Study on Manganese-based Supports for Preparing Low-Temperature SCR deNOx Catalysts

Chemistry and Environment Lab: Tseng, Chih-Fu; Kuo, Lih-Wen; Chiang, Ping-Hung; Chen, Shin-Yi
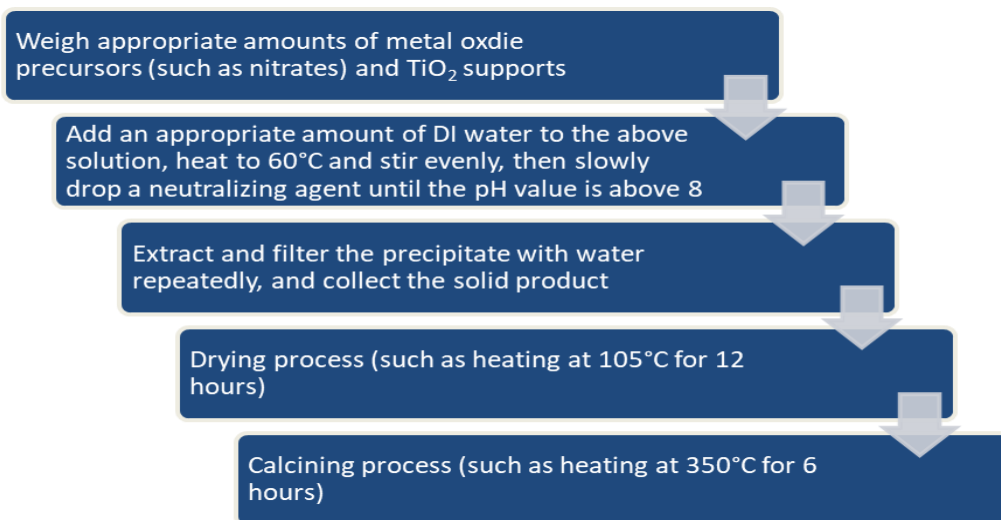
1. Introduction

SCR (Selective Catalyst Reduction) means that under a certain temperature, an appropriate amount of O_2, and in the presence of a catalyst, a reducing agent (such as NH_3 or urea) selectively converts NO_x to N_2 and H_2O in the flue gas in order to achieve purification. Recently, more and more scholars have devoted themselves to researching low-temperature (80~200°C) selective catalytic reduction technology. The development of low-temperature SCR catalyst systems can expand the operating temperature range. It can applied to lower-temperature flue gas treatment to reduce energy consumption. In addition, the low-temperature SCR system can be installed downstream of a baghouse or an electrostatic precipitator to avoid fouling, erosion, and chemical poisoning caused by fly ash. If it is installed downstream of flue gas desulfurization, it can avoid SO_2 poisoning and NH_4HSO_4 formation. They both can effectively extend the catalyst's lifetime and reduce operation and maintenance costs.

2. Experimental Results

The SCR denitration catalyst based on MnO_x has excellent low-temperature (<200°C) activity. In this study, Mn and Ce were selected as the main active metals to ensure the low-temperature activity of the catalyst, and it was combined with Fe auxiliary metal to try to resist water vapor. By modifying the recipe of the catalyst, the amount of catalyst can be more refined, the equipment volume when implementing low-temperature catalysts can be reduced, and the cost of the technology can be improved.

In this study, we synthesized the catalysts using the co-precipitation method. We weighed an appropriate amount of TiO_2 as a carrier (you can choose not to add it), an active metal precursor, and an appropriate amount of water and mixed them evenly. Heat and stir evenly. The neutralizer(such as sodium carbonate, ammonium carbonate, etc.) is slowly dropped into the solution until the solution becomes neutral. After filtration, we collected the precipitate and rinse it with pure water. The precipitate was dried in an oven and then calcined. The catalyst product was obtained, and the experimental process is shown in Figure 1. In addition, this study also designed and developed mass-production equipment for kilogram-level catalysts, as shown in Figure 2.

Source: Graphed by TPRI

Figure 1 Catalyst preparation process
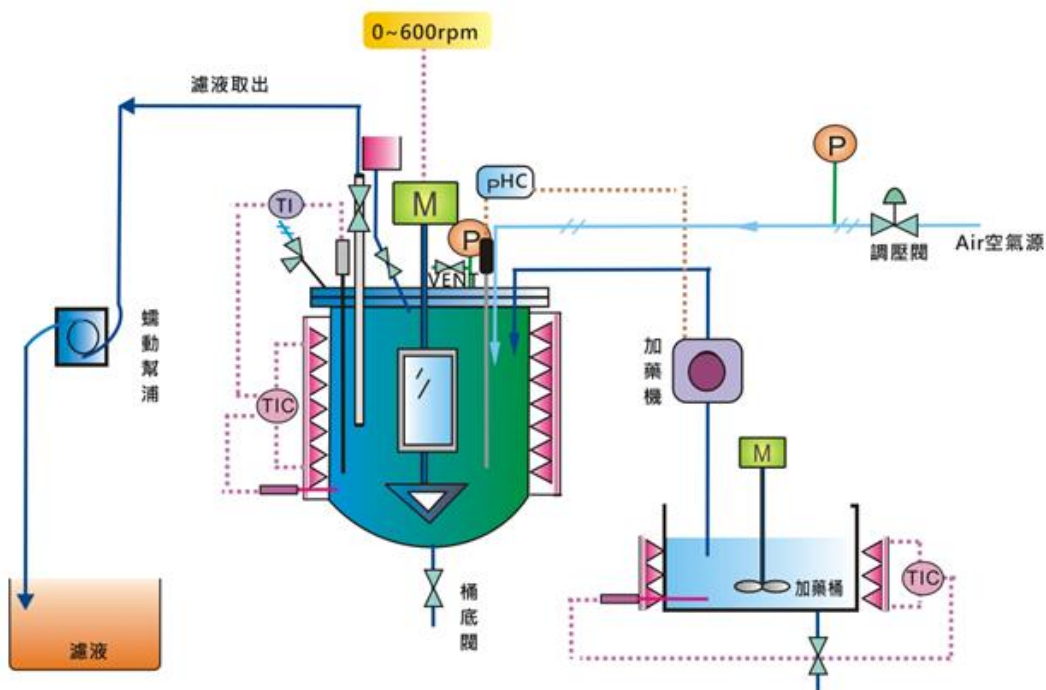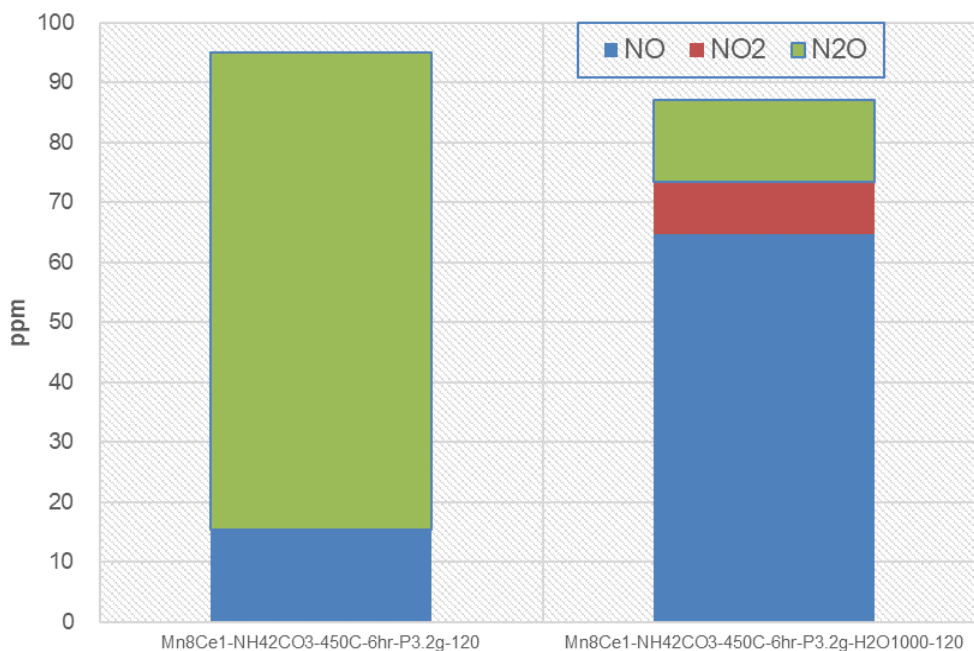

Source: Graphed by TPRI

Figure 2 Catalyst mass production equipment

Cerium has superior oxygen storage capacity and surface acidity, which can increase the oxygen content of chemical adsorption on the catalyst surface. It is helpful for the oxidation of NO. The catalyst Mn_8Ce_1 was synthesized in this experiment. $(NH_4)_2CO_3$ was used as the neutralizing agent in the preparation process. The calcination temperature was 450℃. The simulated flue gas conditions were NO: 204 ppm, NH_3: 204 ppm,

O_2: 3.3%, H_2O: 0~10 %, flow rate: 2000sccm (in N_2 balance), T: 120°C, and SV: 37500 mL/g·hr. The outlet emission concentration was measured, as shown in Figure 3. The results showed that the main product of the catalytic reaction is N_2O under the condition of $H_2O= 0\%$. This indicates that the catalyst activity is extremely strong. The denitration efficiency is about 64.7% under the condition of $H_2O=10\%$. This indicates that this catalyst recipe has enough water resistance.

Source: Graphed by TPRI

Figure 3 The outlet emission concentration of the catalyst when using $(NH_4)_2CO_3$

According to the previous experiment, the optimal catalyst recipe is Mn:Ce = 8:1. In this study, we added Fe metal oxide, which is expected to increase the catalyst denitration efficiency and water and sulfur resistance. The catalysts $Mn_8Ce_1Fe_4$ and $Mn_8Ce_1Fe_2$ were synthesized in this study. The catalysts' denitration efficiency and N_2 selectivity were measured, as shown in Table 1 when the recipe was changed to MnCeFe. The results showed that the denitration efficiency of the $Mn_8Ce_1Fe_2$ catalyst is 93.95%, but the N_2 selectivity is only 61.67% under the condition of $H_2O= 0\%$. The $Mn_8Ce_1Fe_2$ catalyst also has a high denitration efficiency (90.02%) and N_2 selectivity(76.31%) under the condition of $H_2O= 10\%$. If we compare the $Mn_8Ce_1Fe_2$ catalyst and the Mn8Ce1Fe4 catalyst, the $Mn_8Ce_1Fe_2$ catalyst has a higher denitration efficiency despite the presence or absence of moisture or different calcination conditions.

Table1 The results of catalyst activity when changing the Fe ratio

Source: Made by TPRI

Mn8Ce1Fe4 and Mn8Ce1Fe2	Inlet NO	Outlet NO	Outlet NO$_2$	Outlet N$_2$O	Outlet NOx	SV	η	N$_2$ Selectivity	Temp
Mn8Ce1Fe4-400C-6hr-P3.2g-120-1090330	204	23.45	1.1	39.82	24.55	37500	87.97	55.01	120
Mn8Ce1Fe4-400C-6hr-P3.2g-H2O1000-120-1090330	204	36.97	10.16	10.98	47.13	37500	76.90	79.52	120
Mn8Ce1Fe2-400C-6hr-P3.2g-120-1090330	204	12.35	0	36.73	12.35	37500	93.95	61.67	120
Mn8Ce1Fe2-400C-6hr-P3.2g-H2O1000-120-1090330	204	9.58	10.77	16.37	20.35	37500	90.02	76.31	120
Mn8Ce1Fe4-350C-6hr-P3.2g-120-1090331	204	18.86	2.1	43.43	20.96	37500	89.73	51.40	120
Mn8Ce1Fe4-350C-6hr-P3.2g-H2O1000-120-1090331	204	42.24	8.73	12.07	50.97	37500	75.01	78.52	120
Mn8Ce1Fe2-350C-6hr-P3.2g-120-1090331	204	15.14	1.37	47.11	16.51	37500	91.91	49.02	120
Mn8Ce1Fe2-350C-6hr-P3.2g-H2O1000-120-1090331	204	46.66	4.8	13.55	51.46	37500	74.77	79.09	120

We tried to change the Ce ratio and study the catalyst denitration efficiency and water resistance. The catalysts Mn$_8$Ce$_4$Fe$_1$ and Mn$_8$Ce$_8$Fe$_1$ were synthesized in this experiment. The denitration efficiency and N$_2$ selectivity were measured, as shown in Table 2. The results showed that the Mn$_8$Ce$_4$Fe$_1$ catalyst(calcination temperature 400 ℃) has a higher denitration efficiency of 93.18% and N$_2$ selectivity of 84.69% than the Mn$_8$Ce$_4$Fe$_1$ catalyst(calcination temperature 400 ℃). Mn$_8$Ce$_8$Fe$_1$ catalyst (calcination temperature 450 ℃) has a higher denitration efficiency of 91.72% and N$_2$ selectivity of 86.33% than Mn$_8$Ce$_4$Fe$_1$ catalyst(calcination temperature 400 ℃). Moreover, it was also found that when Cerium is added less, the higher denitration efficiency can be obtained by decreasing the calcination temperature. When Cerium is added more, increasing calcination temperature can obtain higher denitration efficiency.

Table 2 The results of catalyst activity when changing the Ce ratio

Source: Made by TPRI

Mn8Ce4Fe1&Mn8Ce8Fe1	Inlet NO	Outlet NO	Outlet NO$_2$	Outlet N$_2$O	Outlet NOx	SV	η	N$_2$ Selectivity	Temp
unit		ppm, 3.3%O$_2$				mL/g*h	%	%	℃
1120119-Mn8Ce4Fe1-400C-6hr-P3.2g-H2O1000-120C	191	0	13.03	7.12	13.03	37500	93.18	84.69	120
1120317-Mn8Ce4Fe1-350C-6hr-P3.2g-H2O1000-120C	191	56.52	12.97	10.09	69.49	37500	63.65	72.75	120
1120412-Mn8Ce8Fe1-400C-6hr-P3.2g-H2O1000-120C	191	15.32	17.03	2.76	32.35	37500	83.08	85.80	120
1120412-Mn8Ce8Fe1-450C-6hr-P3.2g-H2O1000-120C	191	0	15.83	4.07	15.83	37500	91.72	86.33	120

3. Conclusion

This study has found the current best recipe for a low-temperature SCR catalyst. The denitration efficiency can reach more than 90% under 120℃ reaction conditions. It has great potential to be used in flue gas denitration treatment. In future work, the support TiO$_2$ can be replaced with other porous materials, such as fly ash or waste catalysts. It effectively reduces raw material costs and has a circular economy and carbon reduction value. We can use the current best recipe to coat with honeycomb support, and it can be applied to the Datan low-temperature SCR pilot for the denitration test, as shown in Figure 4. It is expected that the commercial products of low-temperature catalysts can be manufactured.
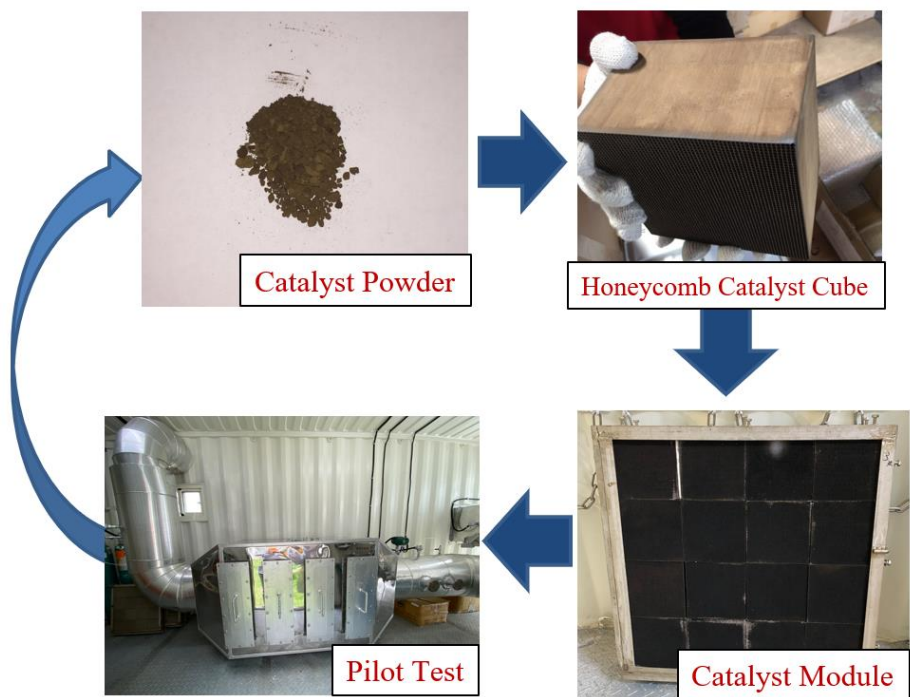
Source: Graphed by TPRI

Figure 4   Cycle diagram of catalyst production and test