



Multipollutant Control of Hg^0/NO from Coal-Combustion Flue Gases Using $\text{MnO}_x\text{-CeO}_x/\text{meso-porous SiO}_2$ from waste rice husk

**Kuan-Hung Liu¹, Ming-Yin Chen¹, Hong-Ping Lin²,
Hsing-Cheng Hsi^{1,*}**

¹ *Institute of Environmental Engineering, National Taiwan University, Taipei, Taiwan*

² *Department of Chemistry, National Cheng-Kung University, Tainan, Taiwan*

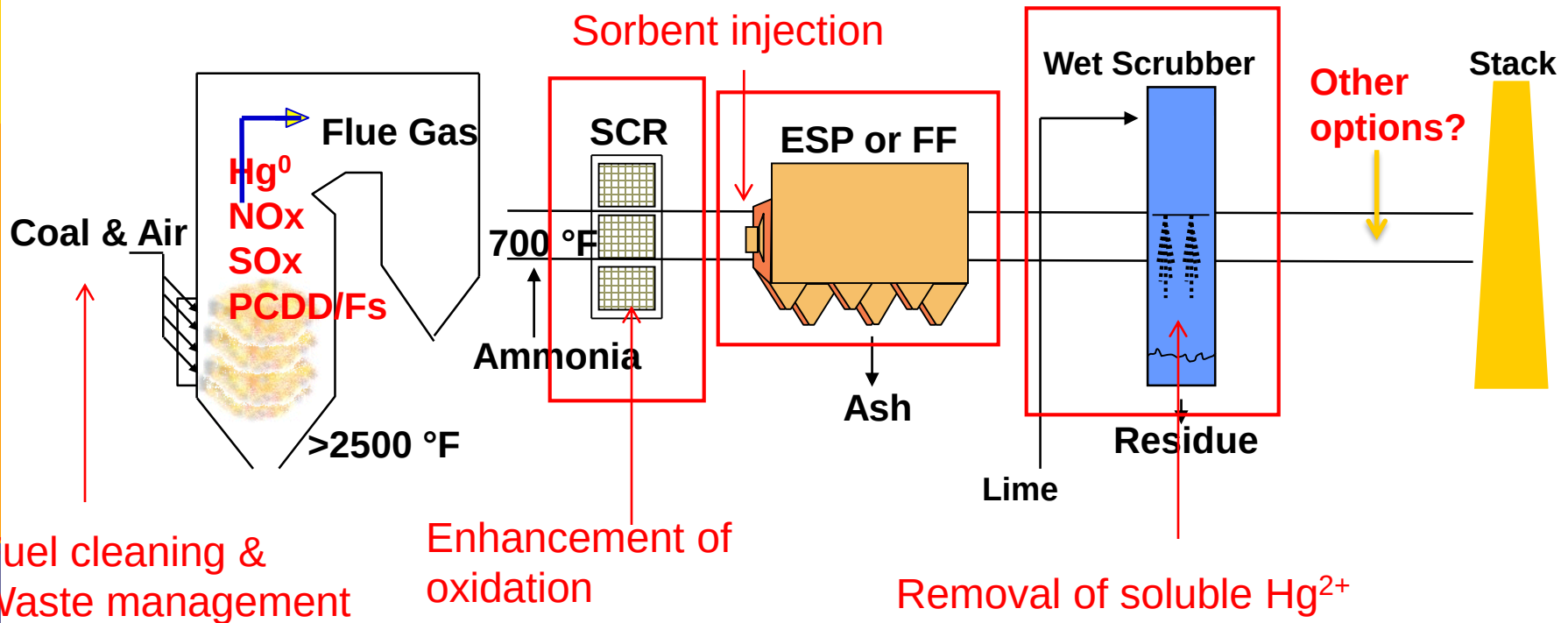


國立台灣大學

環境工程學研究所

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National Taiwan University

Control strategies for Hg/other pollutants multi-control



Catalysts/adsorbents for Hg and NO_x control

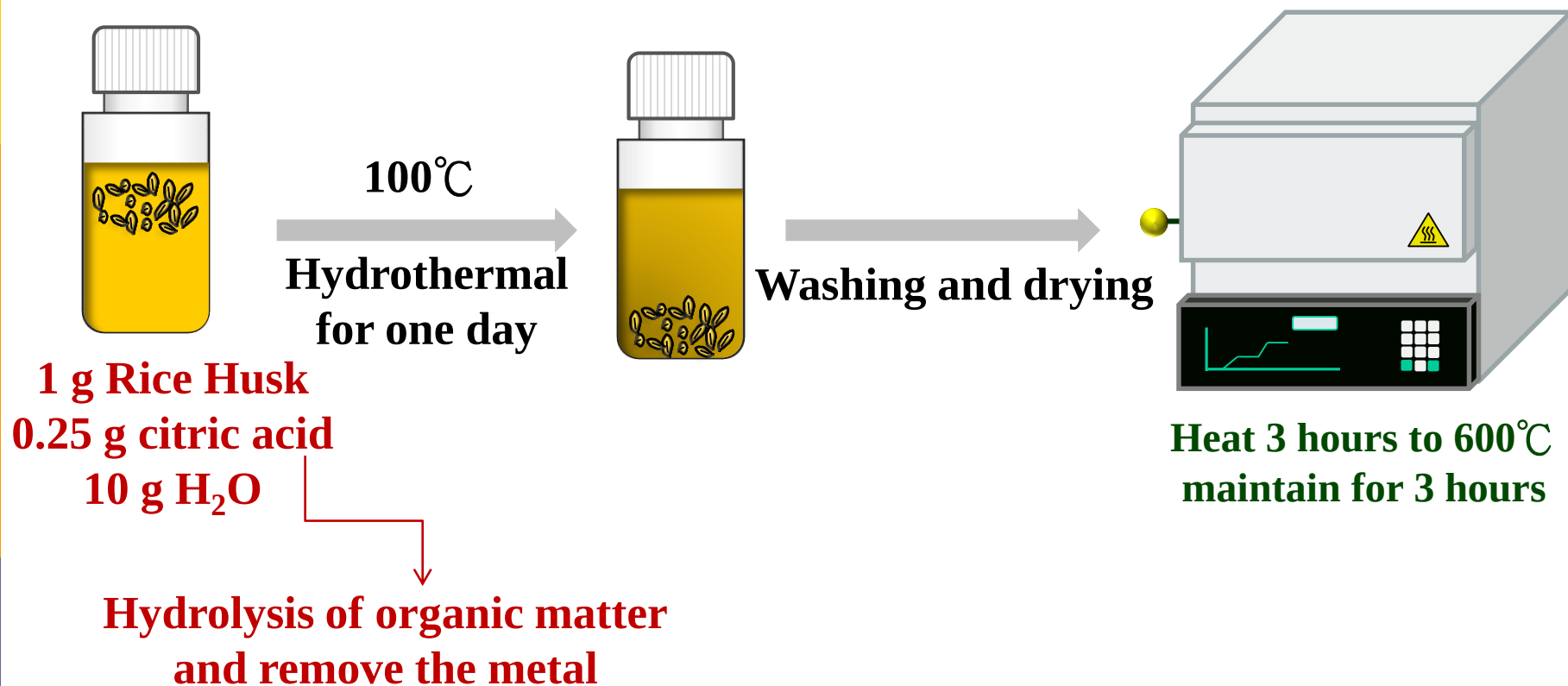
- 1) **Mn/TiO₂** provided the best performance with **100% N₂ selectivity** at **120 °C**. The catalytic performance for various transition metal oxides supported on TiO₂ decreased in the following order: **Mn > Cu ≥ Cr ≥ Co > Fe ≥ V >>> Ni**. (Pefia et al., 2004)
- 2) Wu et al. (2012) showed that **Hg⁰ oxidation efficiency** can reach higher than **90% at 200 °C** over **MnO_x-CeO₂/TiO₂** catalysts under simulated flue gas condition.
- 3) **MnO_x-CeO₂/γ-Al₂O₃** catalyst exhibited high Hg⁰ oxidation activity(**80%**) at low temperatures (**100–250 °C**) under the simulated flue gas. (Wang et al., 2014)
- 4) Ce/TiO₂–SiO₂ catalyst with a **Ti/Si** mass ratio of **3/1** exhibited superior NH₃–SCR activity and high N₂ selectivity in the temperature range of **250–450 °C**. It also exhibited **strong resistance to SO₂ and H₂O poisoning**. (Liu et al., 2012)

From waste to resource: prepare SiO_2 catalysts from rice husk for Hg/NO_x control

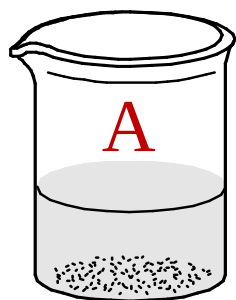
- 1) Preparation and characterization of metal oxide-impregnated mesoporous SiO_2 catalysts.
- 2) To gain a better understanding of the adsorption or oxidation of multipollutant (i.e., Hg^0 , NO) using the metal oxide-impregnated SiO_2 catalysts under simulated coal-combustion flue gases condition.
- 3) Comprehending the influence of the temperature and inlet mercury concentration on the adsorption/oxidation/reduction equilibrium and kinetics of surface-modified catalyst.



Preparation of metal oxide-impregnated SiO₂ catalysts



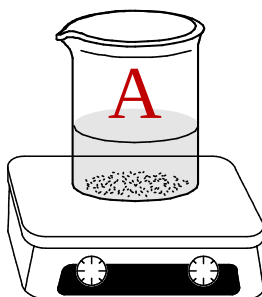
Preparation of metal oxide-impregnated SiO₂ catalysts



$\text{Mn}(\text{NO}_3)_2 / \text{H}_2\text{O} = \text{X g} / 300 \text{ g H}_2\text{O}$
 $\text{Ce}(\text{NO}_3)_3 / \text{H}_2\text{O} = \text{Y g} / 300 \text{ g H}_2\text{O}$

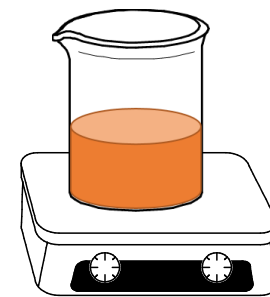


Rice Husk SiO₂



0.6 M Na₂CO₃

adjust to pH=9

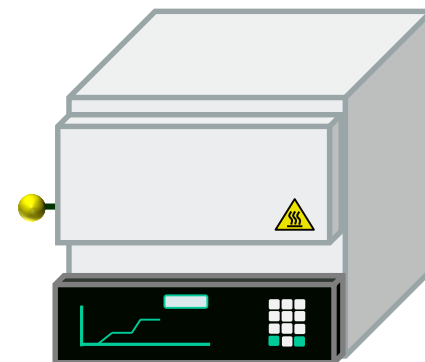
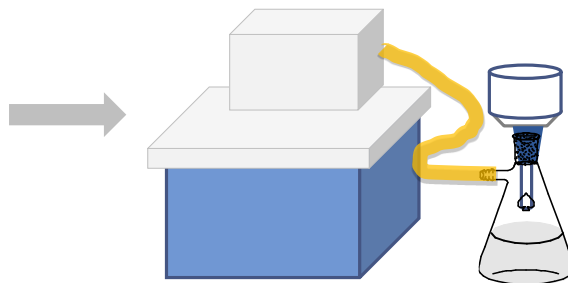


Stir 2 hr



100°C

Hydrothermal for one day



Heat 2 hours to 400°C
maintain for 2 hours

Hg Removal Test Parameters

Catalyst weight	Testing T	Flow rate
10 mg	150 、 250 and 350 °C	1.5 L/min

Flue gas condition	O ₂	HCl	SO ₂	NO	H ₂ O	CO ₂	N ₂
	6 vol%	50 ppm _v	200 ppm _v	200 ppm _v	10 vol%	12 vol%	balanced

Hg⁰ concentration = 30, 65, 100 ± 5 µg/Nm³

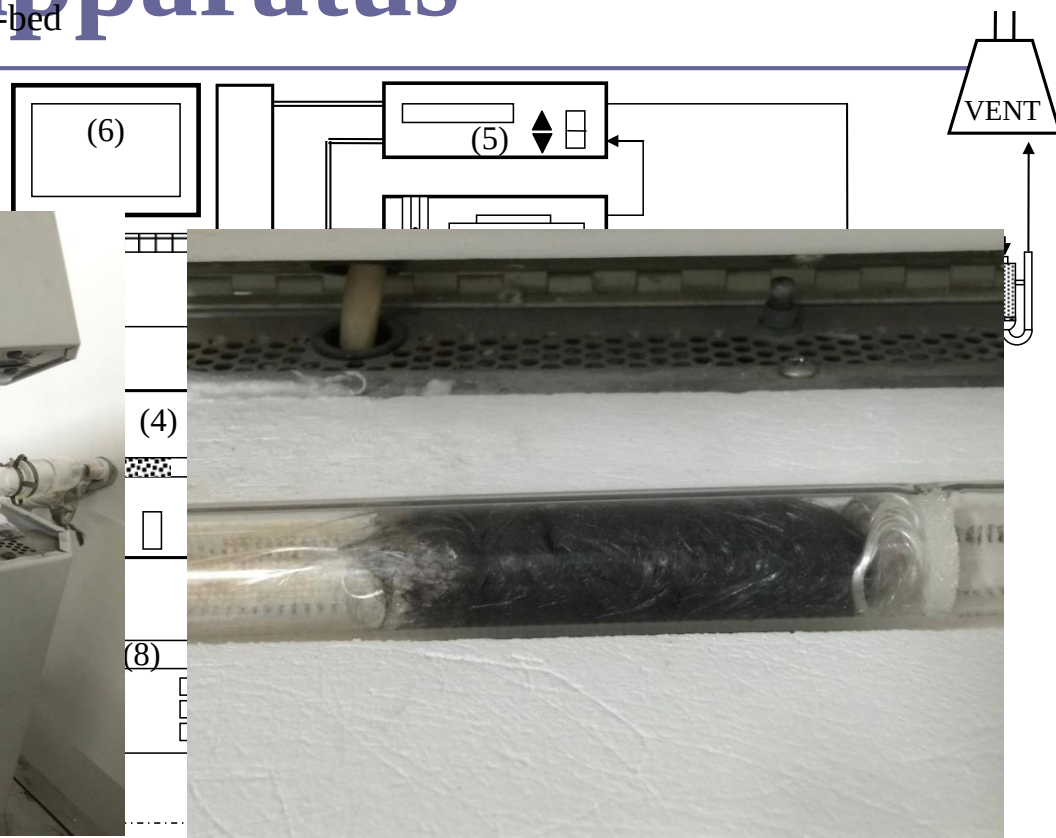
NO_x Removal Test Parameters

Catalyst weight	Testing T	Flow rate
1 g	150 ~ 400 °C	1.5 L/min

Gas condition	O ₂	NO	NH ₃	N ₂
	6 vol%	200 ppm _v	200 ppm _v	balanced

- (1) Gas mixing chamber-1
- (2) Gas mixing chamber-2
- (3) Hg⁰ vapor generator
- (4) Temperature-controlled; a adsorption fixed-bed
- (5) Gold/amalgamation/CVAFS\
- (6) Computer system
- (7) Cooler/condenser
- (8) SO₂/NO continuous monitoring system

Experiment apparatus



⊗ Hand valve

⊗ Electromagnetic valve

⊥ Three way valve

▨ Adsorbent

⊕ Four way valve

⊥ Rotameter

— Gas

- - - Water vapor

== Electrical signal

N₂

NO

SO₂

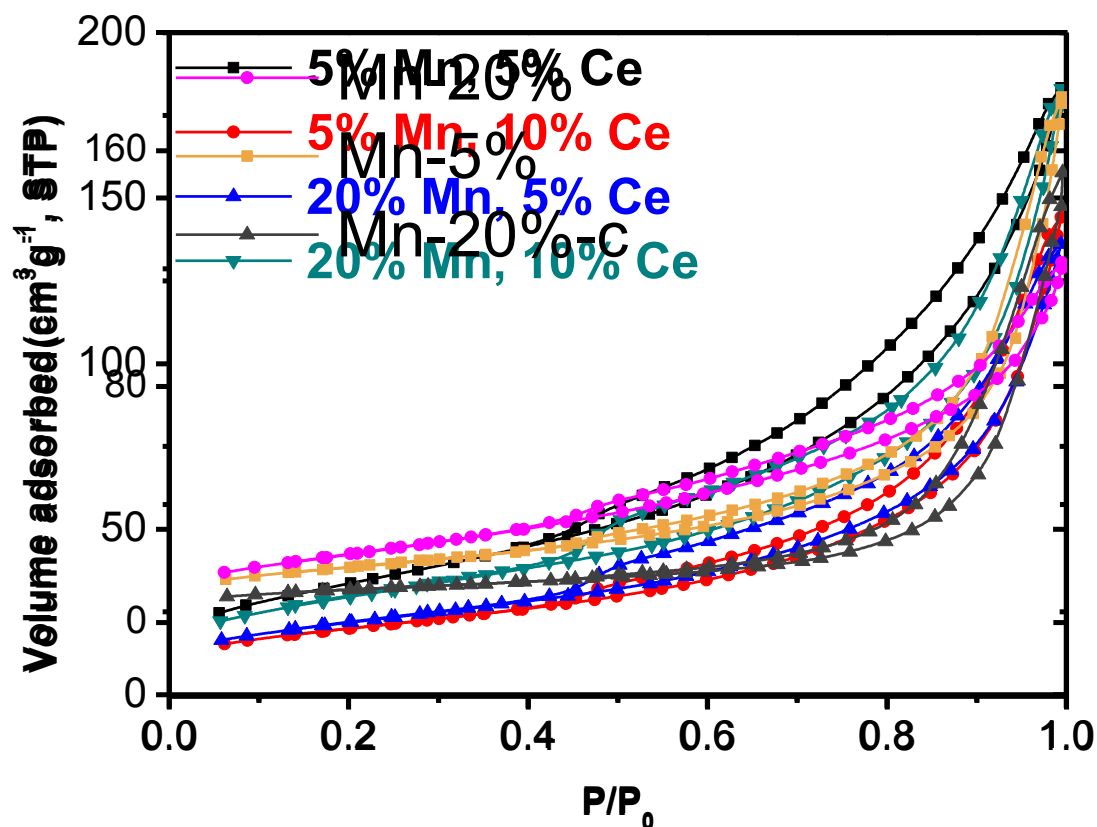
O₂

HCl

CO₂

N₂

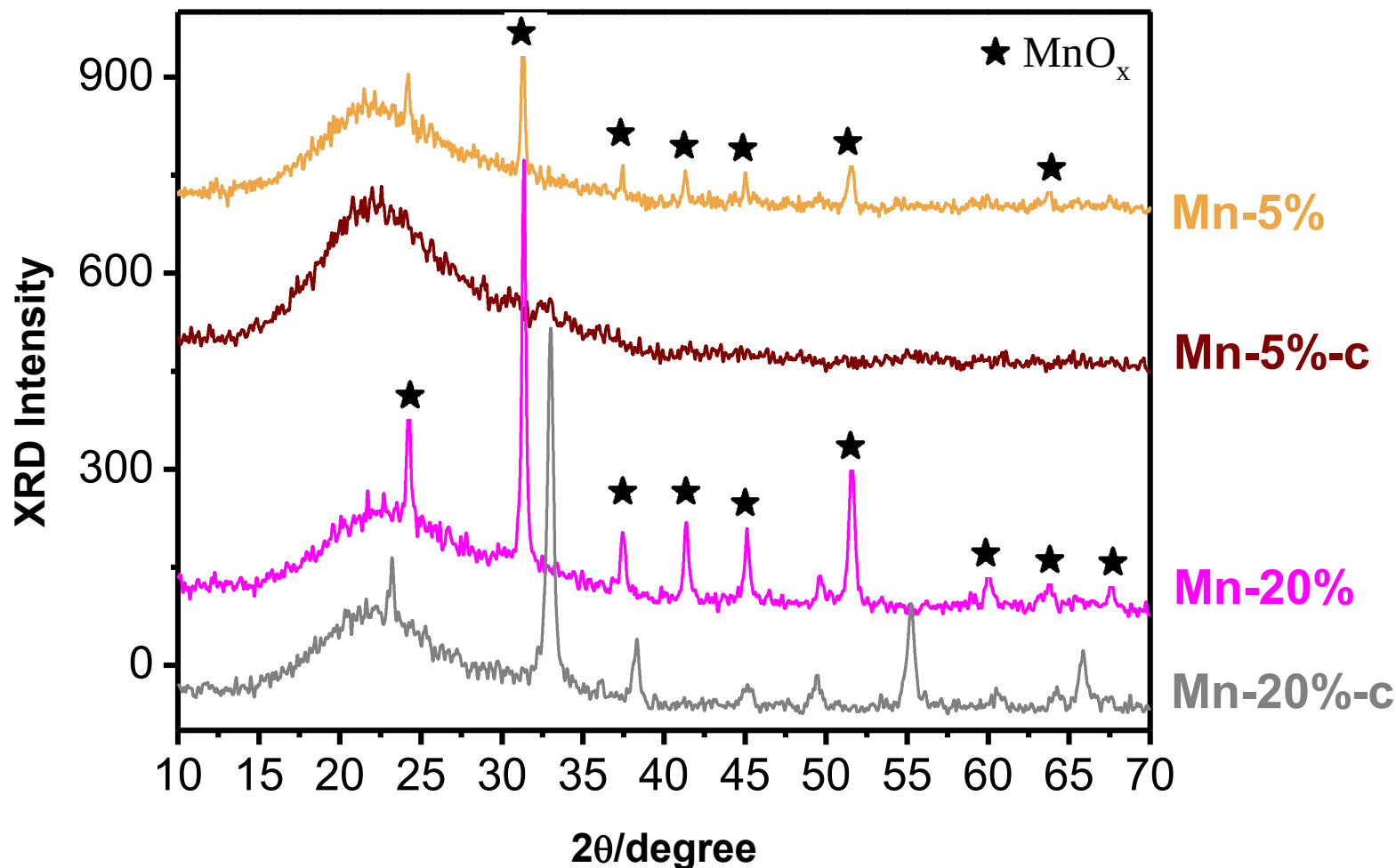
N₂ adsorption of MnO_x-(CeO_x)/SiO₂



Mn %, Ce %	Surface area (m²/g)
5, 5	123
5, 10	72
20, 5	79
20, 10	107

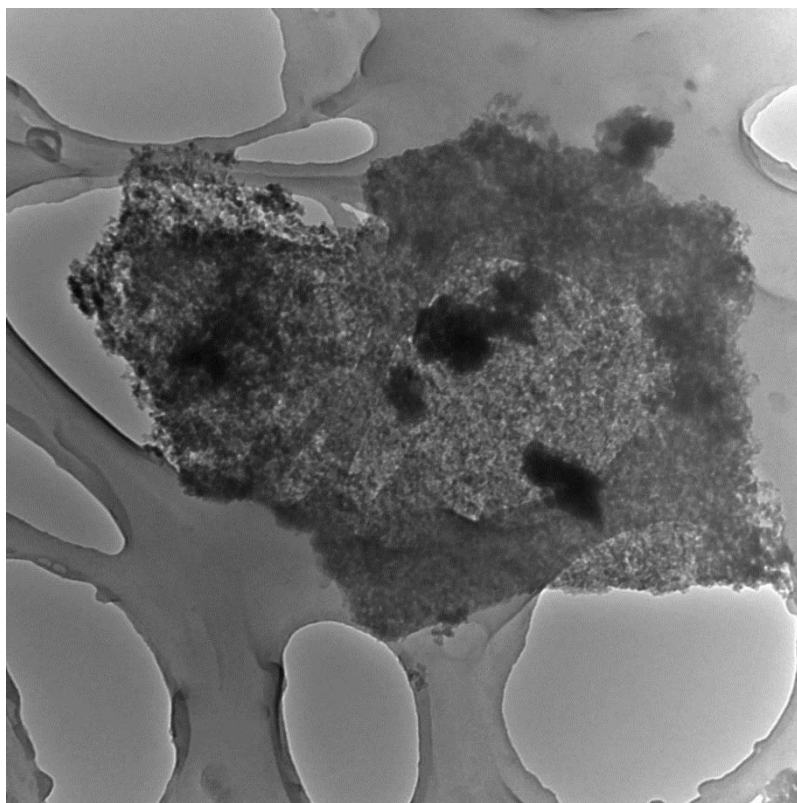
Mn %	Surface area (m²/g)
5	48
20	39

XRD patterns of $\text{MnO}_x\text{-CeO}_2/\text{SiO}_2$



TEM images of $\text{MnO}_x\text{-CeO}_x/\text{SiO}_2$

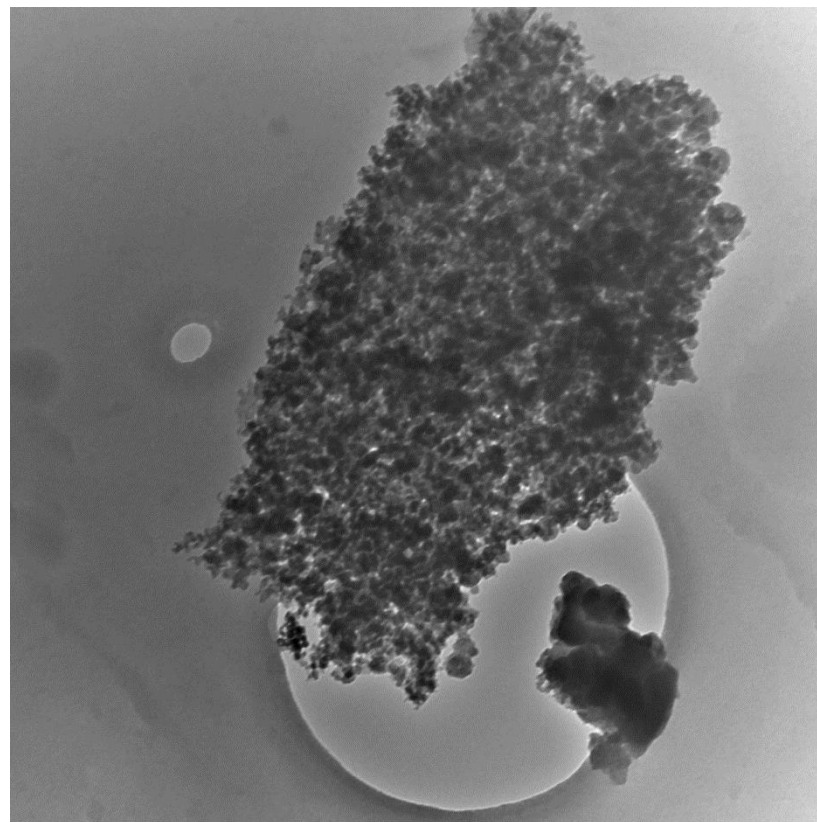
$\text{MnO}_x(20\%)\text{-CeO}_x(5\%)/\text{SiO}_2$



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TEM Mode: Imaging

100 nm
HV=80.0kV
Direct Mag: 80000x

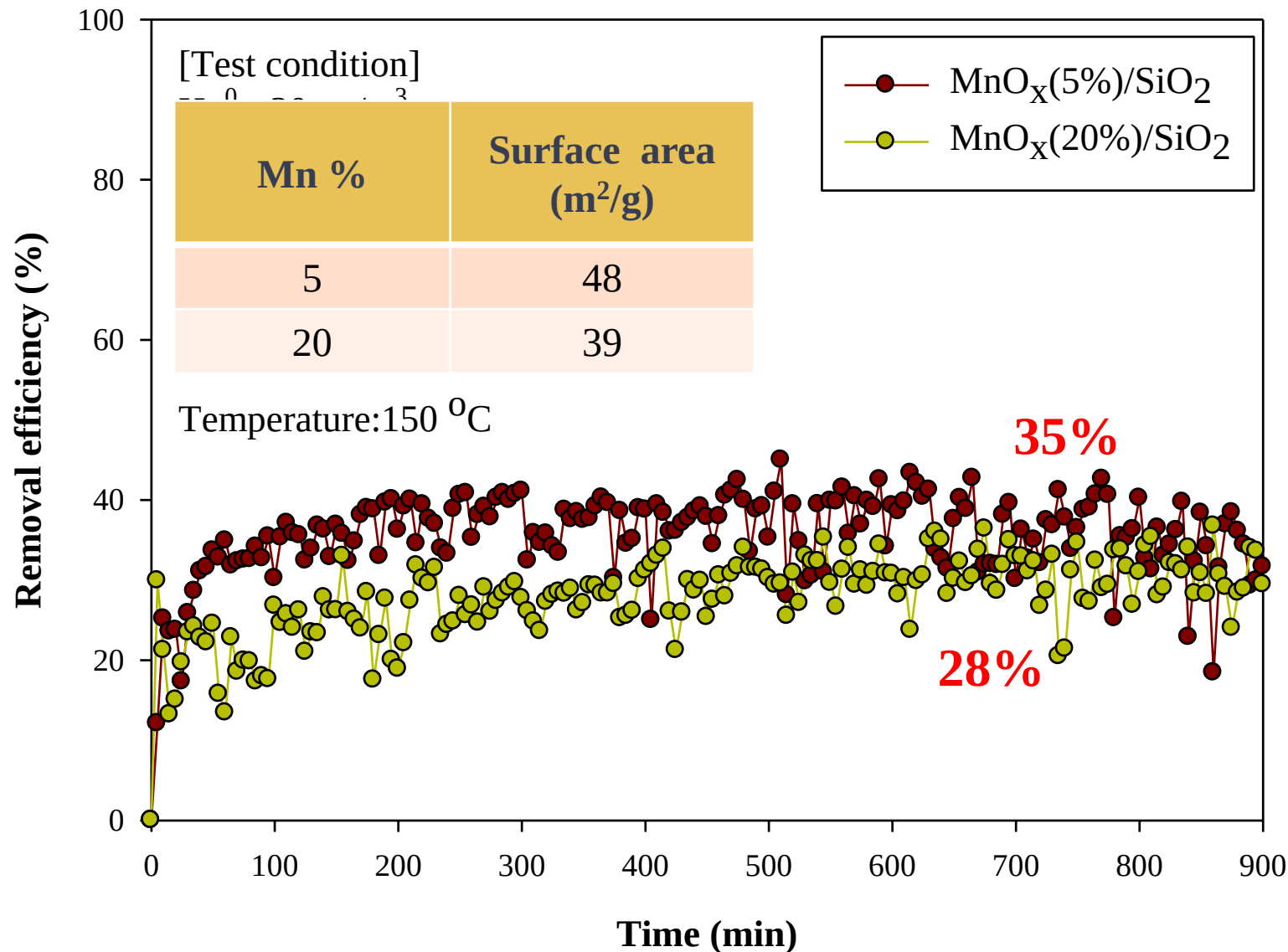
$\text{MnO}_x(20\%)\text{-CeO}_x(10\%)/\text{SiO}_2$



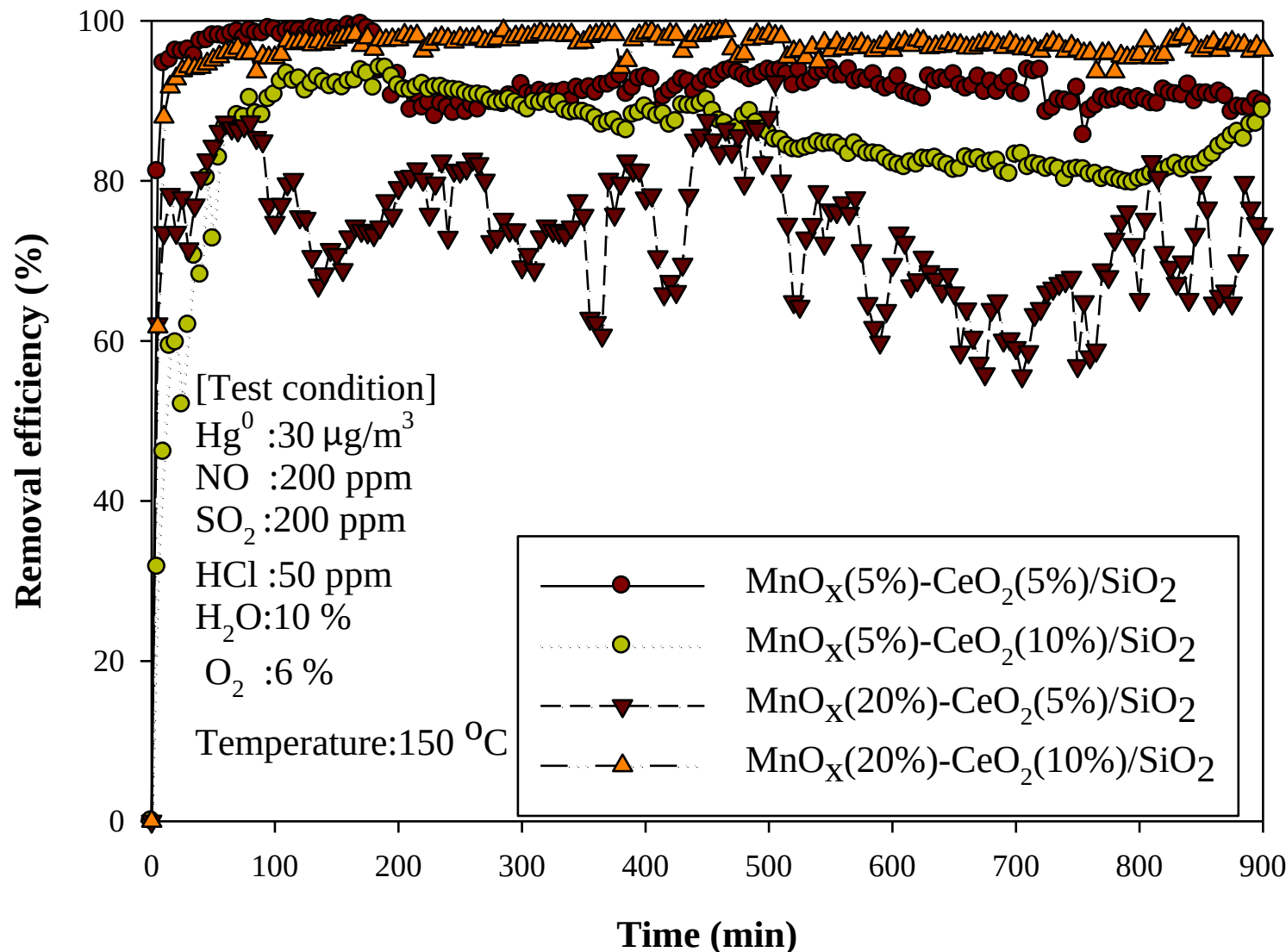
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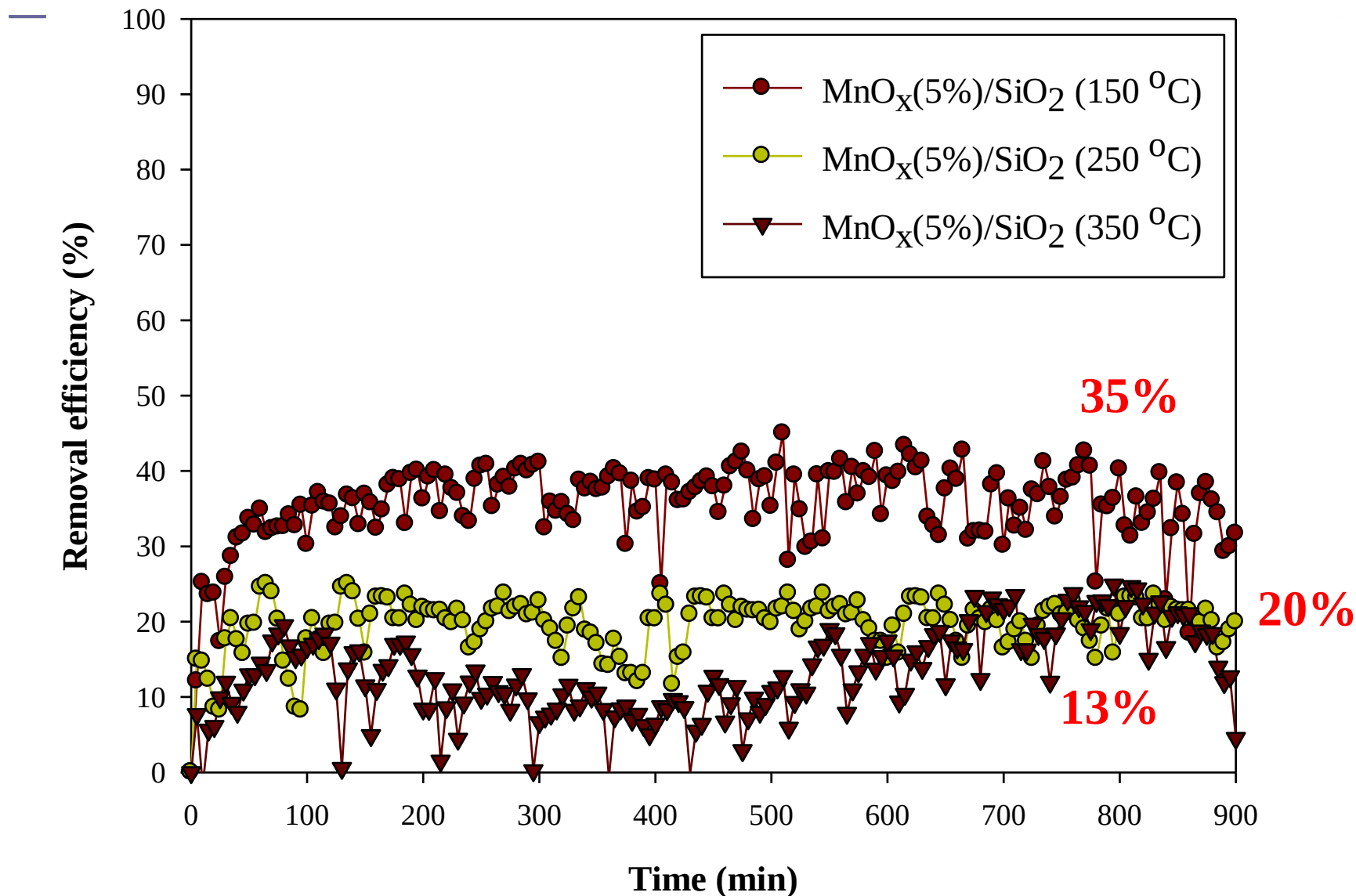
T-Hg removal test at 150 °C



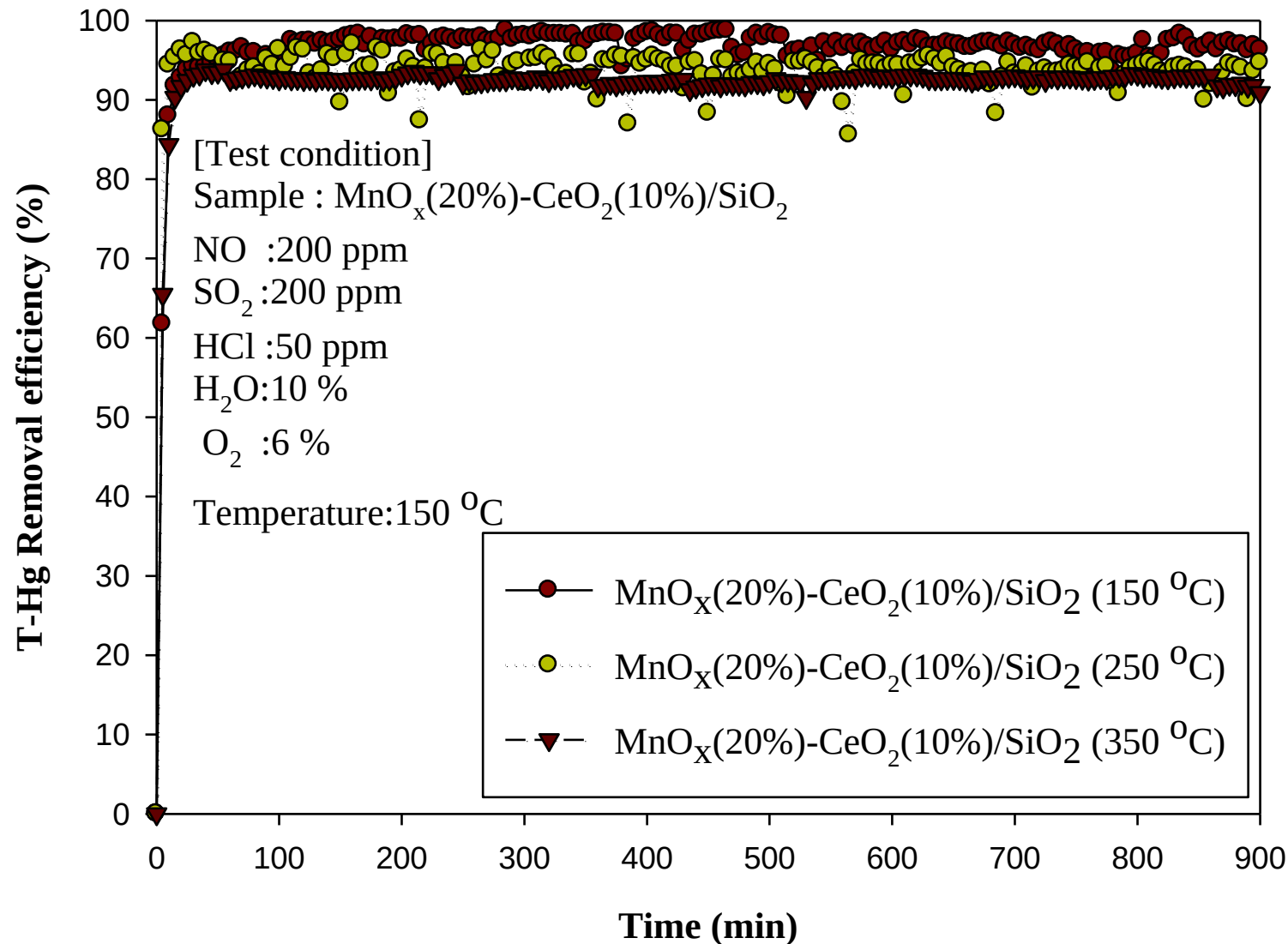
T-Hg removal test at 150 °C



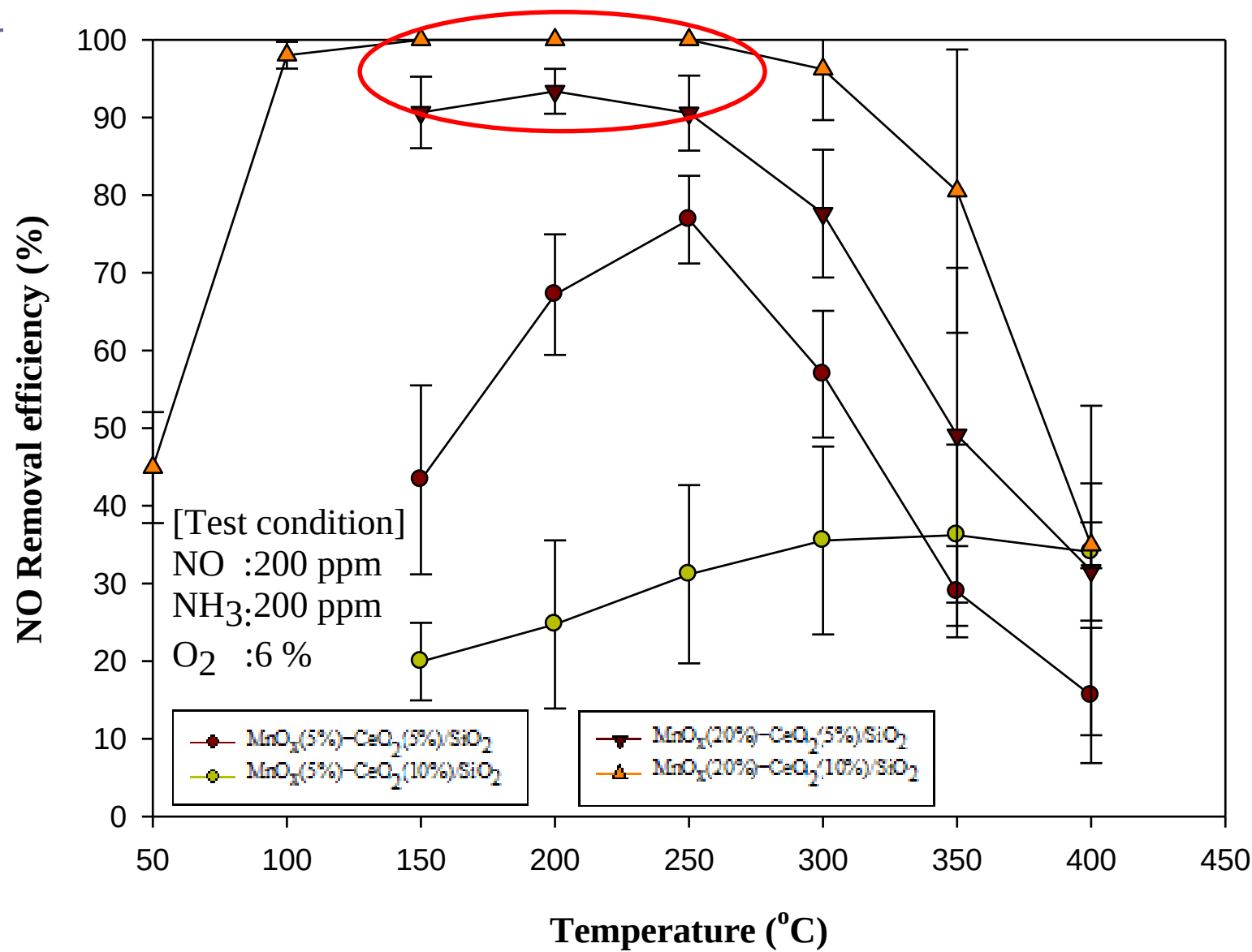
T-Hg removal test of $\text{MnO}_x(5\%)/\text{SiO}_2$ at different temperatures



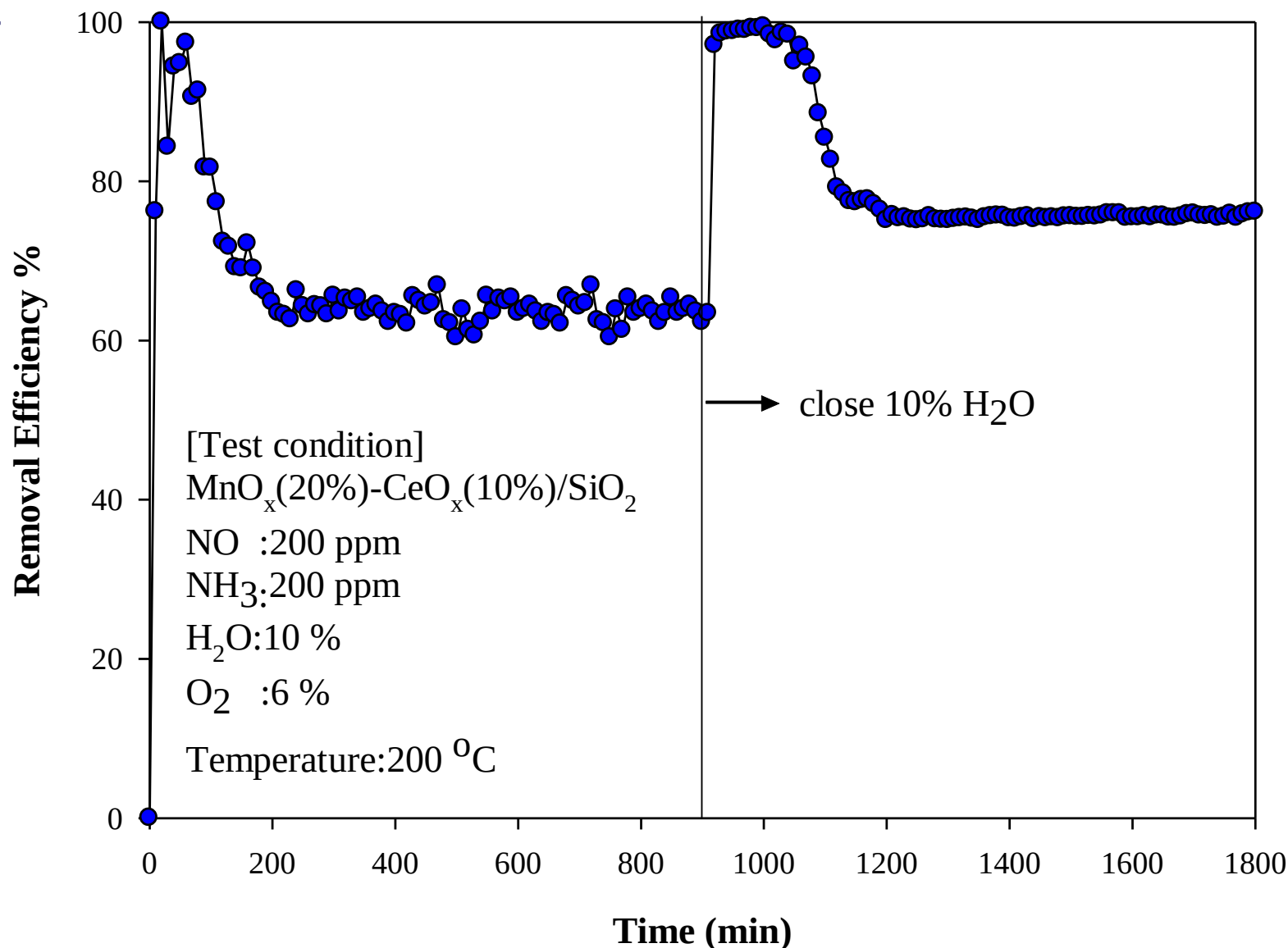
T-Hg removal test of $\text{MnO}_x(20\%)\text{-CeO}_2(10\%)/\text{SiO}_2$ at different temperatures



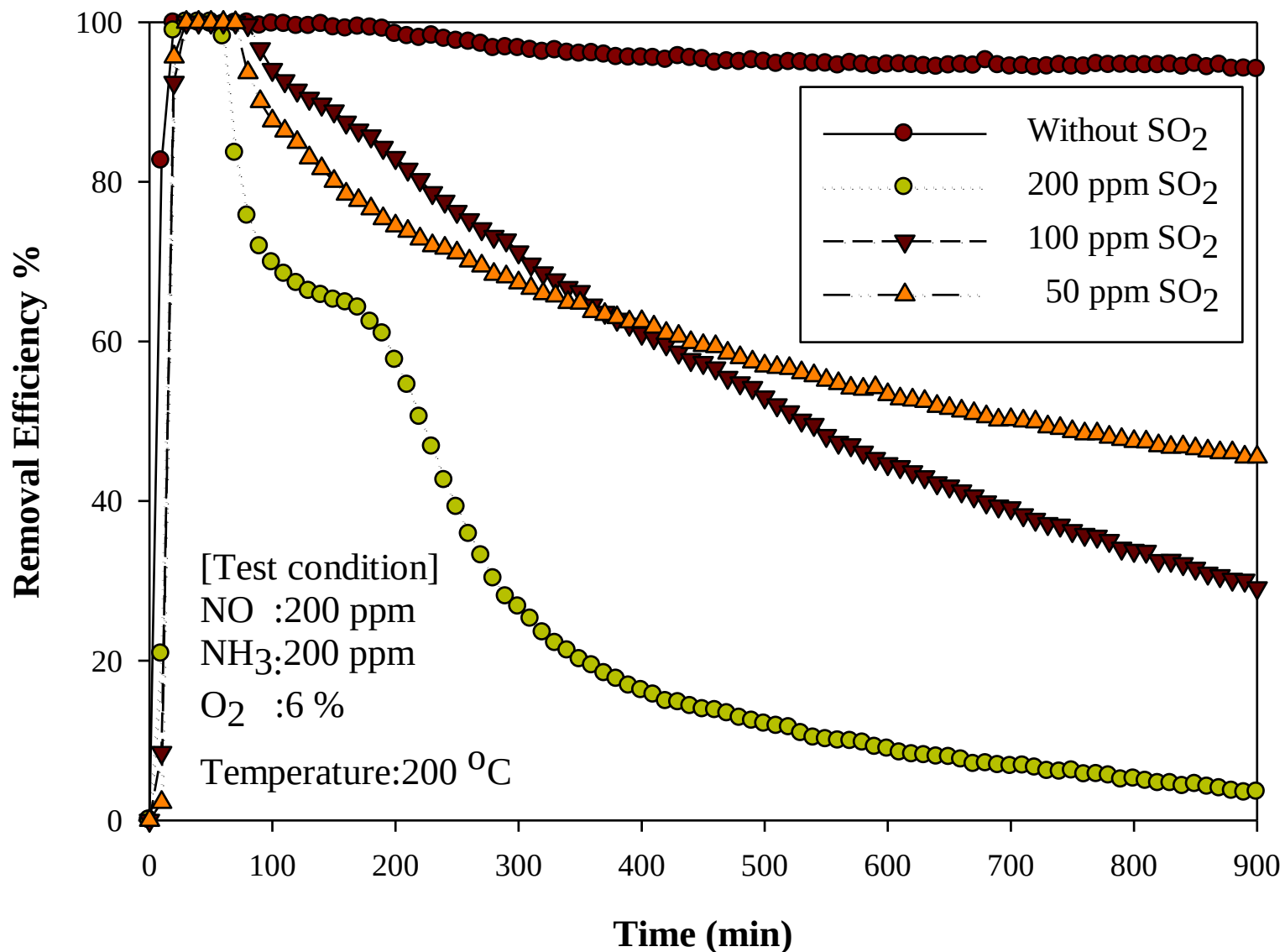
DeNO_x test over MnO_x-CeO₂/SiO₂ catalysts



H₂O resistibility for MnO_x(20%)-CeO_x(10%)/SiO₂



SO₂ resistibility for MnO_x(20%)-CeO_x(10%)/SiO₂



Summary-MnO_x/SiO₂ sample results

- 1) MnO_x(5%)/SiO₂ shows better removal efficiency of T-Hg than MnO_x(10%)/SiO₂ at 150 °C.
- 2) As the **temperature increases**, the removal efficiency of T-Hg of MnO_x(5%)/SiO₂ become **worse**.
- 3) **MnO_x/SiO₂** catalysts show a better deNO_x efficiency between **200 to 300 °C**. At low temperature, it has **better deNO_x efficiency than a commercial SCR catalyst**.

Summary-MnO_x-CeO_x/SiO₂ sample results

- 4) MnO_x(20%)+CeO_x(10%)/SiO₂ demonstrates **excellent Hg removal efficiency (100%)** under a broad operational temperature, even at a temperature up to **350 °C**.
- 5) MnO_x(20%)+CeO_x(10%)/SiO₂ demonstrates **excellent deNO_x efficiency (100%)** under a broad operation window (**100–250 °C**) .
- 6) MnO_x(20%)+CeO_x(10%)/SiO₂ shows **good durability of H₂O**. However, it will **be poisoned by SO₂** within one hour.



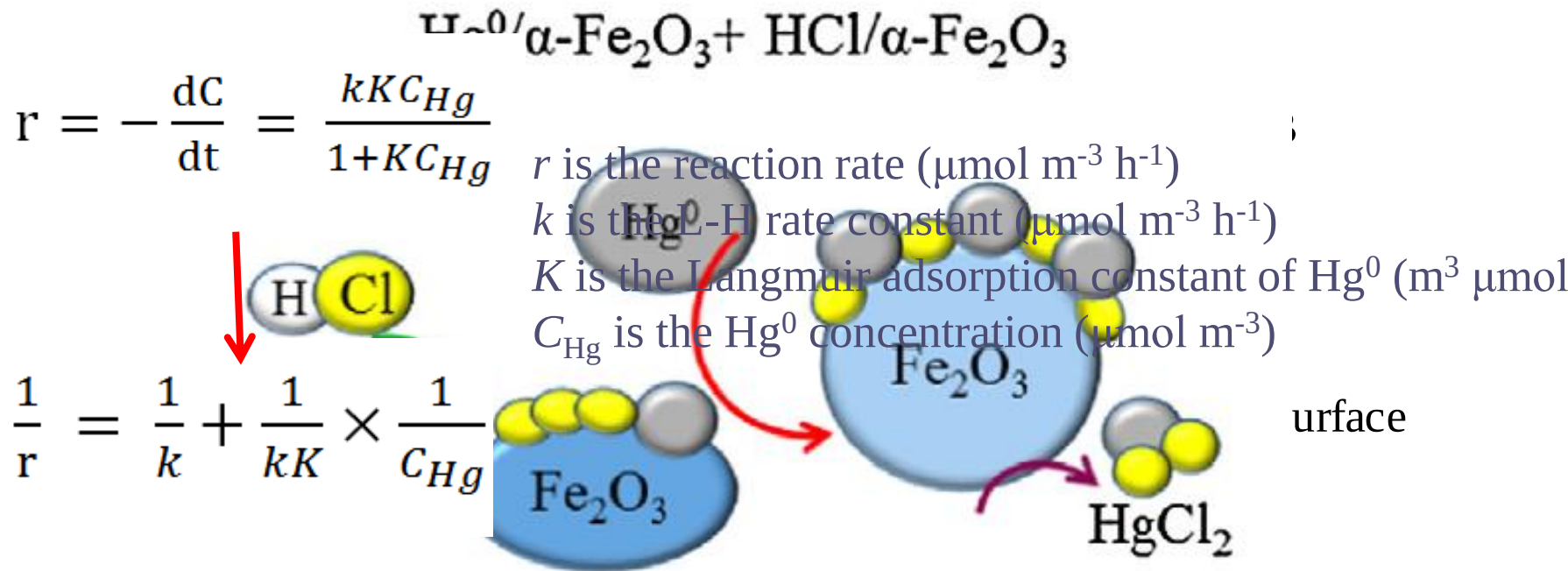
Funding support from the Ministry of Science and Technology, Taiwan under contract no. **MOST 104-2221-E-002-020** is greatly appreciated.

Mercury removal mechanism

Hg⁰ oxidation mechanism by SCR catalysts may be described as follows:

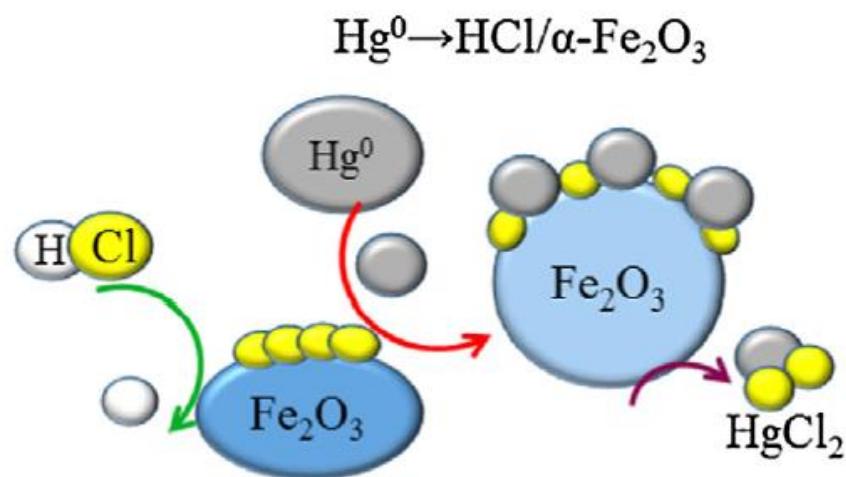
- (1) Langmuir-Hinshelwood (L-H) mechanism
- (2) Eley-Rideal mechanism
- (3) Mars-Maessen mechanism

(1) Langmuir-Hinshelwood mechanism

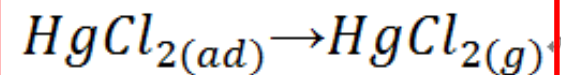
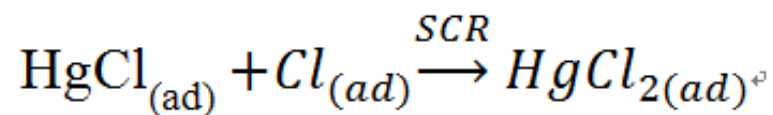
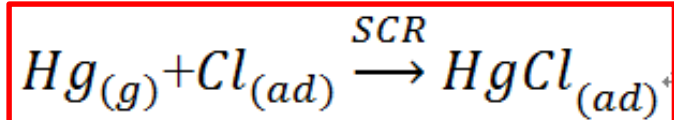
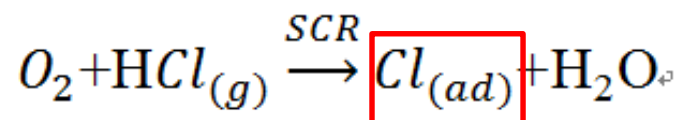
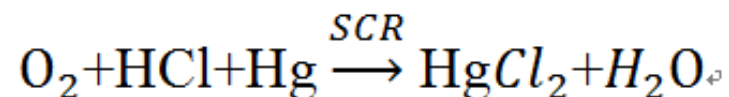


(T. Liu et al., 2016)

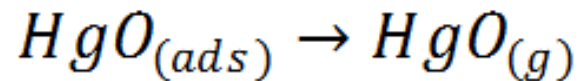
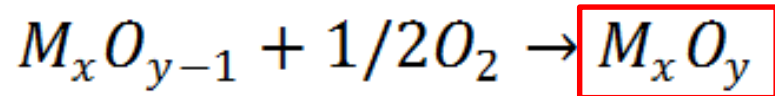
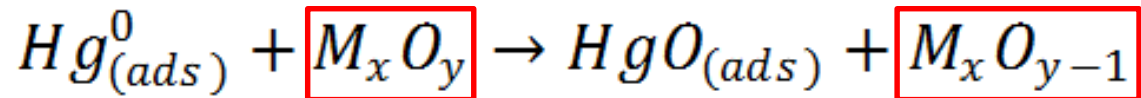
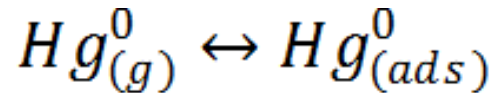
(2) Eley-Rideal mechanism



(Liu et al., 2016)



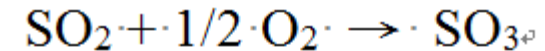
(3) Mars-Maessen mechanism.



NO_x and SO_x removal mechanism

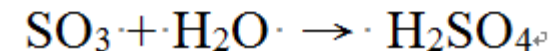
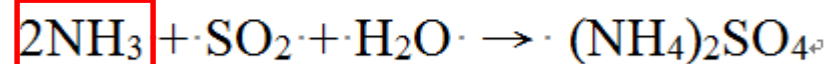
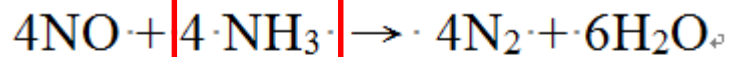
1) Thermal NO_x → over 1540 °C

2) Fuel NO_x → 600~900 °C

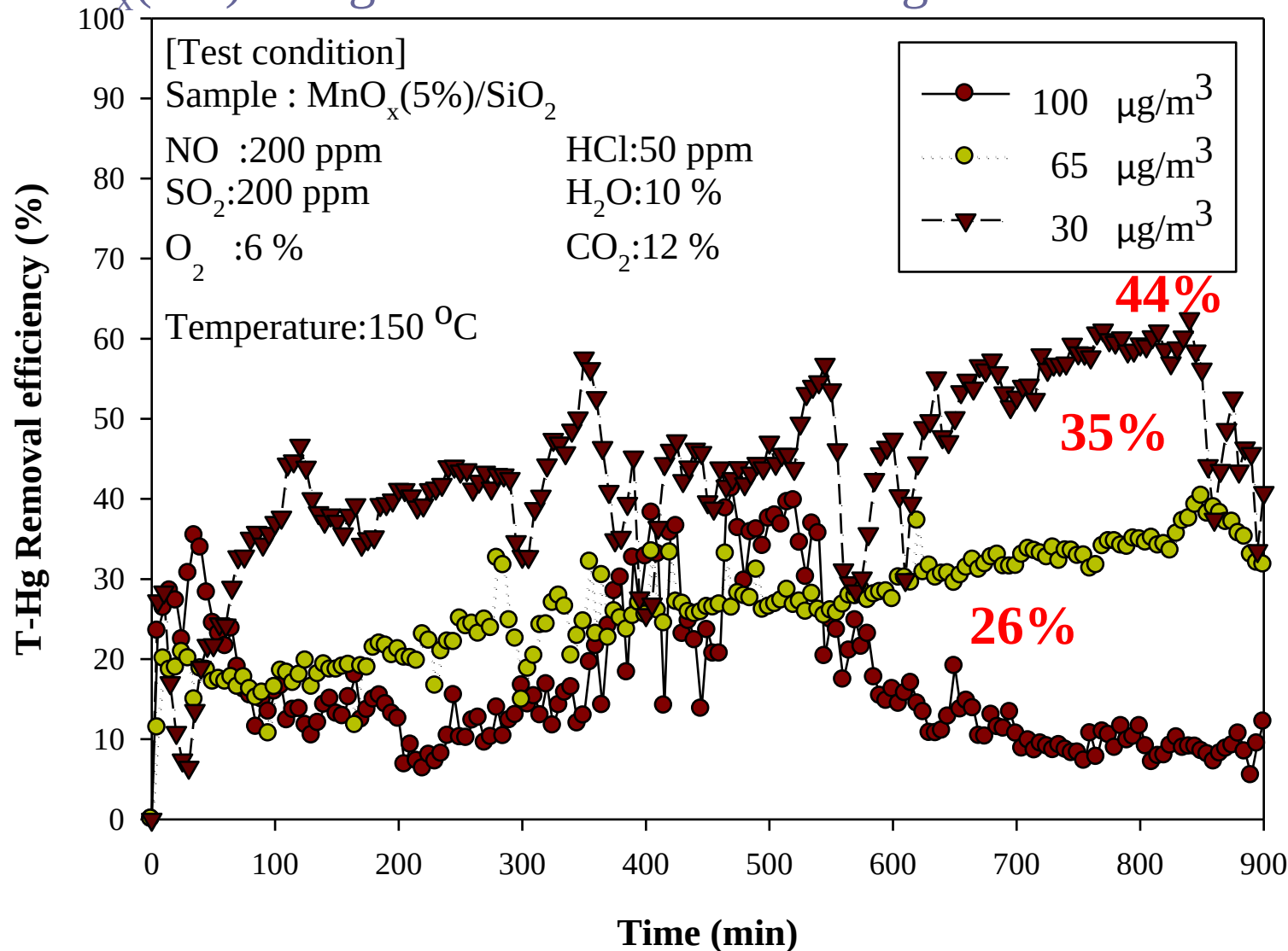


a. Low-NO_x burning

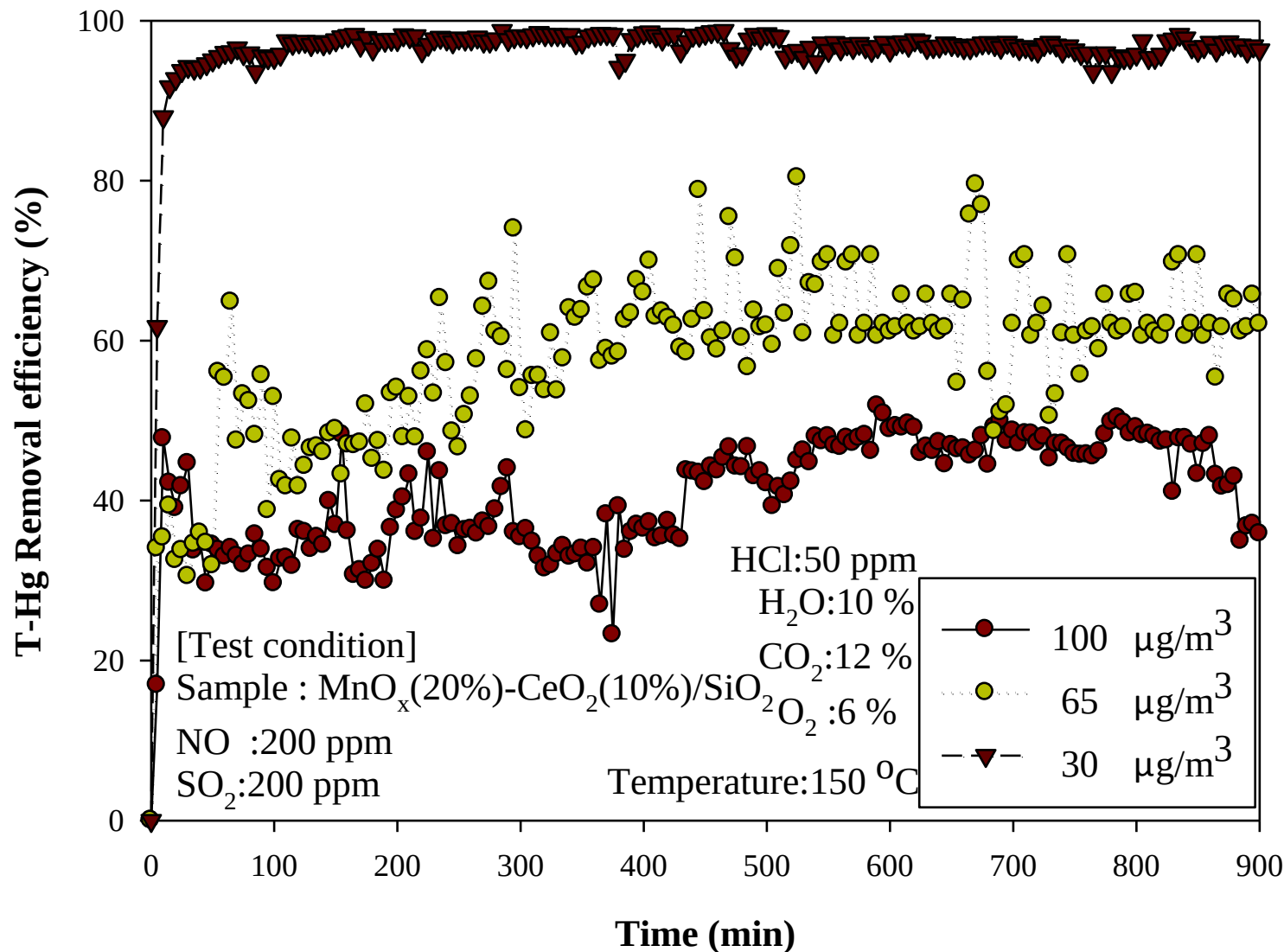
b. Selective Catalytic Reduction; SCR $\text{NH}_3 + \text{SO}_3 + \text{H}_2\text{O} \rightarrow \cdot \text{NH}_4\text{HSO}_4$



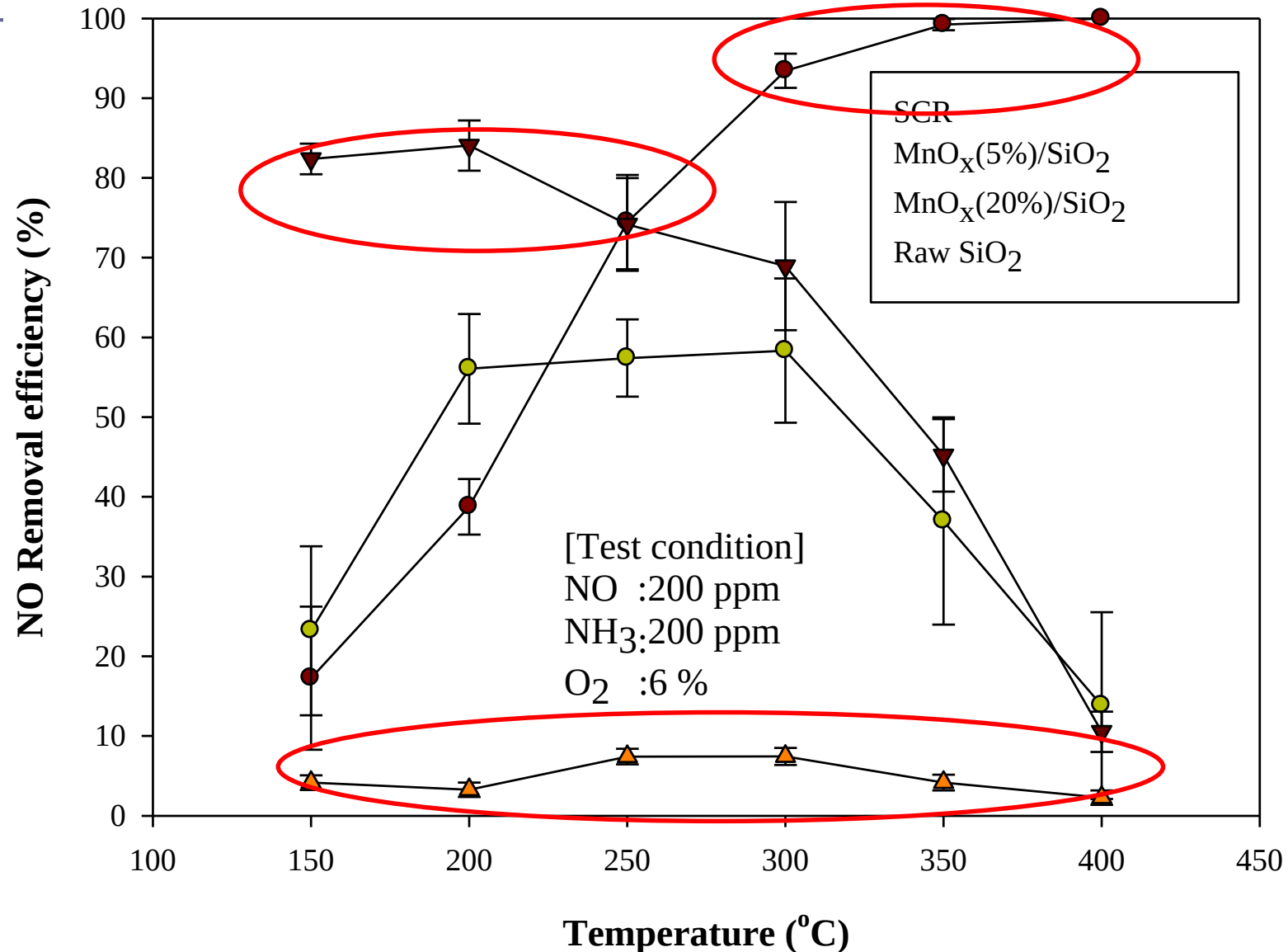
MnO_x(5%) T-Hg Test at different inlet Hg⁰ concentration



MnO_x(20%)-CeO₂(10%)/SiO₂ T-Hg Test at different inlet Hg⁰ concentration



deNO_x Test over MnO_x/SiO₂ catalysts



NH₃ parameter

MnO_x(20%)-CeO_x(10%)/SiO₂

