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Zeolite supported PtRh catalysts for CO oxidation and NO reduction: Evidence for bimetallic particles formation and synergism effect

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PtRh bimetallic particles, evidenced by EXAFS at Pt L_3-edge and Rh K-edge, were prepared in the supercages of NaY zeolites. Bimetallic catalysts, PtRh/NaY, were more reactive in CO-O_2 and CO-NO reactions than their corresponding monometallic catalysts, Pt/NaY and Rh/NaY.

Keywords: PtRh bimetallic catalysts; EXAFS; CO-O_2 reaction; CO-NO reaction

1. Introduction

Bimetallic catalysts are often superior to monometallic catalysts due to the enhancement of selectivity and/or stability in catalytic reactions, such as the incorporation of Re with Pt on chlorinated alumina for reforming reactions of naphtha [1] and the addition of Cu to Ru on silica for the dehydrogenation of cyclohexane [2]. The superior performance of bimetallic catalysts are rationalized by the modification of surface structure and surface composition as the results of the formation of bimetallic or alloy particles. In general, supported bimetallic catalysts are prepared by co-impregnation methods. A study by energy dispersed X-ray spectroscopy of CuRu/SiO_2 by Shastri et al. to examine the metallic composition of each particle indicated that the compositions among the particles are not homogeneous [3].

Pt and Rh on refractory oxide is another widely used industrial bimetallic catalyst for the removal of CO, NO and hydrocarbons in automobile emission

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systems and NH_3 decomposition. Oh et al. recently employed a two-step impregnation method to prepare PtRh bimetallic catalyst on Al_2O_3 [4]. It was found that catalysts prepared by the two-step method are much more reactive in CO oxidation than those prepared either by co-impregnation or by physical mixture of two monometallic catalysts. It was then concluded that PtRh bimetallic particles might be formed on Al_2O_3 by the two-step method though physical evidence for the bimetallic particles was not given. In this paper, we like to report that (1) small bimetallic PtRh particles with near uniform composition, as evidenced by EXAFS, can be easily prepared in the supercages of NaY zeolite and (2) a synergistic effect was observed on the reduced PtRh/NaY catalysts in CO oxidation and NO reduction.

2. Experimental

2.1. PREPARATION

Four metal containing NaY samples, (A) Pt/NaY, (B) Pt_2Rh_1/NaY, (C) Pt_1Rh_2/NaY and (D) Rh/NaY were prepared by ion exchange of NaY with an aqueous solution containing $Pt(NH_3)_4Cl_2$ or/and $Rh(NH_3)_5Cl_3$. The numbers 1 and 2 in Pt_1Rh_2/NaY and Pt_2Rh_1/NaY are the atomic ratios between Pt and Rh in the catalysts. The exchange reactions were carried out at 80°C overnight. The numbers of moles of metals in these four catalysts were kept nearly constant and their loadings, as analyzed by Toray Research Corporation of Japan are listed in table 1.

The pretreatment conditions for the four catalysts prior to the CO oxidation, NO reduction and chemisorption were as follows. Calcination was carried out in oxygen with a flow rate of 1000 ml/min/g zeolite from 20°C to 300°C at a heating rate of 0.5°C/min and held at 300°C for 2 h [5]. It was followed by purging with He during cooling. Finally, they were reduced by hydrogen from 20°C to 400°C (10°C/min) and held at 400°C for 2 h.

Chemisorption of hydrogen and CO were carried out in a volumetric system at room temperature. The pressure of H_2 and CO were in the range of 10 to 80

Table 1
Chemisorption of hydrogen and CO on NaY containing Pt, Rh or PtRh

Catalysts	Loading (wt%)	H/M	CO/M
A. Pt/NaY	Pt 5.5%	0.92	0.57
B. Pt_2Rh_1/NaY	Pt 3.7%, Rh 0.92%	0.91	0.84
C. Pt_1Rh_2/NaY	Pt 1.9%, Rh 1.9%	0.95	1.31
D. Rh/NaY	Rh 2.8%	0.74	1.48

M = Pt + Rh.

Torr. The amount of adsorption was obtained by extrapolation to pressure at zero Torr and substraction of physisorbed quantities.

2.2. REACTIONS

The CO oxidation and NO reduction on the four catalysts were carried out in a flow microreactor. About 200 mg samples mixed with 1.0 g quartz sand were used in each reaction. The activities of a physical mixture of Pt/NaY and Rh/NaY with equal amount of Pt and Rh were also examined. The gas stream was composed of 5 ml/min of oxygen and 2.5, or 5 or 10 ml/min of CO, which were diluted by helium in a blender to give a total flow rate of 100 ml/min. The activities were determined by the temperatures at which 50% CO was converted in the temperature runup experiments. The temperature increment was 10°C every 30 min between 140°C and 340°C. The CO oxidation activities of the used catalysts were remeasured after they were cooled to 140°C and the temperatures for 50% CO conversion were also recorded.

NO reduction by CO was also carried out in the same manner as in the CO oxidation. The gas streams were composed of 2.5 ml/min NO, 2.5 or 7.5 ml/min CO and helium to a give total flow rate 100 ml/min. The activity was also determined by the temperatures at which 50% NO was converted.

2.3. EXAFS CHARACTERIZATION

The structures of freshly reduced and used Pt, Rh and bimetallic PtRh particles in NaY were characterized by EXAFS at both Pt L_3-edge and Rh K-edge. The X-ray absorption measurements were carried out in the Photon Factory of Japan at Tsukuba city. In order to obtain a total absorption coefficient, $\mu\chi$, of each sample less than 3, the calcined samples were mixed with appropriate amounts of boron nitrite in air. The mixed sample was further dehydrated at 300°C in flowing oxygen, purged with He and reduced from 20°C to 400°C by hydrogen. Detailed experimental procedures and analysis of EXAFS results were described in detail in previous publications [6,7].

3. Results and discussions

3.1. HYDROGEN AND CO CHEMISORPTION

The results of H_2 and CO chemisorption on the reduced catalysts are listed in table 1. The ratios of H/M, where M = Pt + Rh, are between 0.75 and 0.95, which indicates the presence of highly dispersed Pt, Rh and PtRh particles in zeolites. The size of metal particles should be smaller than 13 Å.

3.2. EXAFS CHARACTERIZATION

The X-ray absorption for the four catalysts at both Pt L_3-edge and Rh K-edge were measured. Due to the small adsorption coefficient and low loading of Rh in (B) Pt_2Rh_1/NaY, the raw data of X-ray absorption at Rh K-edge was not good enough for reliable analysis. Detailed EXAFS analysis of Pt_1Rh_2/NaY was made.

The Fourier transforms of catalyst (C) Pt_1Rh_2/NaY at Pt L_3-edge and Rh K-edge are shown in fig. 1. There are two peaks with equal intensity in the Fourier transform of the Pt edge, which strongly suggests that both Pt and Rh are the first coordinative shell atoms of platinum. On the other hand for the Rh K-edge, there is a main peak at 2.3 Å (before phase correction) with a shoulder at short distance, which could be due to the interference of Pt atom as the first coordinative shell atom of rhodium. The coordination numbers and bond distances obtained from curve fitting analysis for Pt_1Rh_2/NaY, as well as for Pt/NaY and Rh/NaY, are listed in table 2. It indicates that small bimetallic

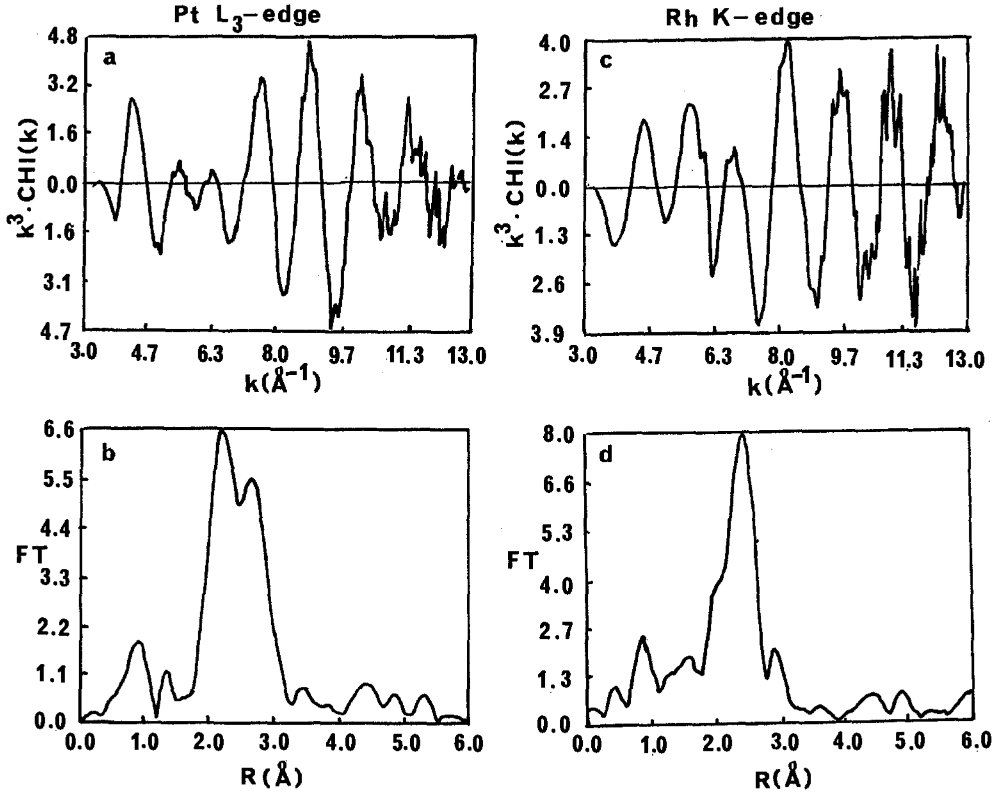

Fig. 1. EXAFS $k^3\ \chi(k)$ functions and Fourier transforms of Pt_1Rh_2/NaY at Pt L_3-edge (a, b) and Rh K-edge (c, d).

Table 2
Structural parameters of Pt, Rh and PtRh particles in NaY zeolites

Catalysts	Bonding pairs	Coordination numbers	Bonding distance (Å)	Debye Waller
Pt/NaY	Pt-Pt	6.4+1.0	2.76	0.07
Rh/NaY	Rh-Rh	5.6+1.0	2.69	0.09
Pt_1Rh_2/NaY	Pt-Pt	4.1+0.7	2.69	0.08
	Pt-Rh	3.5+0.6	2.69	0.09
	Rh-Rh	4.0+1.2	2.68	0.09
	Rh-Pt	2.6+0.4	2.70	0.09

PtRh particles are formed in (C) Pt_1Rh_2/NaY and they may have alloy type structure.

3.3. CO OXIDATION AND NO REDUCTION

Fig. 2 shows the activities for CO oxidation on these four catalysts. In general, bimetallic PtRh catalysts, especially (C) Pt_1Rh_2/NaY, are more reactive than the monometallic Pt/NaY and Rh/NaY since the temperatures to reach 50% CO conversion are lower for bimetallic catalysts. The activity of a physical mixture of equal amounts of Pt/NaY and Rh/NaY was also examined. Its *T*(50% CO), not shown in fig. 2 but listed in table 3, are slightly higher than those of Pt/NaY but much lower than those of Rh/NaY.

Results for the reduction of NO on these four catalysts are shown in fig. 3. Similar to the results for CO oxidation, bimetallic PtRh catalysts (B) and (C) are also more reactive than the monometallic catalysts in NO reduction.

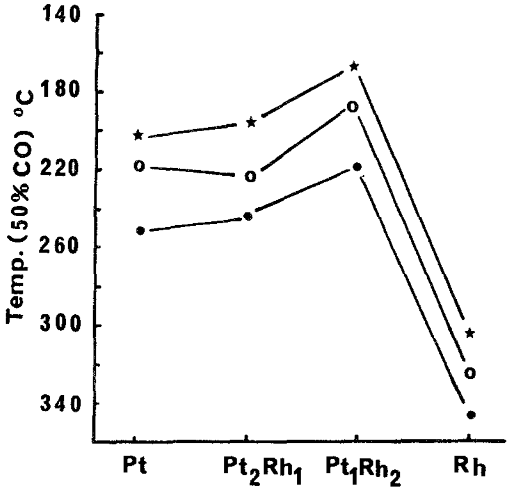

Fig. 2. CO-O_2 reaction reactivities of Pt/NaY, Rh/NaY and PtRh/NaY with gases stream CO/O_2/He = 2.5/5/92.5 ml/min (∗); 5/5/90 ml/min (o); 10/5/85 ml/min (●).

Table 3
CO oxidation activities, T(50% CO) of fresh and used (in parenthesis) NaY zeolites catalysts containing Pt, Rh or PtRh

gases O_2/CO	Catalysts A Pt	 B Pt_2Rh_1	 C Pt_1Rh_2	 D Rh	 E Pt+Rh
5 ml/2.5 ml	200(180)	185(165)	160(145)	300(240)	210(180)
5 ml/5 ml	215(200)	215(205)	180(160)	325(285)	225(215)
5 ml/10 ml	250(245)	245(225)	200(180)	340(300)	265(220)

As shown in figs. 2 and 3 for the two monometallic catalysts, Pt/NaY has higher activity for CO oxidation while higher or comparable (slightly lower) activity for NO reduction was observed on Rh/NaY. Taylor reported that Pt is more active in low temperature oxidation of CO and hydrocarbons and Rh is the component most active in NO reduction [8,9].

In spite of the importance of bimetallic PtRh catalysts in automobile emission, very limited information is available on their activities on CO oxidation and NO reduction. Van den Bosch-Driebergen et al. [10,11] studied the CO oxidation and NO reduction on PtRh alloy supported on SiO_2, in which PtRh alloy particles have an average size around 100 Å. It was concluded that activity was dependent on the bulk and surface composition and enhanced activity was not observed. It was well correlated to the studies on PtRh alloy single-crystal surfaces [12]. On the other hand, Oh et al. reported that higher CO oxidation activity was observed on the PtRh/Al_2O_3 prepared by the two-step procedure, which might be due to the formation of small PtRh bimetallic particles [4]. Our current study indicates that a synergetic effect indeed exists in the PtRh

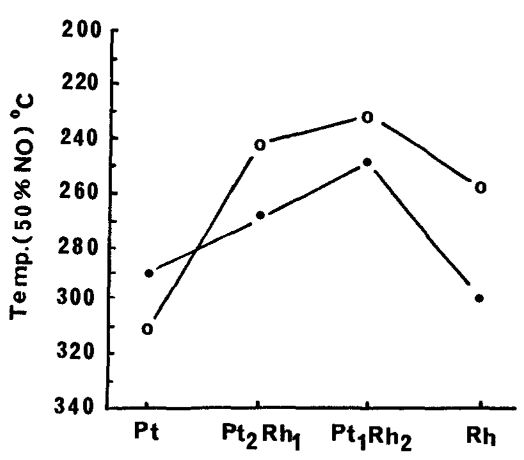

Fig. 3. CO-NO reaction reactivities of Pt/NaY, Rh/NaY and PtRh/NaY with gases stream CO/NO/He = 2.5/2.5/95 ml/min (●); 7.5/2.5/90 ml/min (○).

bimetallic catalysts and is consistent to what Oh et al. reported. The discrepancy between PtRh alloy on SiO_2 [9,10], Al_2O_3 [4] and NaY might be due to the particle size effect [13].

The temperature to reach 50% conversion of CO on the used catalysts are also included in table 3. Among all the four catalysts and the physical mixture of (Pt + Rh)/NaY, the used catalysts are always slightly more active, i.e. lower $T(50\%)$, than the freshly reduced catalysts. The difference of $T(50\%)$ between fresh and used catalysts is about 15 to 20°C.

Since these four exchanged catalysts were calcined at 300°C to remove the amine ligands, both Pt(II) and Rh(III) ions should be still in the supercages. During reduction at elevated temperature, Pt and Rh atoms would migrate along the supercages/channels till stable clusters or particles are formed. The composition of bimetallic PtRh particles might be dependent on the relative distribution of both cations in the zeolite crystals.

4. Conclusions

(1) Based on the EXAFS studies, it is concluded that bimetallic PtRh particles formed in the supercages may have alloy structure. They are formed by the random collision of reduced Pt and Rh atoms in supercages.

(2) As determined by H_2 and CO chemisorption and EXAFS, the PtRh bimetallic particles in zeolite are smaller than 13 Å, the dimension of supercage.

The small bimetallic particles might be responsible for the higher activities of CO oxidation and NO reduction observed.

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