Local Structure Analysis of de-NOx Catalyst Prepared by the Glycothermal Method

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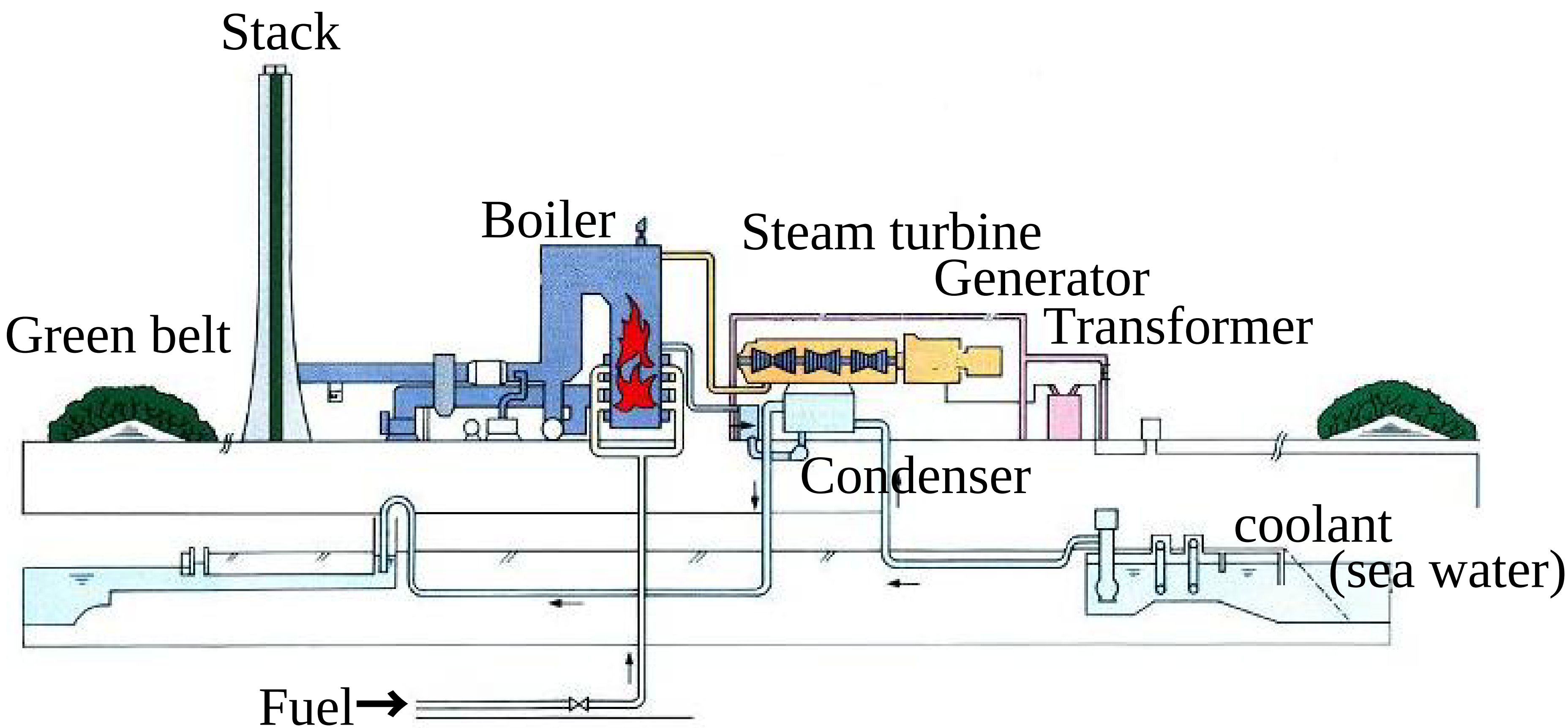
1. Introduction (1) The outline of the Thermal Power Station



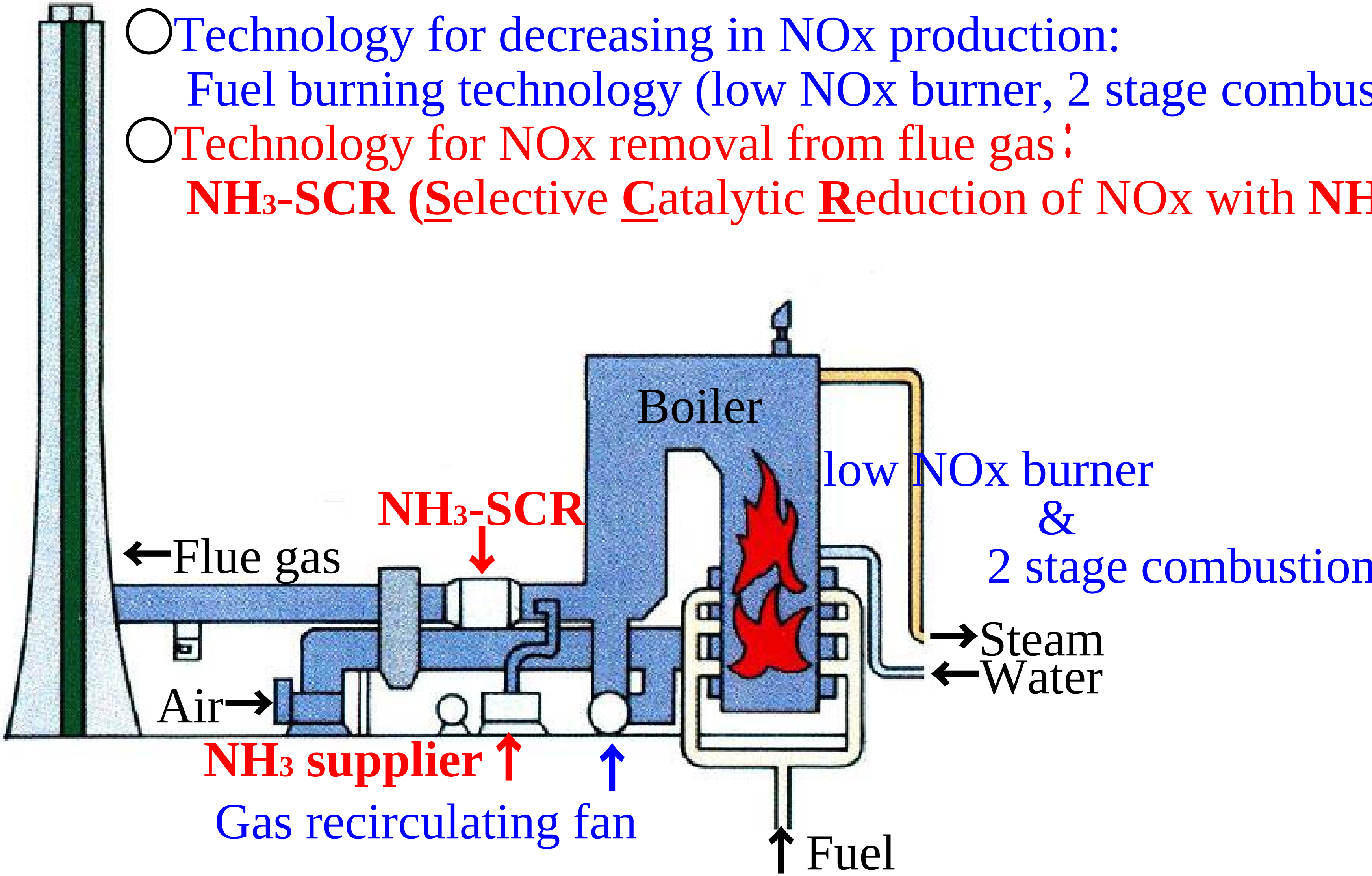
There are many kinds of pollution sources at the thermal power station.
The measures are taken in accordance with the cause of pollution.
(Ex. Sound isolation wall, Low emission boiler, Green belt, etc.)

1. Introduction (2) NOx reducing Technology

Stack

○Technology for decreasing in NOx production:
Fuel burning technology (low NOx burner, 2 stage combustion)

○Technology for NOx removal from flue gas:
NH_3-SCR (**S**elective **C**atalytic **R**eduction of NOx with **NH_3**)

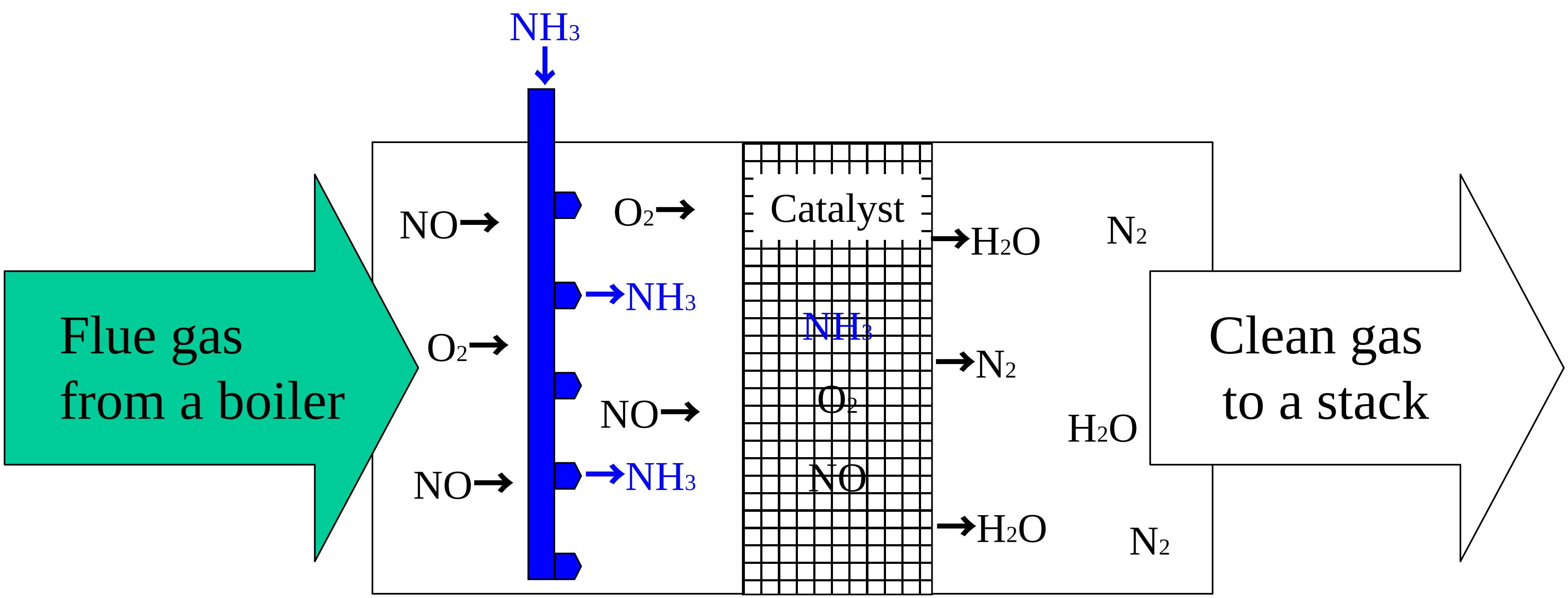


(3)What is NH_3-SCR?

Nitrogen Oxide (NO) reacts with ammonia on the catalyst.

$$NO + NH_3 + (1/4)O_2 \rightarrow N_2 + (3/2)H_2O$$

NH_3-SCR is widely used at thermal power stations.
However, as it is not easy to handle NH_3,
new de-NOx catalysts without NH_3 are required.



2. New catalyst

(1) Catalyst for CH_4-SCR

1. CH_4 is the main component of natural gas (NG).

2. NG is used as a clean fuel at the thermal power station.

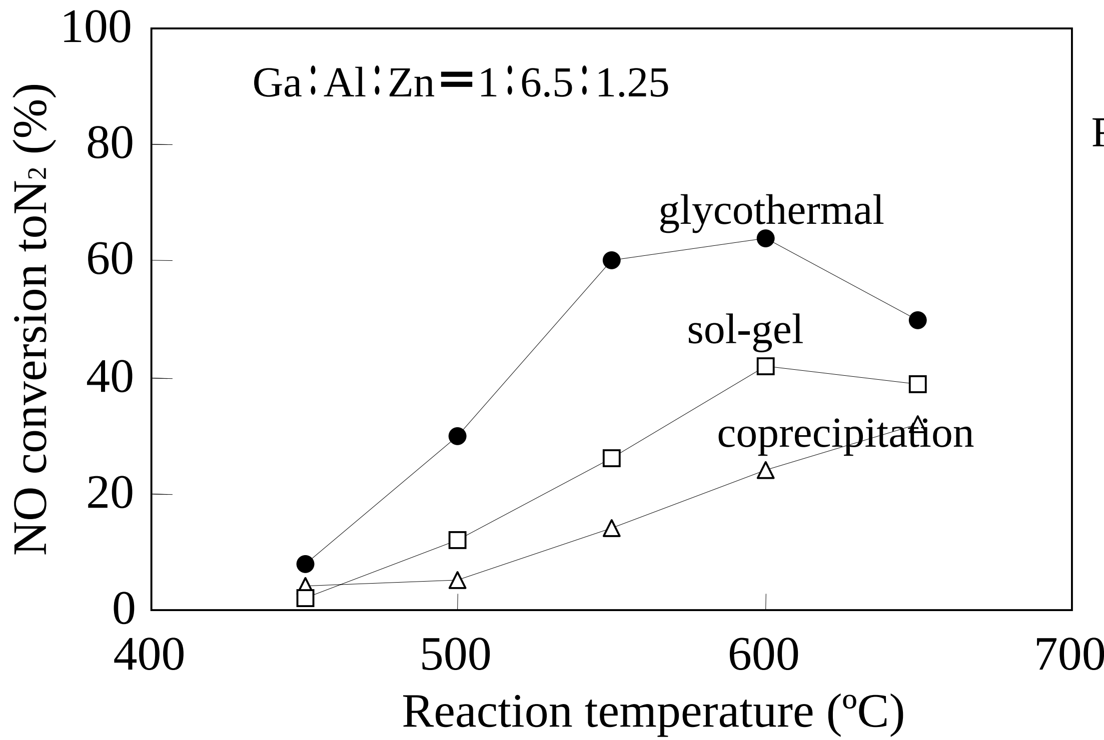
3. NO can be reduced selectively with CH_4 on the many kinds of catalyst.
   (1) Metal-modified zeolite catalyst (ex. Co-zeolite, Pd-zeolite)
   high activity, high selectivity, low durability
   (2) Metal-modified metal oxide catalyst(ex. Pt/Al_2O_3, Co/Al_2O_3,)
   low activity, low selectivity, **high durability**
   (3) Metal oxide (ex. Al_2O_3)
   low activity, high selectivity, **high durability**

It is the better way to improve the activity of metal oxide,
because the stable operation is required at thermal power station.

2. New catalyst

(2) ZnO-Ga_2O_3-Al_2O_3

The CH4-SCR performance of ZnO-Ga_2O_3-Al_2O_3 catalysts prepared by some method were investigated and the results are shown in this Figure.



Reaction condition:
- NO 1,000ppm
- CH_4 2,000ppm
- O_2 6.7%
- H_2O 2.5%
- He balance

Performance order
glycothermal > sol-gel > coprecipitation
→Why ?

3.Experimental (1) Samples and XAFS measurement

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1. Samples

(1) Metal composition

Ga/Al/Zn (molar ratio)

= 1/6.5/1.25, 1/1/1, 1/4/1, 1/4/0.1

(2) Preparation method

glycothermal, sol-gel, and coprecipitation methods

2.XAFS measurement

(1) Edge

Zn-K (9.66 keV), Ga-K (10.38 keV)

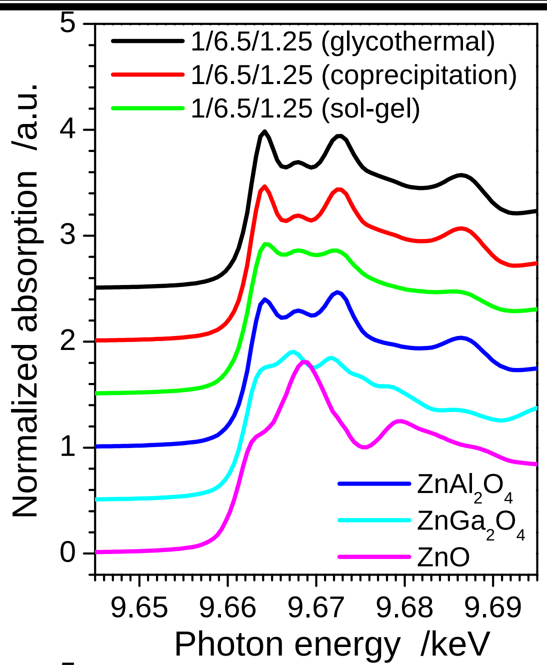
(2) Beamline

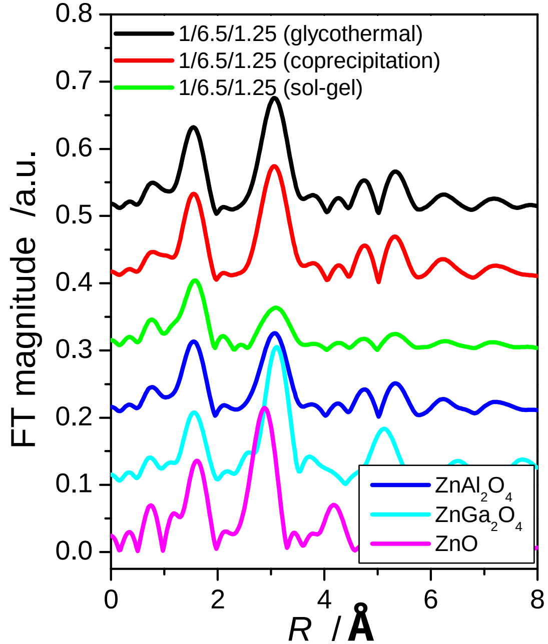
SPring-8 BL16B2

(3) Measurements

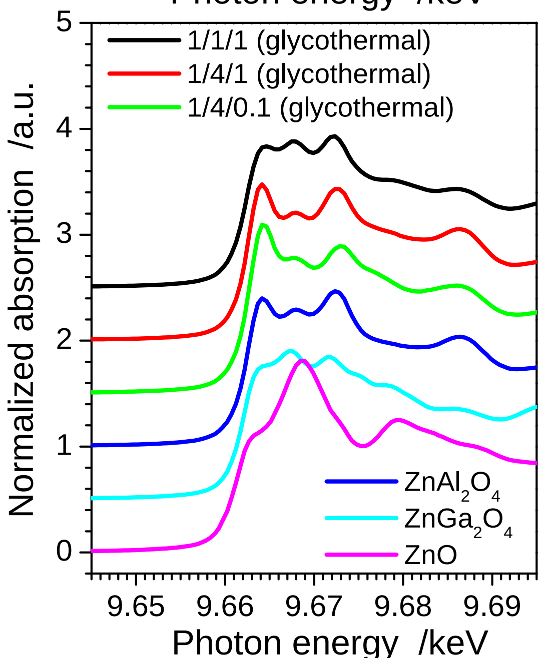
All samples by transmission mode in air at room temperature

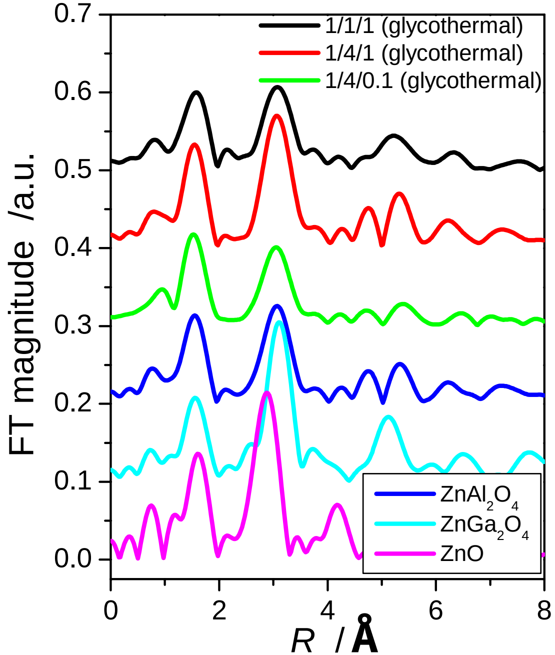
4. Result (1) Zn-K edge





Ga/Al/Zn molar ratio	CN	R(Å)
1/6.5/1.25 (GT)	4.0(3)	1.941(3)
1/6.5/1.25 (C)	3.8(3)	1.942(3)
1/6.5/1.25 (S)	3.7(4)	1.960(4)
1/1/1 (GT)	4.1(2)	1.975(2)
1/4/1 (GT)	3.9(2)	1.943(2)
1/4/0.1 (GT)	3.9(5)	1.953(4)

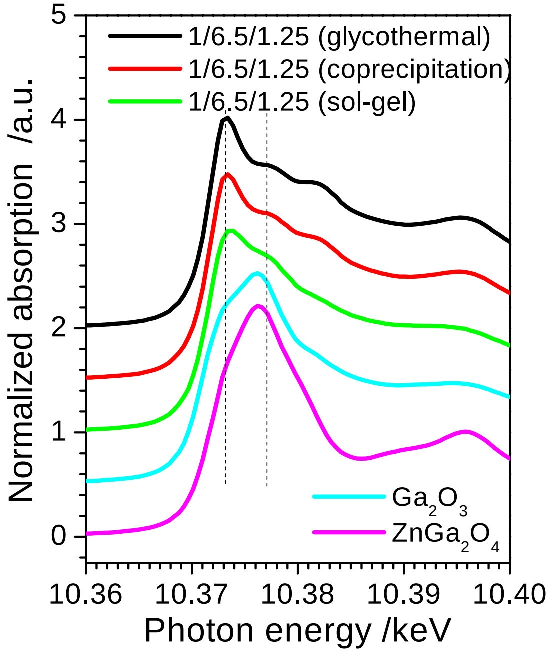


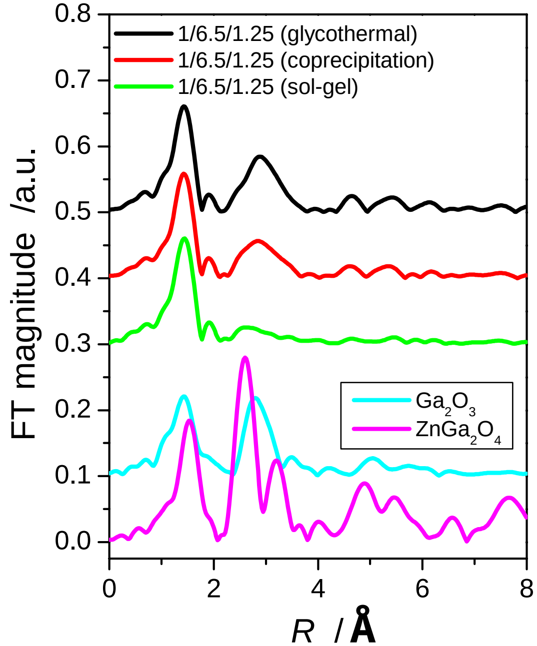


XANES spectra showed that Zn^{2+} ions were not in ZnO but in the spinel structure.

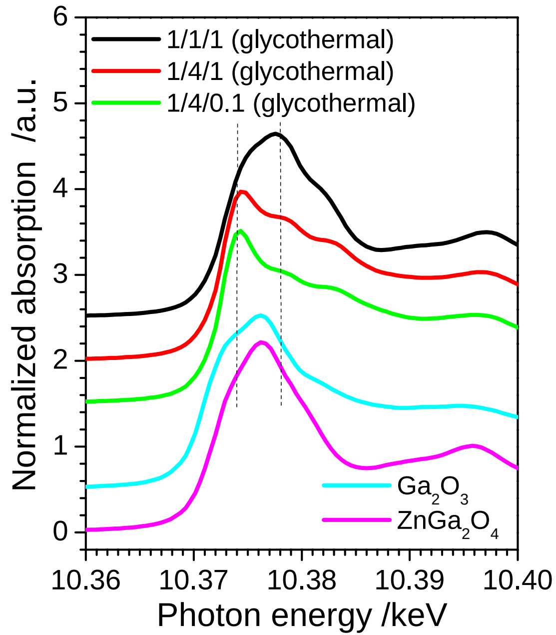
Zn^{2+} occupied tetrahedral sites regardless of the preparation method and the metal content.

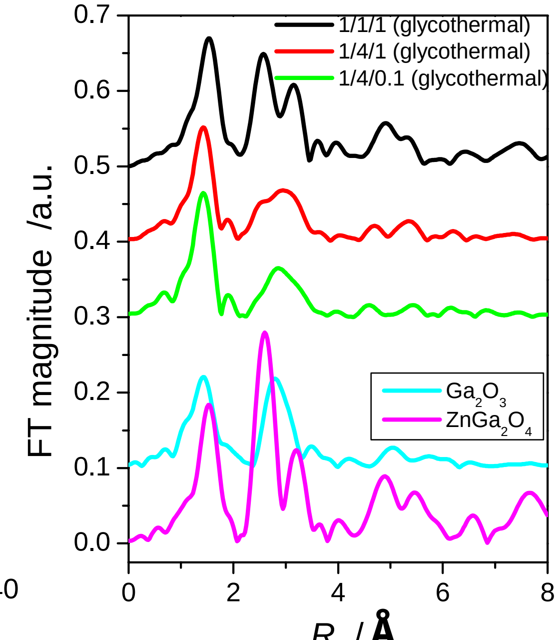
4. Result (2) Ga-K edge





Ga/Al/Zn molar ratio	CN	R(Å)
1/6.5/1.25 (GT)	3.8(4)	1.868(5)
1/6.5/1.25 (C)	3.7(5)	1.870(5)
1/6.5/1.25 (S)	3.9(5)	1.874(5)
1/1/1 (GT)	5.7(3)	1.959(3)
1/4/1 (GT)	4.2(6)	1.882(6)
1/4/0.1 (GT)	3.6(4)	1.862(5)



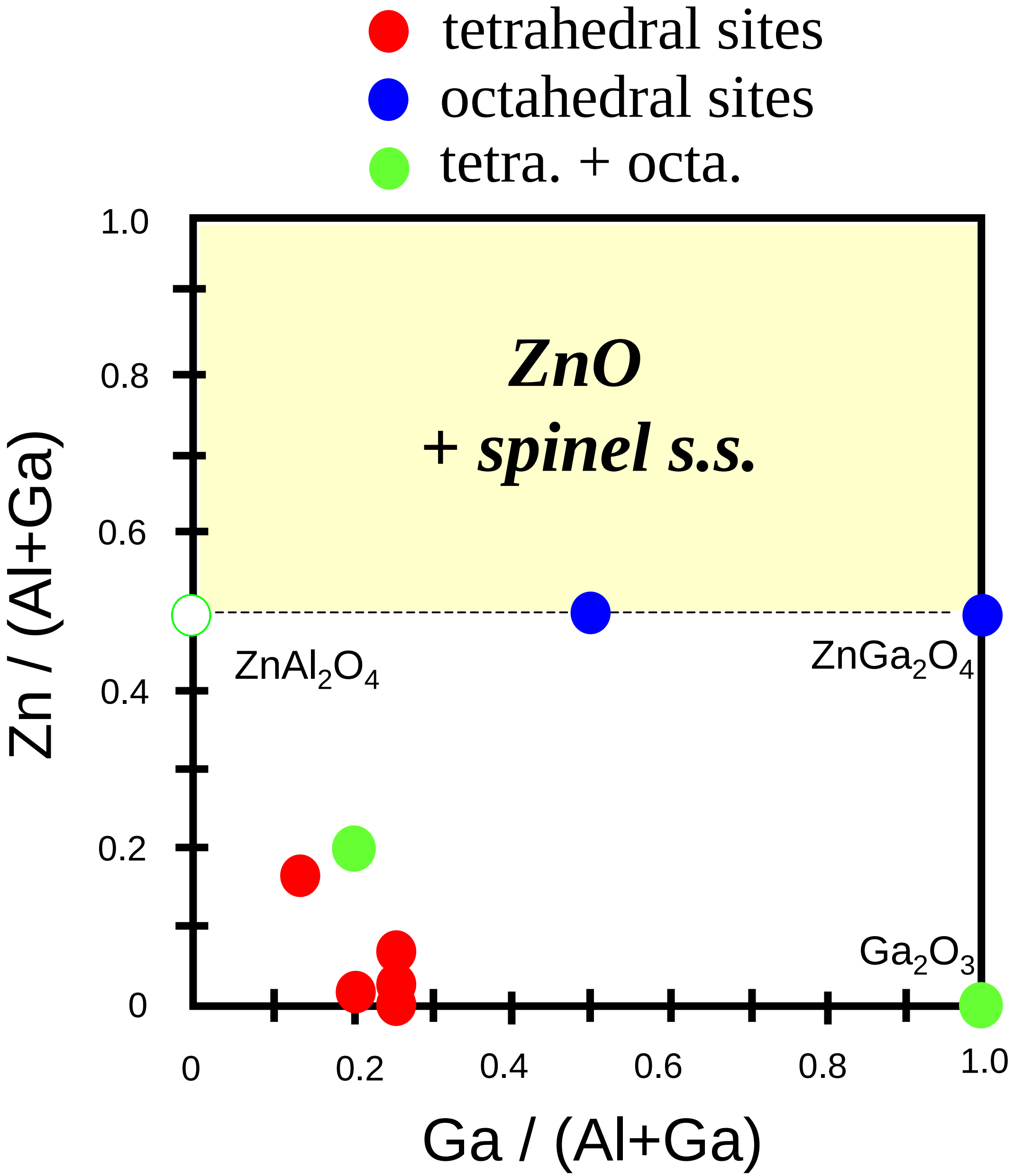


Difference among the three preparation methods was not clearly elucidated.

Occupation sites of Ga^{3+} varied with Zn^{2+} and Al^{3+} content.

4. Result

(3) Occupation site of Ga^{3+}



In the catalysts having high activities, Ga^{3+} ions occupied the tetrahedral sites. However, Ga^{3+} ions moved to the octahedral sites when Zn^{2+} content was high and/or Al^{3+} content was low.

Both Zn^{2+} and Ga^{3+} prefer to occupy the tetrahedral sites, but Zn^{2+} has a stronger tendency to occupy the tetrahedral sites than Ga^{3+}.

5. Summary

XAFS analysis of $ZnO-Ga_2O_3-Al_2O_3$ catalysts prepared by glycothermal, coprecipitation and sol-gel methods was carried out.

Difference among the three preparation methods was not clearly elucidated.

Both Zn^{2+} and Ga^{3+} prefer to occupy the tetrahedral sites, but Zn^{2+} has a stronger tendency to occupy the tetrahedral sites than Ga^{3+}.