Promoting Effects of Sn on NO Dissociation and NO Reduction with H_2 on Rh–Sn/SiO_2 Catalysts

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The Rh–Sn/SiO_2 catalysts prepared by the selective reaction of Me_4Sn with Rh/SiO_2 show remarkably high activities for NO dissociation and NO catalytic reduction with H_2 as compared with Rh/SiO_2.

Pollutants such as NO, hydrocarbons and CO from automobile exhaust gas have been removed by so-called 'three way' multicomponent catalysts containing noble metals such as Pt and Rh and also metal oxides such as cerium oxide. However, local and global environmental problems demand the development of new efficient catalytic systems for NO removal. The addition of typical sp-metals such as Sn to noble metals often changes the metal catalysis owing to geometrical and electronic isolation of the metal sites/ensembles. It has been demonstrated that Sn changes the catalytic activities of Pt and Rh for CO oxidation and ethyl acetate hydrogenation,[1–4] because of the advantageous interaction of Sn with oxygen atom.[5] These results prompted us to investigate the promoting effect of Sn on Rh catalysis for NO reaction on the basis of the characterisation of Rh–Sn and Sn–O bonds by EXAFS (extended X-ray absorption fine structure). In many cases, alloy catalysts have been prepared by a co-impregnation method, which makes it difficult to control the surface composition particularly for Sn alloy systems. In this report, a reactive chemical-vapour-deposition technique was adopted to prepare Rh–Sn/SiO_2 catalysts. We found that the Rh–Sn bimetallic catalysts prepared from Rh metal particles on SiO_2 and Me_4Sn vapour showed extremely high activities for NO dissociation and NO–H_2 reaction.

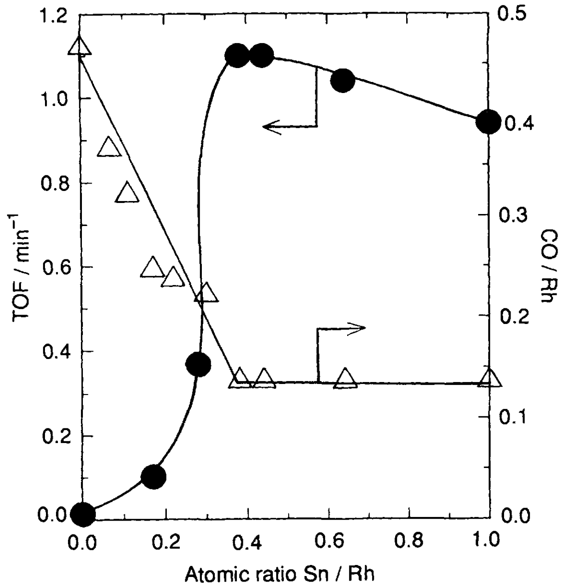

Fig. 1 The turnover frequency (product molecules per min per surface Rh atom) for $N_2 + N_2O$ formation in NO–H_2 reaction at 373 K (●) and the uptake of CO adsorption at 273 K (△) on Rh–Sn/SiO_2; NO : H_2 = 2.66 kPa: 13.3 kPa, P_{CO} = 13.3 kPa, Rh: 1.0 wt%

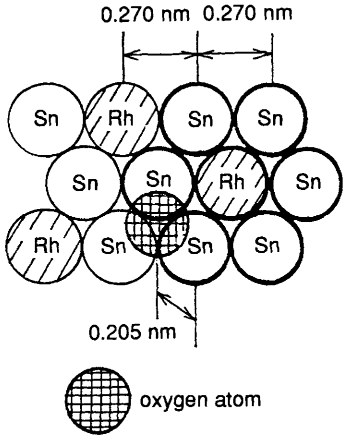

Fig. 2 A surface structure model of Rh–Sn/SiO_2 (Sn/Rh ⩾ 0.4); an oxygen atom (produced by NO dissociation at the steady state of reaction) is tentatively placed at the threefold hollow site composed of three Sn atoms

SiO_2 was immersed in a methanol solution of $RhCl_3 \cdot 3H_2O$, followed by drying at 393 K for 12 h and reduced with H_2 at 573 K. The obtained Rh particles on SiO_2 were treated with Me_4Sn vapour at 423 K, at which temperature no Me_4Sn reacted with the SiO_2 support. The catalysts were reduced with H_2 at 573 K for 1 h, followed by evacuation before each run. The loading of Rh was always 1.0 wt% and the Sn/Rh ratio was varied in the range 0–1. NO dissociation and the NO–H_2 reaction were carried out in the temperature range 273–393 K in a closed circulating system (dead volume 200 cm^3), producing N_2O and N_2, which were analysed by gas chromatography.

NO dissociation on Rh–Sn/SiO_2 (Sn/Rh = 0.45) at room temperature took place almost instantaneously. The product at NO pressures as low as 40 Pa was N_2 and at the higher pressures (*e.g.* 2.66 kPa) N_2 and N_2O were produced. The rapid dissociation stopped when one third of surface Sn atoms were oxidized with oxygen atoms from NO, exhibiting an Sn–O distance of 0.205 nm by EXAFS. On the other hand, NO molecularly adsorbs on Rh/SiO_2, and it does not decompose significantly below 373 K. The initial rate of NO–H_2 reaction on Rh–Sn/SiO_2 (Sn/Rh = 0.45) was so high that we could not follow it, which coincides with the instantaneous decomposition of NO as mentioned above. After the initial stage of reaction, the catalytic NO reduction proceeded steadily. Fig. 1 shows the variation of the NO–H_2 steady-state rate (turnover frequency = TOF) with Sn/Rh composition. The TOFs [product molecules min^{-1} (surface Rh atom)$^{-1}$] were calculated from the amount of adsorbed CO which is assumed to be equal to the number of surface Rh atoms (Fig. 1). The catalytic activity (TOF) of Rh–Sn/SiO_2 (Sn/Rh = 0.45) was 75 times as large as that of Rh/SiO_2 [25 times for the activity (g catalyst)$^{-1}$]. It has been reported that on Rh/SiO_2 NO dissociation occurs by the assistance of adsorbed H atoms, which is a rate-determining step.[6] In contrast, on Rh–Sn/SiO_2 the removal of the oxygen atoms on Sn (formed by NO dissociation) by H_2 is the slowest step. The promoter effect of Sn for the catalysts prepared by the reaction of Me_4Sn with Rh/SiO_2 was six times as great as that in the catalysts prepared by a co-impregnation method.

While the surface composition changed linearly in the range of Sn/Rh ⩽ 0.4, the TOF for NO–H_2 reaction increased in an S-shape form as shown in Fig. 1. This implies that particular Rh–Sn bimetal ensembles are required for the high activity. According to Sn K-edge EXAFS spectra, all the Sn atoms are bonded to Rh metal particles (Sn–Rh and Sn–Sn = 0.270 nm). When the catalysts (Sn/Rh ⩽ 0.4) were exposed to O_2 at room temperature, all Sn atoms were oxidized, exhibiting Sn–O bonds, which indicates that the Sn atoms are located at the surface of the Rh–Sn bimetallic particles. From the CO adsorption and EXAFS data, together with the transmission electron microscopy (TEM) image (average particle size = 2.5 ± 0.3 nm), the surface composition for the Rh–Sn/SiO_2 with Sn/Rh = 0.4 is estimated to be Rh : Sn = 1 : 3. The Rh–Rh coordination number and the Debye–Waller factor determined by Rh K-edge EXAFS analysis also suggest the formation of Sn–Rh bimetallic surface layers.[7] These results lead to a surface structure model with a hexagonal arrangement of Sn atoms surrounding a Rh atom, based on a stable fcc(111) plane as shown in Fig. 2. IR observation of adsorbed CO for Rh–Sn/SiO_2 (Sn/Rh > 0.2) revealed only a linear CO peak, no bridge CO peak being observed, which coincides with the active ensemble structure composed of isolated Rh atoms and also shows the onset of the sharp increase in the reaction rate shown in Fig. 1 (Sn/Rh > 0.2). At Sn/Rh ⩾ 0.4, the surface composition was constant (Fig. 1) and the excess Sn atoms were diffused into the Rh particles as proved by the EXAFS analysis.[7] The dissolved Sn atoms had little influence on the catalytic properties of the surface bimental ensembles.

Received, 15th October 1992; Com. 2/05520A

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