

XAFS measurements with simultaneous monitoring of products for catalytic reactions

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1 Introduction

QXAFS is an efficient method to monitor time-resolved change of catalysts with the in-situ condition. For this purpose simultaneous monitoring of products from the catalyst layer is required for establishing the correlation between catalytic activities and XAFS results. The development of XAFS system with simultaneous monitoring of products is reported here. The system is applied to pulsed reaction sequence for partial oxidation of methane by Ni/CeO₂ catalyst.

2 Experiment

Schematic drawing of QXAFS-Pulse system is shown in Fig. 1. Sample is prepared as a pellet with BN and sustained with quartz wool at the midpoint of quartz tube. Both ends of quartz tube are connected with T-joints with

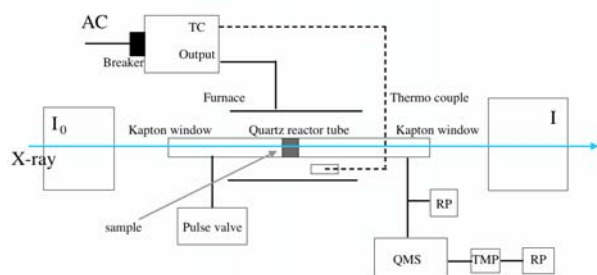


Fig. 1: Schematic drawing of QXAFS-Pulse system

a Kapton window and connection with gas pulse valve and QMS chamber. Two gas pulse valves driven by solenoid are equipped with 5 ms open time. QMS chamber is evacuated by turbo molecular pump and 5 mass signals can be monitored simultaneously. The quartz tube is positioned between I₀ and I chambers, so that transmission XAFS measurements are conducted. The quartz tube is surrounded with a coaxial furnace and temperature can be controlled in the range RT and 900 °C. 5 wt% Ni/CeO₂ catalyst was prepared by an impregnation method with Ni acetate as a precursor and calcined at 800 °C. EXAFS measurements of Ni-K edge were carried out at KEK-IMMS-PF BL9C.

3 Results and Discussion

QXAFS-pulse reaction experiments were performed for Ni/CeO₂ catalyst. Reaction temperature was 800 °C. Pulsed gas mixture (CH₄:O₂=2:1) was fed to the catalyst layer and K-edge XANES spectra were recorded after each pulse as shown in Fig. 2 and mass signals recorded simultaneously are shown in Fig. 3.

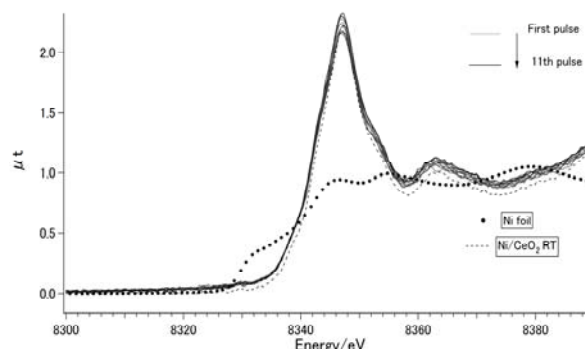


Fig. 2: Ni K-edge XANES spectra obtained by QXAFS – pulse experiments

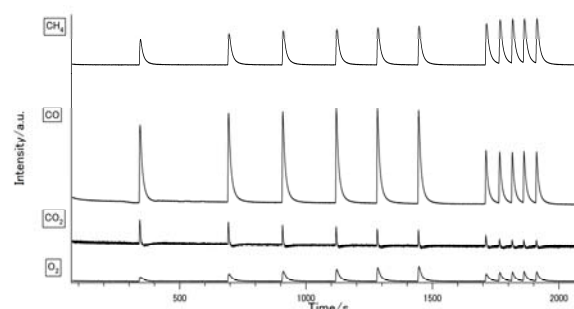


Fig. 3: Responses of products in QXAFS - pulse experiments

In Fig. 2, XANES spectrum recorded for the Ni foil is also shown as a dotted curve. As-prepared Ni/CeO₂ catalyst exhibits Ni oxidized state distributed on CeO₂ support as confirmed by the strong white line without pre-edge feature in contrast to Ni foil. Intensity of white line is slightly decreasing with increasing pulses, indicating slight reduction of NiO species. From mass signals (Fig. 3) catalyst working condition can be monitored. Unreacted CH₄ signal is increasing gradually, meaning that reaction is not in steady state and activity is decreasing. Unreacted O₂ is also increasing. H₂ and H₂O signals were not detected as a product signal. CO and CO₂ signals were detected. CO formation can be attributed to the reaction with lattice oxygen of CeO₂ and CH₄, while CO₂ formation can be attributed to reaction with NiO and CH₄. O₂ fills the oxygen vacancy sites [1].

Reference

[1] W.S.Dong et al, *Catal. Lett.*, 2002, 78, 1.

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