

## ***In situ* EXAFS study on nickel metal particles dispersed on Loy Yang brown coal**

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The structure of nickel catalysts supported on Loy Yang brown coal by an ion-exchanging method during thermal treatment was studied by a XAFS technique. The exchanged nickel species aggregated to metal particles during pyrolysis and hydrogasification. The aggregation behaviour of nickel species depended on the amount of nickel loaded and/or treatment atmospheres.

**Keyword: Coal; Catalyst; Metal particle.**

### **1. Introduction**

Brown coals have oxygen-containing surface functional groups. By exchanging protons of surface groups with metal cations, atomically dispersed catalysts can be loaded on coals. The activity of catalysts so prepared for coal utilisation processes (e.g. gasification and liquefaction) is higher than that of catalysts prepared by other conventional methods (e.g. mixing and impregnation) (Murakami, Ozaki & Nishiyama, 1995). Although atomically dispersed catalysts can be obtained by ion-exchanging methods, the catalysts aggregate to large particles during coal conversion process at high temperatures. It is important to characterize the structure of catalysts under in-situ conditions for developing highly active catalysts. X-ray diffraction (XRD) is one of the conventional methods to determine the structure of catalysts, however it is less effective for highly dispersed and/or low concentration systems. X-ray absorption fine structure (XAFS) is a powerful technique to determine the local structure of X-ray absorbing atoms under in-situ conditions. In this paper we report the structure of nickel catalysts on Loy Yang brown coal under in-situ conditions by a XAFS technique.

### **2. Experimental**

#### **2.1. Sample Preparation.**

Loy Yang brown coal from Victoria, Australia, was used in this study. Details of sample preparation were described previously (Shirai, Murakami & Nishiyama, 1997). Raw coal was ground below 250  $\mu\text{m}$  particle size, washed with deionized water, dried at 323 K under vacuum. The analyses for this coal are as follows:

C 67.6% (daf), H 5.2% (daf), N 0.8% (daf), O 26.4% (diff), and ash 0.2% (dry). Acid-washed coal (AW) was prepared by stirring the raw coal into 0.5 M hydrochloric acid for 24 h. A coal sample was stirred into aqueous solution of nickel chloride at a concentration of 10000 ppm and the pH of the solution was adjusted by adding ammonia or hydrochloric acid. After the pH stopped changing and remained unchanged for 5 h, the exchange reaction was judged to be at equilibrium. The quantity of exchanged nickel cations was determined by extracting the cations from the sample by hydrochloric acid.

#### **2.2. Gas Analysis.**

Pyrolysis and hydrogasification experiment was carried out in a fixed bed type pyrolyzer under helium or hydrogen flow at a heating rate of 5 K/min from 373 to 1173 K and the C1 gases evolved were analyzed by a gas chromatograph attached to the pyrolyzer.

#### **2.3. XAFS.**

Details of XAFS analysis were described previously (Shirai, Murakami & Arai 1999). Data were collected at beam line BL-10B and 12C at the Photon Factory of National Laboratory for High Energy Physics, Tsukuba. The storage ring was operated with an electron energy of 2.5 GeV. Data were recorded in the transmission mode in the region of the Ni K edge (8331.7 eV) at room temperature. The transmission spectra were collected using ion chambers that were filled with nitrogen gas.

EXAFS oscillation was extracted from the EXAFS raw data by using a cubic spline method and normalized with the edge height. The  $k^3$ -weighted EXAFS spectra were Fourier transformed to R space. The inversely Fourier filtering data were analyzed by a curve-fitting technique on the basis of the single-scattering plane-wave theory.

Experimentally determined phase shifts and backscattering amplitudes for Ni-Ni and Ni-O were obtained from EXAFS data for Ni foil (Ni-Ni; coordination number (N) = 6, distance (R) = 0.2089 nm) and NiO (Ni-O; N = 12, R = 0.2488 nm), respectively.

### **3. Results and discussion**

#### **3.1. Structure and Catalysis of Nickel Species for Loy Yang Brown Coal during Pyrolysis.**

Fig.1a shows several results of EXAFS Fourier transforms of nickel-loaded Loy Yang brown coals pyrolyzed at different temperatures. Only Ni-O was observed in the 1.4 wt% nickel-loaded sample pyrolyzed at 723 K with curve-fitting analysis (N=5.6 and R=0.201 nm), indicating that nickel species were atomically dispersed. We have reported that nickel carboxylate groups are formed by exchanging protons of carboxyl groups of Loy Yang coal with nickel cations, indicating that nickel species were atomically dispersed on the brown coal after ion-exchanging (Shirai, Arai & Murakami, 1999). The EXAFS result shows that nickel atoms were still atomically dispersed after pyrolyzed at

723 K. After treatment at 773 K, a peak assigned to Ni-Ni metal bonds ( $N=0.6$  and  $R=0.249$  nm) was observed in addition to the Ni-O bond peak ( $N=4.7$  and  $R=0.200$  nm). After treatment at 793 K, the peak intensity of Ni-Ni metal bonds became large. These results indicate that nickel species were reduced and agglomerated during pyrolysis.

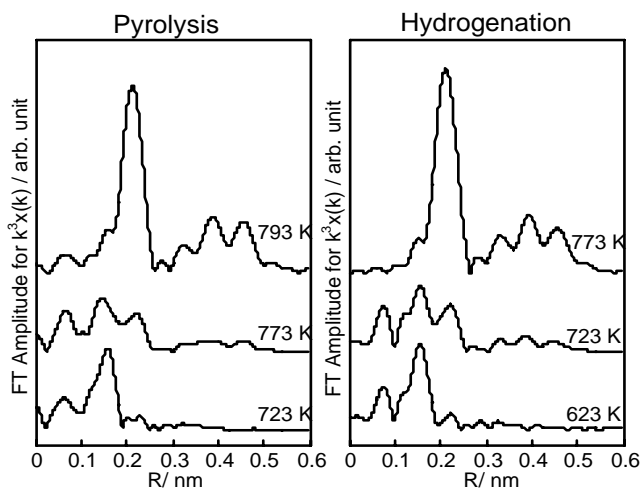


Figure 1

Fourier transforms for EXAFS oscillations of the 1.4 wt% nickel-loaded Loy Yang coal samples pyrolyzed and hydrogenated at various temperatures (No correction for phase shift).

Fig. 2 shows that the dependence of Ni-Ni coordination numbers of the nickel-loaded samples on the pyrolysis temperature. All EXAFS results show that nickel metal particles are formed in the ion-exchanged brown coals, but the transition temperature for the appearance of nickel particles depends on the loading. The agglomeration temperature decreased with increasing amount of nickel species.

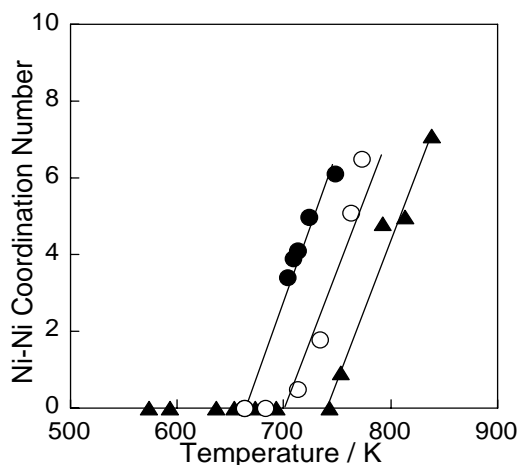


Figure 2

Coordination numbers of Ni-Ni bond as a function of pyrolysis temperature (filled triangles: 1.4 wt% nickel-loaded coal; empty circles: 2.8 wt% nickel-loaded coal; filled circles: 6.4 wt% nickel-loaded coal).

C1 gas ( $\text{CO}$ ,  $\text{CO}_2$ , and  $\text{CH}_4$ ) evolution profiles of the acid washed coal (AW) and several nickel-loaded samples are given in Fig. 3.

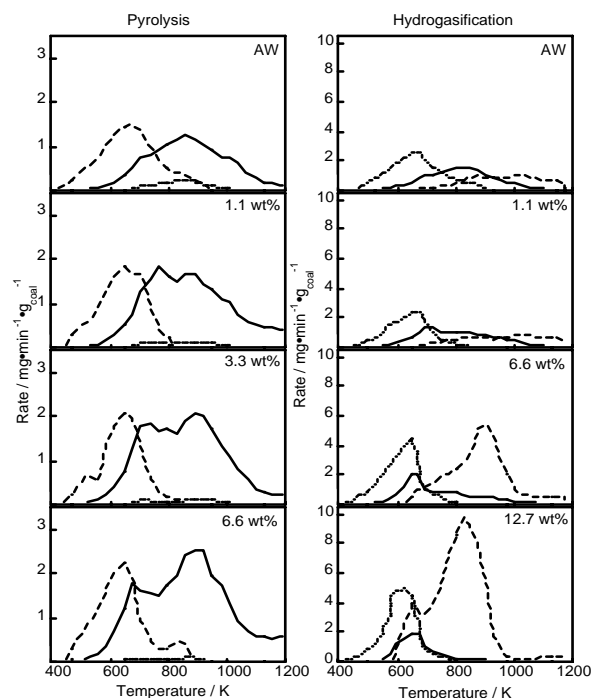


Figure 3

C1 gas evolution profile during pyrolysis and hydrogasification ( $\text{CO}$ : solid line;  $\text{CO}_2$ : dotted line;  $\text{CH}_4$ : broken line).

The  $\text{CO}$  evolution profiles in pyrolysis were drastically changed by supporting nickel and depended on the amounts of nickel species. Only one  $\text{CO}$  evolution peak was observed at 870 K for AW, while two peaks appeared in the  $\text{CO}$  evolution from nickel-loaded coals. The  $\text{CO}$  evolution peaks were deconvoluted with a Gaussian shape to two peaks at 760–670 K ( $\alpha$ - $\text{CO}$ ) and 880 K ( $\beta$ - $\text{CO}$ ). The total amount of  $\alpha$ - $\text{CO}$  evolved increased with increasing nickel loading. The peak top temperature of  $\alpha$ - $\text{CO}$  decreased from 760 K for the 1.1 wt% nickel-loaded sample to 670 K for the 6.6 wt% sample. The amount of  $\text{CO}$  evolved from Loy Yang coal was increased by supporting and with increasing amount nickel species, suggesting that nickel species catalyzed for  $\text{CO}$  evolution from the brown coal. The total amount of  $\alpha$ - $\text{CO}$  evolved increased with increasing nickel loading. The amount of  $\alpha$ - $\text{CO}$  evolved from the 1.1 wt% nickel-loaded sample was two times larger than the amounts of nickel atoms loaded. The peak top temperature of  $\alpha$ - $\text{CO}$  evolution at the loading from 1.1 to 6.6 wt% is the same as the transition temperature for the formation of nickel metal particles (Fig. 4). It is probable that the nickel metal particle formation process closely relate to the  $\alpha$ - $\text{CO}$  evolution during pyrolysis.

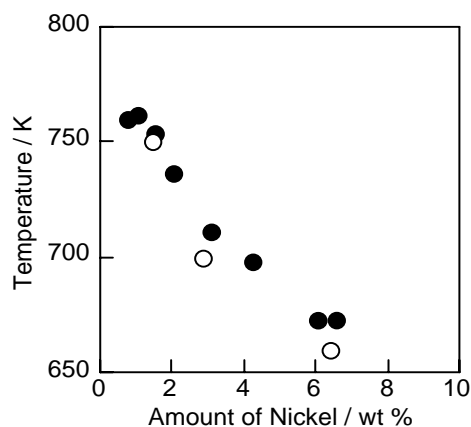


Figure 4

The peak top temperature of  $\alpha$ -CO evolved (filled circles) and the transition temperature (empty circles) for the formation of nickel metal particles as a function of the metal loading.

### 3.2. Structure and Catalysis of Nickel Species for Loy Yang Brown Coal in Flowing Hydrogen

Fig. 1b shows several results of EXAFS Fourier transforms of nickel-loaded Loy Yang coals treated with hydrogen at different temperatures. Only Ni-O was observed in the 1.1 wt% nickel-loaded coal hydrogasified at 623 K with curve-fitting analysis ( $N=0.6$  and  $R=0.201$  nm), indicating that atomically dispersed nickel atoms existed in this sample. After gasification at 723 K, a peak assigned to Ni-Ni metal bonds ( $N=1.0$  and  $R=0.250$  nm) was observed in addition to the Ni-O bond peak ( $N=5.6$  and  $R=0.200$  nm). After treatment at 773 K, the peak intensity of Ni-Ni metal bonds became large. These results indicate that nickel species were reduced and agglomerated during hydrogasification. Fig. 5 shows the dependence of Ni-Ni coordination numbers of the nickel-loaded samples on the hydrogasification temperature. The agglomeration temperature decreased with increasing amount of nickel species. The agglomeration temperature during hydrogasification was lower than that during pyrolysis on samples supporting similar amount of nickel.

C1 gas evolution profiles of AW and several nickel-loaded samples are given in Fig. 3. The  $\text{CH}_4$  evolution profile was affected drastically by large amounts of nickel loaded. The  $\text{CH}_4$  evolution peaks at 860 and 1010 K were broad for AW. The position and amount of  $\text{CH}_4$  did not change in the 1.1 wt% nickel-loaded sample. Large amount of  $\text{CH}_4$  was evolved at 900 K from the 6.6 wt% nickel-loaded sample. The  $\text{CH}_4$  peak shifted to 820 K and the amount became greater for the 12.7 wt%-nickel loaded sample. EXAFS analysis showed that nickel metal particles were formed at 680 K in the 1.1 wt% nickel-loaded sample under hydrogen flow. The amount of  $\text{CH}_4$  evolved from the 1.1 wt% nickel-loaded sample was similar to that of AW under hydrogen flow. The  $\text{CH}_4$  peak appeared at 600 K and had a maximum at 900 K in the 6.6 wt% nickel-loaded. EXAFS

analysis showed that nickel metal particles were formed at 620 K in the 6.6 wt% nickel-loaded sample. Large nickel metal particles formed above 620 K promote the production of  $\text{CH}_4$  in the 6.6 wt% nickel-loaded coal. The peak temperature and amount of  $\text{CH}_4$  evolved from the 12.7 wt% nickel-loaded coal became lower and larger compared with the 6.6 wt% nickel-loaded coal. EXAFS analysis showed that nickel metal particles formed at 580 K and large metal particles were formed above 580 K in the 12.7 wt% nickel-loaded sample. The large nickel metal particles produced  $\text{CH}_4$  from the 12.7 wt% nickel-loaded sample.

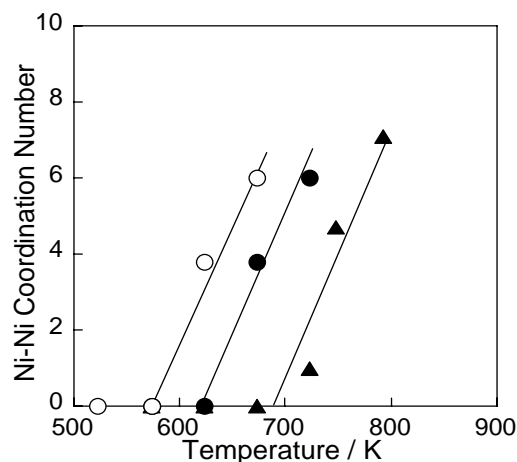


Figure 5

Coordination numbers of Ni-Ni bond as a function of hydrogasification temperature (filled triangles: 1.1 wt% nickel-loaded coal; filled circles: 6.6 wt% nickel-loaded coal; empty circles: 12.7 wt% nickel-loaded coal).

## 4. Conclusions

Pyrolysis and hydrogasification profile of Loy Yang brown coal was affected by nickel loading. The peak top temperature of  $\alpha$ -CO evolution during pyrolysis at loading from 0.77 to 6.6 wt% was the same as the transition temperature for the formation of nickel metal particles suggesting that the aggregation behaviour of nickel particles could affect the evolution of  $\alpha$ -CO during pyrolysis. Above 6.6 wt% of nickel loading, the amount of  $\alpha$ - $\text{CH}_4$  evolution during hydrogasification increasing with nickel loading, suggesting that the large nickel metal particles could promote the production of  $\text{CH}_4$ .

This work was carried out under the approval of PF advisory committee (No.99G252).

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