatures higher than 300 °C, the catalyst showed a stable catalytic reactivity at different SO₂ concentrations, but a significant reduction of SCR activity was observed at a temperature of 250 °C for gas streams containing 250 and 750 ppm SO₂. The decrease of SCR activity with the increase of space velocity has also been reported by other researchers [26]. Pan *et al.* [30] reported that H₂O has a reversible negative effect on NH₃-SCR using a MnO_x/MWCNTs catalyst, while SO₂ was found to have an irreversible deactivation effect.

In this work, our main objective was to investigate the SCR performance under a concentrated CO₂ atmosphere. Mn-Ce/AC with different process conditions, including temperature, SO₂ and H₂O and also space velocity were used. In addition, the performance of SCR catalyst under CO₂ atmosphere was compared to an inert N₂ atmosphere at various process conditions.

2. Experimental

2.1. Catalyst Preparation

Activated carbon (AC, 40–60 mesh, Kecheng Novel Technology Co., Ltd. Beijing, China) was used as catalyst support. It was pre-treated under 67% concentrated HNO₃ for 1.5 h at 80 °C, and washed with deionized water to a pH about 7. The washed AC was dried at 110 °C for 12 h before using as catalyst support. Catalyst support (treated AC) was added to an aqueous solution (100 mL) containing the desired amount of Mn(NO₃)₂ and Ce(NO₃)₃. The solution was stirred for 3 h and left for 2 h without stirring. The precursor was dried at 100 °C for 12 h and finally calcined at 500 °C for 3 h in N₂ atmosphere. Catalysts with different metal additions were prepared in this work: Mn/AC catalysts contained 3, 7, and 9 wt% Mn, respectively; Ce/AC catalysts had a Ce content of 3, 7 and 9 wt%, respectively. Also 7 wt% (Mn-Ce)/AC catalysts were prepared with the following Mn/Ce ratios: 1:4, 1:2, 1:1 and 2:1. The catalysts prepared in this work have BET surface areas around 300 m²·g⁻¹ and pore volumes of about 0.3 cm³·g⁻¹.

2.2. Experimental System

NH₃-SCR tests were carried out in a fixed bed reaction system shown in Figure 1. Simulated gases (NO, NH₃ and O₂ balanced with N₂ or CO₂) with a total flow rate of 1200 mL/min were introduced into the reaction system, where 2 g of catalyst was located. The catalysts were tested at temperatures between 100 °C and 300 °C. The NO concentration was analysed by a Flue Gas Analyzer (350 XL, Testo, Schwarzwald, Germany) The NO conversion was calculated using the following equation:

$$NO_{\text{conversion}} \% = \frac{[NO]_{\text{inlet}} - [NO]_{\text{outlet}}}{[NO]_{\text{inlet}}} \times 100\% \quad (1)$$

where $[NO]_{\text{inlet}}$ is the introduced NO concentration, vol%; $[NO]_{\text{outlet}}$ is the NO concentration in the outlet of the reactor, vol%.

In addition, the influences of space velocity (3408–13,632 h⁻¹), SO₂ content (0–400 ppm) and H₂O content (0%–8%) were also investigated under both CO₂ and N₂ atmospheres.

2.3. Catalyst Characterization

X-ray diffraction (XRD, Bruker, Karlsruhe, Germany) with monochromatized Cu K α radiation was used to obtain the crystal structure of the fresh catalyst with scanning speed of 12 min⁻¹ from 10° to 60°. Scanning electron microscopy (SEM, S-3500N, Hitachi, Tokyo, Japan) and transmission electron microscopy (TEM) (Tecnai-20, Royal Philips, Amsterdam, Netherlands) were used to obtain morphologies of the fresh catalysts. BET surface area and porosity of the fresh catalyst were determined using ASAP2020 equipment (Micromeritics, Norcross, GA, USA); during the analysis, a 0.2 g sample was first degassed under 150 °C before being used for adsorption/desorption of N₂.

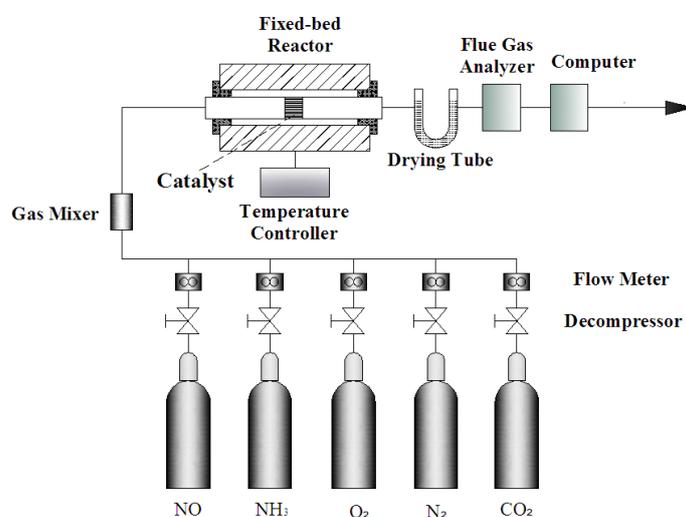


Figure 1. Schematic diagram of the selective catalytic reduction of NO_x with NH₃ (NH₃-SCR) reaction system.

3. Results and Discussion

3.1. Comparison of CO₂ and N₂ Atmosphere with Different Catalysts

NH₃-SCR was carried out at temperatures between 100 °C and 300 °C with Mn/AC, Ce/AC and Mn-Ce/AC catalysts, respectively. As shown in Figure 2, activated carbon (AC) without metal loading showed very low NO reduction activity, with about 35% NO conversion. In addition, with little catalytic impact from catalyst (only using AC), CO₂ showed inhibition of NO conversion in the SCR test.

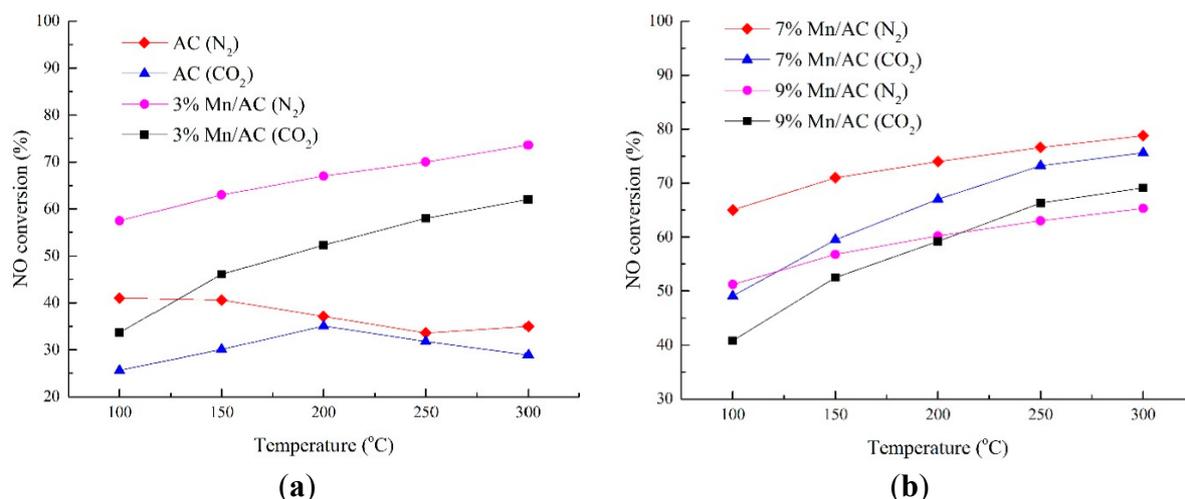


Figure 2. NH₃-SCR using Mn/AC catalyst under CO₂ and N₂ atmosphere. Other conditions: 800 ppm NO; 800 ppm NH₃, 6% O₂ and space velocity 3408 h⁻¹.

With the increase of reaction temperature from 100 °C to 300 °C, NO conversion was increased significantly in the presence of Mn/AC catalyst, for both N₂ and CO₂ atmospheres. The enhanced NO conversion at a relatively higher temperature using Mn-based catalyst has been reported [34–37]. Similar results were also found while using other catalysts (Figures 3 and 4).

From Figure 2, the conversion of NO was between 58% and 70% in the presence of 3% Mn/AC catalyst under N₂ atmosphere; the NO conversion was much lower in the CO₂ atmosphere (33%–58%). Using 7% Mn/AC catalyst, the N₂ atmosphere also gave higher NO conversion (65%–75%) compared with the CO₂ atmosphere (49%–70%). However, it seems that the difference of NO conversion between N₂ and CO₂ atmosphere was reduced at higher reaction temperatures, when the catalyst was changed from 3% Mn/AC (10% difference) to 7% Mn/AC (5% difference).

The advantage of N₂ atmosphere over CO₂ in terms of NO conversion was reduced when the Mn loading in the Mn/AC catalyst was increased to 9%. For example, the same level of NO conversion was observed from Figure 2 for both CO₂ and N₂ atmospheres at 200 °C using the 9% Mn/AC catalyst. When the reaction temperature was increased to 300 °C in the presence of the 9% Mn/AC catalyst, the NO conversion in the CO₂ atmosphere (69%) became higher than under the N₂ atmosphere (64%).

The NO conversion in relation to the reaction atmosphere has also been studied using Ce/AC catalysts. As shown in Figure 3, the difference of NO conversion between the CO₂ and N₂ atmosphere was also affected by the reaction temperature. When the reaction temperature was lower than 200 °C, the NO conversion was higher in the atmosphere of N₂ compared with the CO₂ one. When the reaction temperature was increased to 300 °C, in most of the cases, the N₂ atmosphere gave higher NO conversion compared with the CO₂ atmosphere; except when using the 3%Ce/AC catalyst, where the NO conversion was higher in the atmosphere of CO₂ (80%) compared with the N₂ one (75%).

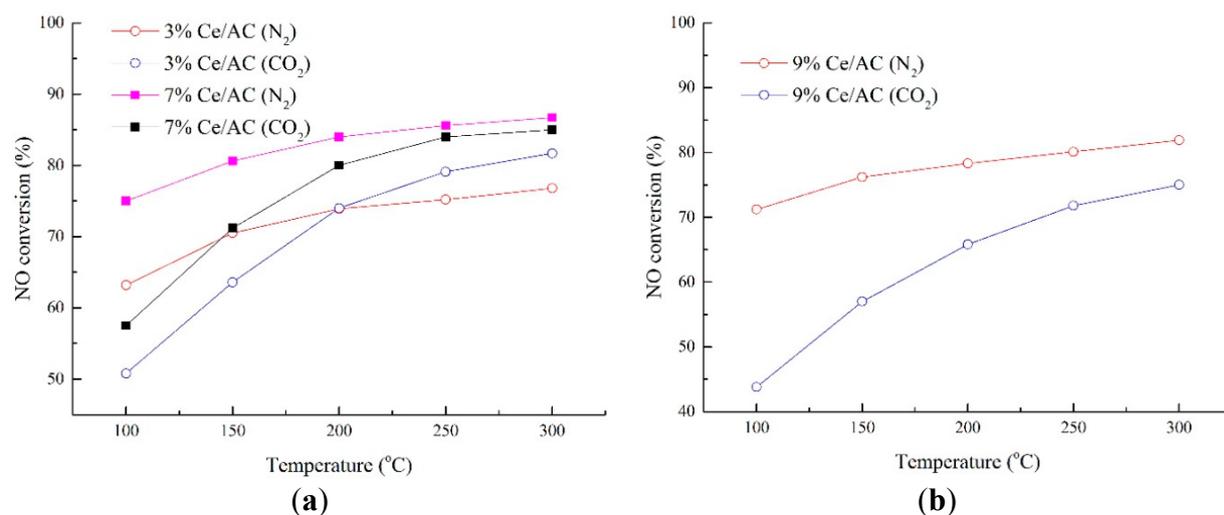


Figure 3. NH₃-SCR using Ce/AC catalyst under CO₂ and N₂ atmosphere: (a) 3% Ce/AC and 7% Ce/AC; (b) 9% Ce/AC. Other conditions: 800 ppm NO; 800 ppm NH₃; 6% O₂ and space velocity 3408 h⁻¹.

The SCR-NH₃ process was enhanced under the CO₂ atmosphere compared with the N₂ atmosphere, when the Mn loading in the catalyst was increased (Figures 2 and 3). This is consistent with the results shown in Figure 4, where the SCR experiments were carried out using Mn-Ce/AC catalysts with different Mn:Ce ratios. From Figure 4, catalyst with low Mn loading e.g., 7% Mn-Ce/AC (Mn:Ce = 1:4) showed a lower NO conversion in the CO₂ atmosphere (57%) compared with the N₂ atmosphere (71%) at the temperature of 100 °C.

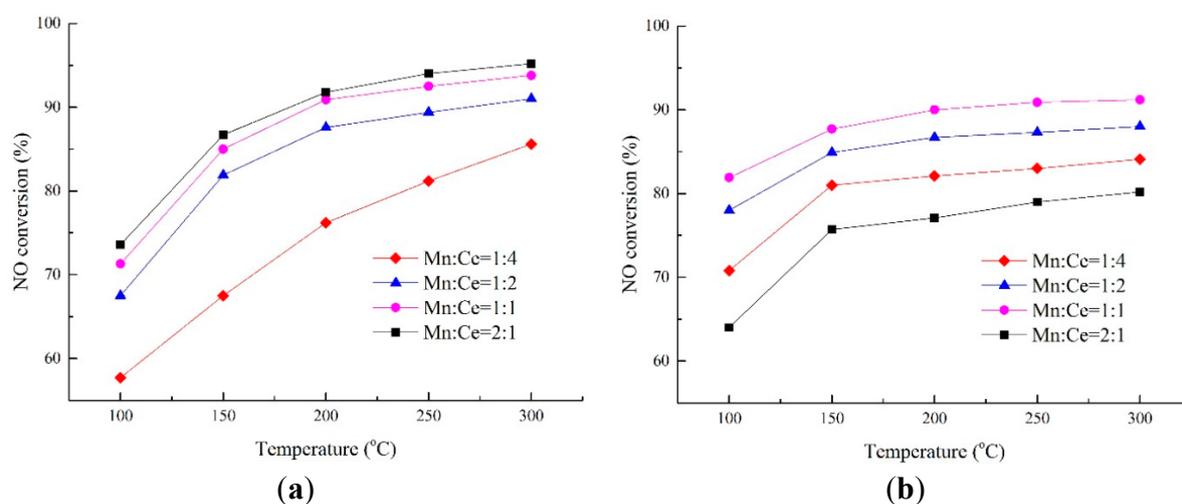


Figure 4. NH₃-SCR using different 7% Mn-Ce/AC catalysts under (a) CO₂ and (b) N₂ atmosphere. Other conditions: 800 ppm NO; 800 ppm NH₃; 6% O₂ and space velocity 3408 h⁻¹.

With the increase of Mn:Ce ratio, the NO conversion was increased for the CO₂ atmosphere, and fluctuated (increased first and then decreased) for the N₂ atmosphere. For example, the NO conversion was around 73% for the CO₂ and only 64% for the N₂ in the presence of the 7% Mn-Ce/AC (Mn:Ce = 2:1) catalyst at 100 °C. In addition, the overall performance of SCR was better in the CO₂ atmosphere compared with the N₂ atmosphere, when the catalyst has higher Mn:Ce ratio.

In summary, in this work we found that the depression of SCR activity under CO₂ atmosphere can be reduced by adding Mn metals in the catalyst system, while the presence of Ce in the catalyst enhanced the CO₂-induced SCR depression.

Mn-based catalysts have been widely researched for SCR, as various types of labile oxygen are present in the catalyst [38–40]. In addition, abundant oxygen vacancies present in amorphous Mn-based catalysts were reported to greatly improve the SCR activity [40]. The enhancement of SCR activity using Mn-based catalyst is also due to the promoted adsorption of NH₃ and NO oxidation to NO₂ [41], which play important roles in SCR [42]. In this work, it seems that amorphous Mn-species were present in the Mn-based catalyst; as shown in Figure 5, XRD analysis of the selected catalysts is presented. Diffraction peaks related to Mn or Ce metals could barely be observed, as little differences could be found from XRD analysis between AC and Mn-Ce/AC. The weak diffraction in the XRD analysis might be due to that the particle size of metal were very small. As shown in Figure 6 (TEM analysis), particles with size about 10 nm were observed in the fresh 7% Mn-Ce/AC (Mn:Ce = 1:4).

Kim *et al.* [24] reported that CO₂-induced deactivation in SCR was due to the adsorption of NH₃ by CO₂, and suppression of the formation of nitrates, which are a key reaction intermediate for NO_x reduction. Yang *et al.* [43] also reported that CO₂ may compete for the adsorbed NH₃, which should be desirable for NO conversion.

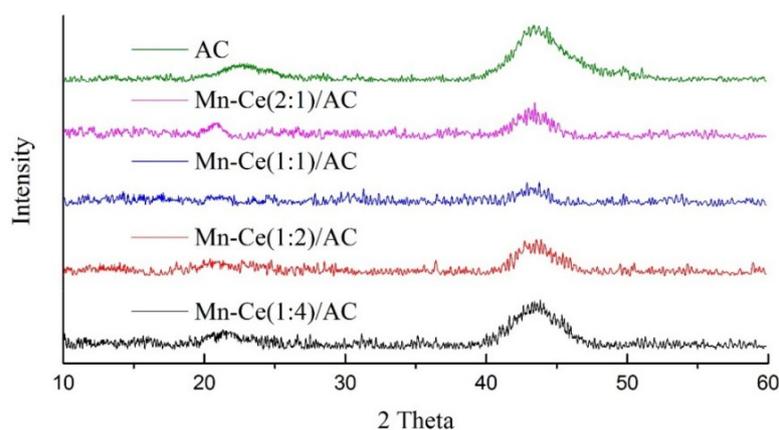


Figure 5. X-ray diffraction (XRD) analysis of the selected catalysts.

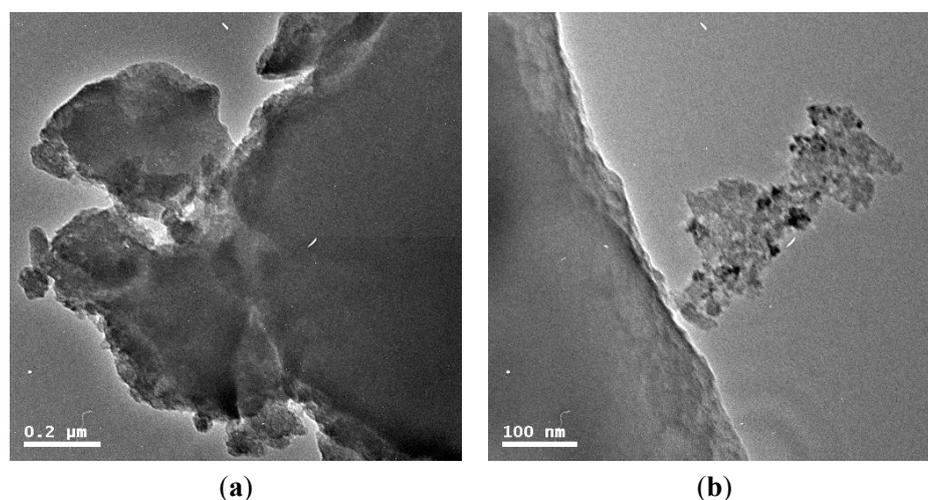


Figure 6. Transmission electron microscopy (TEM) analysis of the selected catalyst: (a) AC; (b) 7% Mn-Ce/AC (Mn/Ce 1:4).

Therefore, in order to reduce the negative effect of CO₂ in SCR, the adsorption of NH₃ by CO₂ should be depressed. In this work, we suggest that the formed Mn-based species might reduce the adsorption of NH₃ by CO₂. The addition of Mn in the catalysts changed some Lewis (weak) acid sites to Bronsted (strong) acid sites, which have been reported to be less affected by CO₂ [43]. It has also been reported that weak acid sites in the catalyst were changed into strong acid sites with the increase of Mn loading [8]. In addition, addition of Ce into MnTi catalyst resulted in an increase of Lewis acid sites, which enhances the inhibiting of CO₂ on SCR [43]; thus the literature supports the results obtained in this work, where catalysts with high Ce loading showed lower NO conversion under the CO₂ atmosphere compared with the N₂ atmosphere (Figure 4).

From the above results, we propose that the performance of SCR in CO₂ atmosphere is affected by the type of catalyst and also the reaction temperature. It is suggested that CO₂ has a more negative effect on SCR at low temperatures. In the following sections, we will discuss the influence of process conditions on SCR in the CO₂ and N₂ atmosphere.

3.2. Selective Catalytic Reduction of NO_x with NH₃ (NH₃-SCR) Test under CO₂ and N₂ Atmosphere with Different Process Conditions

The SCR performance under concentrated CO₂ was compared with a N₂ atmosphere under different process conditions. Figure 7 shows the effect of space velocity on the SCR performance using the 7% Mn/AC and the 7% Ce/AC catalysts. The higher space velocity resulted in a lower NO conversion might be due to the reduction of residence time of the reactants [25,26]. Although Ce-based catalyst has higher SCR activity compared with the Mn-based catalyst, we focus on discussions about the influence of the reaction atmosphere.

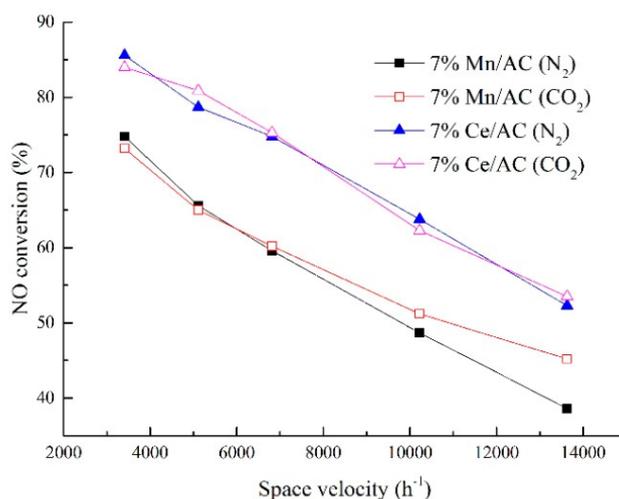


Figure 7. NH₃-SCR using different space velocity under CO₂ and N₂ atmosphere. Other conditions: temperature 250 °C; 800 ppm NO; 800 ppm NH₃ and 6% O₂.

From Figure 7, it seems that for the Mn/AC catalyst, higher NO conversion was observed under the CO₂ atmosphere compared with the N₂ atmosphere, under high space velocity (13,632 h⁻¹). The better SCR performance using CO₂ over N₂ was not observed in the presence of Ce/AC catalysts; this is consistent with the previous discussions that Mn reduces the negative effect of CO₂ while Ce does not. In addition, since the depression of SCR under CO₂ is mainly ascribed to the adsorption of NH₃ by CO₂, thus a higher space velocity could reduce/avoid the negative effects of CO₂. However, the overall NO efficiency could be greatly reduced at higher space velocity.

The influence of CO₂ atmosphere on SCR was also investigated under different SO₂ concentrations. SO₂ is known to have a negative effect on NO conversion due to catalyst poisoning [6,11,30]. As shown in Figure 8, for all of the tested three catalysts (Mn/AC, Ce/AC and

Mn-Ce/AC), the CO₂ atmosphere showed an inhibition of the NO conversion. In particular, the difference of NO conversion between CO₂ and N₂ atmosphere was increased with the increase of SO₂ concentration in the feed gas stream. For example, the NO conversion was similar for both CO₂ and N₂ atmosphere with the SO₂ concentration of 0 ppm; however, the N₂ atmosphere gave about 10% of NO conversion higher than the CO₂ atmosphere when the SO₂ concentration was increased to 400 ppm. Therefore, it is suggested that the presence of SO₂ enhances the inhibition of NO conversion in the CO₂ atmosphere.

The influences of a CO₂ atmosphere on catalytic SCR at different H₂O concentrations are shown in Figure 9. The increase of H₂O content from 0% to 8% resulted in a reduction of NO conversion for all the catalysts; this is consistent with the literature on the effect of H₂O addition [30,44]. It seems that the influence of H₂O concentration on NO conversion is small, when the CO₂ atmosphere is compared with the N₂ atmosphere, although a little higher NO conversion was observed for the N₂ atmosphere with 8% of H₂O. It is suggested that the presence of large amounts of H₂O, which would compete with NO and NH₃ adhering to the AC surface, has a more negative effect on the SCR performance in the CO₂ atmosphere, compared with the N₂ atmosphere.

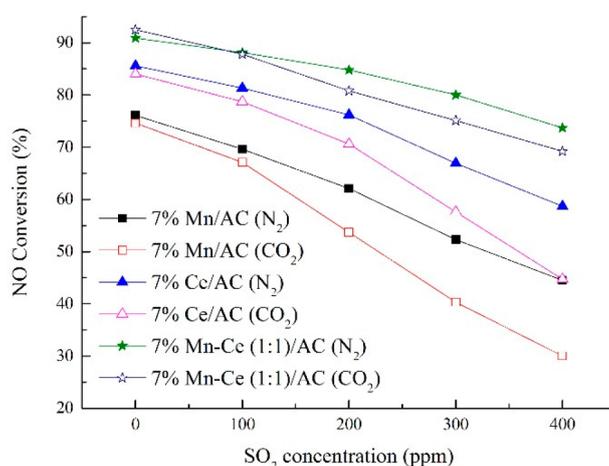


Figure 8. NH₃-SCR using different SO₂ concentrations under CO₂ and N₂ atmosphere. Other conditions: temperature 250 °C; 800 ppm NO; 800 ppm NH₃; 6% O₂ and space velocity 3408 h⁻¹.

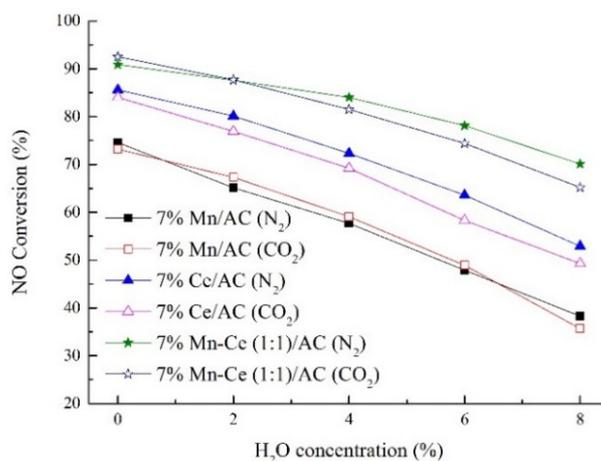


Figure 9. NH₃-SCR using different H₂O concentrations under CO₂ and N₂ atmosphere. Other conditions: temperature 250 °C; 800 ppm NO; 800 ppm NH₃; 6% O₂; 0 ppm SO₂ and space velocity 3408 h⁻¹.

4. Conclusions

In this work, the SCR process in the presence of Mn- and Ce-based catalysts under a concentrated CO₂ atmosphere was investigated in order to obtain information for developing SCR technologies combined with oxy-fuel combustion power plants. It is found that CO₂ can depress the conversion of NO, in particular at low reaction temperatures and with high SO₂ concentration in the feed gas. Under the Mn-Ce/AC catalysis conditions, the results showed that with the increase of Mn loading, the inhibitory effect of CO₂ on NO conversion was reduced, while adding Ce metal in the catalyst system enhanced the depression effect of CO₂ on SCR.

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Conflicts of Interest: The authors declare no conflict of interest.

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