Selective Catalytic Reduction (SCR) of NO_x by NH_3

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1. Objectives

- To familiarize with the experimental set-up used to measure the activity of exhaust gas catalysts at elevated temperatures (200-500°C)
- To be able to summarize and analyze catalytic testing data in the form of tables and graphs
- To compare the catalytic properties of V_2O_5/WO_3-TiO_2 and Cu/SSZ-13
- To decide which catalyst is more suited for a particular application

2. Background

Selective catalytic reduction (SCR) is used to control NO_x emissions from diesel-powered vehicles and power plants. In this process, harmful NO_x is transformed into benign N_2 in the presence of a selective reductant such as ammonia (NH_3). The main reaction involved is termed "standard SCR" and proceeds according to Eq. 1.

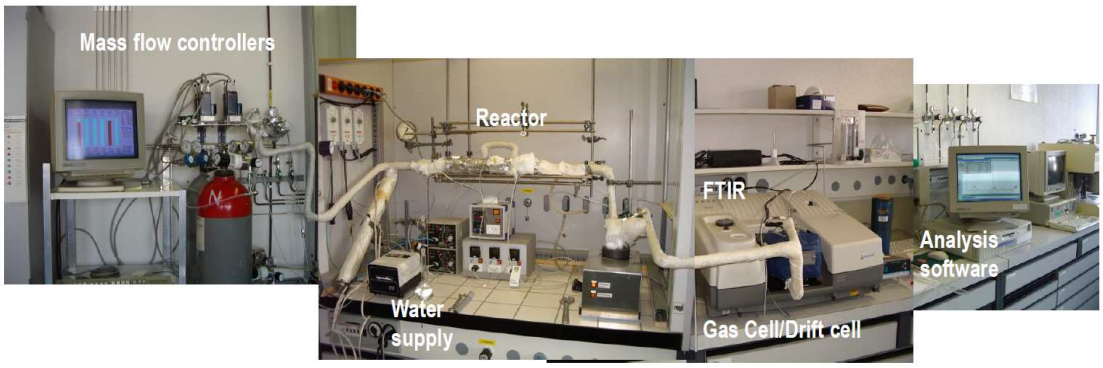
$$4NO + 4NH_3 + O_2 \longrightarrow 4N_2 + 6H_2O \qquad \text{(Eq.1)}$$

Since they were introduced in the 1950s, V_2O_5/TiO_2-based materials have remained to be the most widely used SCR catalysts. Their commercial success stems from their high activity, good resistance to SO2 poisoning, and moderate cost. In practice, WO_3 is added as a promoter to improve the activity and stability of the catalysts. V_2O_5/WO_3-TiO_2 catalysts are commonly processed in the form of monolithic honeycombs for commercial applications. Compared to pellets or any other catalyst form, monoliths resist pressure drop more efficiently, especially at high flow rates. Furthermore, the open channels in the structure ensure that the catalyst can process gas streams with high particulate and dust content.

In this experiment, you will measure the activity of a V_2O_5/WO_3-TiO_2 catalyst toward NO_x reduction under different temperatures and NH_3:NO ratio. You will then compare the performance of this catalyst with that of Cu/SSZ-13, which was tested under the same conditions. Catalyst performances will be compared in terms of activity (i.e. NO_x abatement) and selectivity (undesired by-product production).

3. Methods and materials

The $DeNO_x$ performance of state-of-the-art V_2O_5/WO_3-TiO_2 catalyst in the selective catalytic reduction (SCR) of NO_x will be investigated in a lab-scale experimental set-up. Mass flow controllers, NH_3, NO, N_2, O_2, and H_2 gas cylinders and a homemade computer interface are used to control reactant flow rates. H_2O is generated in-situ from precise flows of H_2 and O_2 through a Pt/Al_2O_3 catalyst (oxidation catalyst). The reactor comprises a stainless steel envelope in which the coated monolith catalyst is inserted. A tube filled with inert material (cordierite) precedes the catalytic bed, to decrease heat and concentration gradients and enhance mixing so that good contact between reducing agent and NO_x is ensured. The set-up is heated in its entirety to avoid water condensation and guarantee homogeneous thermal conditions. Several thermocouples and heaters for gas lines are employed to control the temperature and heat the set-up, respectively. At the output of the reactor, a sampling tube and a pump are installed to probe the output gas mixture and send it towards the analytical part of the set-up. Gas concentrations are analyzed employing an FTIR spectrometer equipped with a heated gas cell. In this way, while the gas mixture is moving through the cell, the IR beam strikes it and is continuously reflected inside the tube. This allows to achieve an appropriately long IR path inside the gas-mixture (ca. 2 m) and thus to obtain reliable data also at very low concentrations. Finally, using a proper calibration, gas species concentrations are extracted from the IR spectrum so that catalytic data can be attained. Pictures of the experimental set-up are displayed in Figure 1 and Figure 2 for clarity.



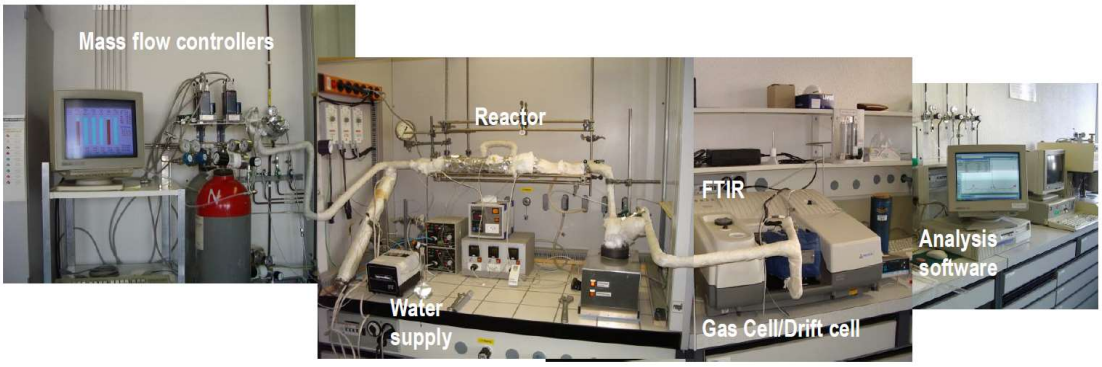


Figure 1: Experimental set-up

Figure 2: Custom-made interface used to control the gases flow rates (left panel) through Mass Flow controller (MFCs, right panel).

4. Experimental procedure

1. Using a caliper, measure the dimensions and calculate the volume of the sample. Given that the desired gas hourly space velocity (GHSV) is 50,000 h^{-1}, calculate the required flow of the model gas in $L \cdot h^{-1}$ and input the value in the gas control software.
2. Wrap the sample in a ceramic paper, and put it in the catalyst holder. Insert the sample toward the middle of the tubular reactor. Install the glass cover of the reactor with the sampling tube for IR analysis.
3. Turn on the heaters for the gas inlet (200 °C), water generator (150 °C), reactor (550 °C), and gas outlet (150 °C).
4. Open the gas cylinders for H_2, NH_3, and NO. Using the gas control software, introduce 10 vol% O_2, 5 vol% H_2O, 500 ppm NO, and 400 ppm NH_3 into the reactor.
   (Generally, points 1-4 are done before your arrival to save time for your experiment)
5. Add liquid nitrogen into the compartment for the HgCdTe (MCT) detector of the IR spectrometer. CAUTION Wear a laboratory coat, goggles, and the special gloves for liquefied gases when handling liquid nitrogen.

6. Purge the inlet of the IR cell with N_2 gas. Measure a background spectrum. As it is done in the in-situ FTIR experiment, the background is required to obtain the IR spectrum of interest. In this case, the background is a flat line, i.e. the gas-phase IR spectrum of N_2. Afterward, during the real experiment, the background will be subtracted from the IR spectrum of interest, i.e. the one containing the NO, NH_3, and H_2O signals.
7. Once the reactor temperature reaches 550 °C, turn NH_3 flow to 0. Connect the outlet of the reactor to the IR spectrometer and close the purging N_2 gas line. Start the gas analysis with the IR spectrometer which will return the concentrations of NO, NO_2, N_2O, H_2O, and NH_3.
8. Measure the SCR activity at 550 °C and vary the NH_3 concentration from 0, 300, 400, 500, and finally to 600 ppm.
9. Repeat the same measurement at 450 °C, but obtain an additional data point at 550 ppm NH_3.
10. Repeat the same measurement at 350 °C, but obtain an additional data point at 475 ppm NH_3.
11. Repeat the same measurement at 250°C, but obtain additional data points at 150 and 250 ppm NH_3.

In each experiment, the data point is collected under steady-state conditions. When the NH_3 concentration or the temperature is changed, the system will move through a transient condition, and then will reach a new steady-state situation characterized by constant concentrations of NH_3, NO, and H_2O after the catalyst. The custom-made analysis software (Figure 1, right panel) is used to understand when steady-state conditions are met.

5. Catalytic results

In the following table, the catalytic data collected under the conditions previously explained (bullet points 8 to 11) are reported for the V_2O_5/WO_3-TiO_2 catalyst.

550 °C					
Inlet [ppm]		**Output [ppm]**			
NH_3	NO	NH_3	NO	NO_2	N_2O
0	500	0	454.6	46.5	0.1
300	500	0	274.5	23.3	23.5
400	500	0	227.1	19.1	32.7
500	500	0	190.2	14.4	42.7
600	500	1.3	161.4	10.6	52.8
450 °C					

Inlet [ppm]		Output [ppm]			
NH_3	NO	NH_3	NO	NO_2	N_2O
0	500	0	481	20.8	0
300	500	0	197.4	7.5	1.3
400	500	0	102.5	4.1	2
500	500	7.9	22.2	0.7	2.8
550	500	33.7	8	0.6	3
600	500	68.6	4.1	1	3.4
350 °C					
Inlet [ppm]		**Output [ppm]**			
NH_3	NO	NH_3	NO	NO_2	N_2O
0	500	0	492	7.7	0
300	500	0	200	2.1	0
400	500	0	99.8	1.6	0.2
475	500	2.1	26.4	0.6	0.1
500	500	10.9	10.1	0.5	0.1
600	500	100.7	2.5	0.5	0.3
250 °C					
Inlet [ppm]		**Output [ppm]**			
NH_3	NO	NH_3	NO	NO_2	N_2O
0	500	0	495.6	3.7	0.2
150	500	0	349.4	1.4	0.1
250	500	0.7	252.5	0.9	0
300	500	7.6	209.3	0.6	0.2
400	500	65.3	162.4	1.3	0.1
500	500	155.3	153.2	0.9	0.1
600	500	254.6	150.2	1.2	0

In the following are the data collected with Cu-SSZ-13.

Cu-SSZ-13 CATALYST

DeNOx at 10 ppm of NH_3 slip

Temperature [°C]	NO conversion [%]
550	19.7
450	70.7
350	84.7
250	92.5

N_2O production at NH_3:NO=1

Temperature [°C]	N_2O Concentration [ppm]
550	28.5
450	23.6
350	19
250	20.5

6. Report

1.1. Calculate the $DeNO_x$ (i.e., NO conversion) of V_2O_5/WO_3-TiO_2 according to the following formula:

$$NO\ conversion\ =\ 100 \cdot \frac{(NOin\ -\ NOx, out)}{NOin}$$

1.2. Plot the $DeNO_x$ of V_2O_5/WO_3-TiO_2 at different temperatures as a function of NH_3:NO ratio.

1.3. Interpolate the $DeNO_x$ at 10 ppm NH_3 slip linearly (i.e., when the $NH_{3,out}$ concentration is 10 ppm) from the measured data (if not possible, just explain why).

1.4. Plot the $DeNO_x$ at NH_3:NO = 1 and at 10 ppm NH_3 slip as a function of temperature.

1.5. Plot the N_2O emission at NH_3: NO = 1 as a function of temperature.

1.6. Compare the $DeNO_x$ at 10 ppm NH_3 slip and N_2O emission of V_2O_5/WO_3-TiO_2 and Cu/SSZ-13. Answer the following questions:

a. Based on just $DeNO_x$, which of the two catalysts is more active? In which temperature range would you favour V_2O_5/WO_3-TiO_2 over Cu/SSZ-13?

b. N_2O is a greenhouse gas that is 300 times more potent than CO_2. Based on the N_2O emission data, which of the two catalysts is better?

c. In mobile applications, the temperature of the exhaust gas can vary significantly. When a car is just started, the exhaust gas is relatively colder. Also, when a car is used for just a short period (i.e., short-distance driving within the city), the temperature rarely reaches a high value. Which of the two catalysts will be more suitable for this type of application?

d. In stationary power plants, the exhaust temperature of gas turbines used for power production can reach around 450 to 500°C. During normal operation, the exhaust gas temperature is typically controlled to be within this range. Which of the two catalysts will be more suitable for this type of application?