Catalytic Synthesis of Unsaturated Nitriles from NO–Alkane or NO–Alkene on Pt–Sn/SiO$_2$

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The Pt–Sn/SiO$_2$ catalysts prepared by selective bimetallic CVD reaction of SnMe$_4$ with Pt particles on SiO$_2$, characterized by EXAFS (extended X-ray absorption fine structure), yield acrylonitrile from NO + propene and methacrylonitrile from NO + isobutene and NO + isobutane with good selectivities, typically 70–93%, in contrast to negligible activity and selectivity (about one order of magnitude lower) with the monometallic Pt/SiO$_2$ catalyst.

Utilization of NO for the synthesis of unsaturated nitrile compounds from light alkanes and alkenes has received much attention from chemical as well as industrial points of view. NO + alkane/alkene reactions to produce the corresponding unsaturated nitriles are known as nitroxidation, which proceed on binary oxide catalysts, such as NiO–Al$_2$O$_3$, PbO–ZrO$_2$, Cr$_2$O$_3$–Al$_2$O$_3$, Ag$_2$O–SiO$_2$, *etc.*[1–4] In contrast to the accumulated performance of mixed metal oxides, noble metals like platinum have not been employed in this reaction because of the low NO dissociation activity of noble metals at low temperatures and the high oxidation activity of the oxygen atoms formed by NO dissociation on noble metals at high temperatures leading to combustion of hydrocarbons. Furthermore, undesirable cracking reactions of C–C bonds also occur with noble metals at such reaction temperatures. In this study we prepared Pt particles with Pt–Sn bimetallic layers at the surface by a selective bimetallic reaction of Pt particles on SiO$_2$ with SnMe$_4$ vapour by a CVD technique in a similar way to Rh–Sn systems.[5,6] The Pt–Sn bimetallic catalyst exhibited selective syntheses of acrylonitrile from propene + NO and methacrylonitrile from isobutene + NO or isobutane + NO at much lower temperatures than those for metal oxide catalysts.[1–4]

In many cases, alloy catalysts have been prepared by co-impregnation methods, which make it difficult to control surface composition, while use of organometallic compounds such as SnR$_4$ can provide comparatively well-defined surface layers of bimetallic particles.[5–8] The Pt/SiO$_2$ catalyst was prepared by a usual impregnation method using an aqueous solution of H$_2$PtCl$_6$, followed by calcination with O$_2$ for 1 h and reduction with H$_2$ for 1 h at 673 K. SnMe$_4$ vapour as a Sn source was reacted with the Pt/SiO$_2$ sample for 30 min at 423 K, under which conditions SnMe$_4$ reacted preferentially with Pt particles, rather than the SiO$_2$ surface, as confirmed by TPD experiments for both Pt/SiO$_2$ and SiO$_2$. The NO + hydrocarbon reactions were carried out in a closed circulating system (dead volume: 180 cm^3) equipped with a gas chromatograph and a quadrupole mass spectrometer for product analysis.

In the NO + propene reaction acrylonitrile was selectively produced over the Pt–Sn/SiO$_2$ catalyst (Sn/Pt = 0.17) at 573 K. The rate of acrylonitrile formation on Pt–Sn/SiO$_2$ was 7 times faster than that for Pt/SiO$_2$ as shown in Table 1. The selectivity toward acrylonitrile on Pt–Sn/SiO$_2$ was 77.4%, whereas it was as low as 9.6% on Pt/SiO$_2$. Acetonitrile formation as a byproduct reaction was suppressed by addition of Sn. The selectivity of acrylonitrile increased with an increase of propene pressure and it became 85% at 16 kPa of propene, with NO pressure held at 1.3 kPa. The superiority of the Pt–Sn/SiO$_2$ catalyst was also observed with the combustion byproduct reaction of propene to CO + CO$_2$ being dramatically suppressed as compared to the Pt/SiO$_2$ catalyst (Table 1). In addition, the rate of formation of N$_2$ and N$_2$O on Pt–Sn/SiO$_2$ was much lower than that for Pt/SiO$_2$. Thus, propene was selectively converted to acrylonitrile by NO on Pt–Sn/SiO$_2$, whereas on Pt/SiO$_2$ the majority of propene was merely oxidized to CO and CO$_2$ and NO was decomposed mainly to N$_2$ and N$_2$O without incorporation into the hydrocarbon, as shown in Table 1.

The rate and selectivity for acrylonitrile formation depended on the Sn content in Pt–Sn/SiO$_2$. Both rate and selectivity increased with Sn content, and reached their maxima around Sn/Pt = 0.2, and retained their values at Sn/Pt $\geqslant$0.2.[9] The adsorbed amount of CO decreased linearly upon Sn addition to Pt/SiO$_2$ until Sn/Pt = 0.2 and at Sn/Pt $\geqslant$ 0.2 became constant, showing a break at Sn/Pt = 0.2. The decrease in the adsorbed amount of CO coincides with the amount of Sn added to the Pt/SiO$_2$, taking into account the increase in the total number of metal atoms involved in each bimetallic particle. At the saturation surface of Sn/Pt = 0.2, we can estimate the surface composition to be Pt : Sn = 2 : 3. A model ensemble structure is shown in Fig. 1. The Sn–Pt and Sn–Sn bond distances were determined to be 0.263 and 0.260 nm, respectively, by Sn K-edge EXAFS analysis.[9] EXAFS spectra at the Sn K-edge were measured in the transmission mode at the BL-14A station of the Photon Factory in the National Laboratory for High Energy Physics (KEK) with a positron energy of 2.5 GeV and a maximum storage ring current of 350 mA (Proposal No. 94G028). The EXAFS measurements were performed at 300 K. The resulting data were analysed by a curve-fitting technique using the

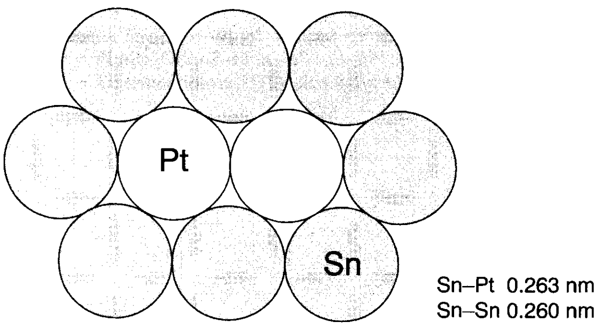

Fig. 1 A surface structure model of Pt–Sn/SiO$_2$ (Sn/Pt = 0.2)

Table 1 Initial rates (r)^a and (%) selectivities (S) for the formation of each product in NO + C$_3$H$_6$ reaction on Pt/SiO$_2$ and Pt–Sn/SiO$_2$ catalysts

	C$_2$H$_3$CN		MeCN		CO		CO$_2$		N$_2$		N$_2$O	
Catalyst	r	S	r	S	r	S	r	S	r	S	r	S
Pt/SiO$_2$	0.07	9.6	0.28	25.7	0.83	38.1	0.58	26.6	0.92	58.8	0.47	30.0
Pt–Sn/SiO$_2$ (Sn/Pt = 0.17)	0.49	77.4	0.13	13.7	0.0	0.0	0.17	8.9	0.28	42.4	0.07	10.6

^{a} 10^{-6} mol min^{-1} (g cat)$^{-1}$; T = 573 K, NO = 1.3 kPa, C$_3$H$_6$ = 5.3 kPa.

parameters derived from the FEFF calculation for Sn–Sn and Sn–Pt bonds.[10]

NO Dissociation (NO 1.3 kPa) on the Pt–Sn/SiO_2 catalyst (Sn/Pt = 0.17) at 573 K occurred almost instantaneously, forming only N_2 in the initial stage of decomposition, and Sn was oxidized up to O/Sn = 0.5, (Sn–O 0.198 nm). Then both N_2 and N_2O were produced in the following stage, as surface oxidation proceeded further. These results indicate that NO dissociates on Pt–Sn ensemble sites to produce SnO_x species, leaving N(a). In the NO + propene reaction, NO dissociation was largely inhibited by the presence of propene, while propene reduced some of the SnO_x species at the bimetallic surface to the metallic state as established by Sn K-edge EXAFS.[9]

The catalytic performance of Pt–Sn/SiO_2 was tested for other hydrocarbons, such as ethene, isobutene, *cis*- and *trans*-but-2-ene, propane and isobutane. The activities and selectivities are summarized in Fig. 2, where the results for Pt/SiO_2 are also shown for comparison. Methacrylonitrile formation from NO + isobutene was dramatically promoted by the addition of Sn to Pt/SiO_2. The selectivity towards methacrylonitrile increased from 8% for Pt/SiO_2 to 93% for Pt–Sn/SiO_2. The Pt–Sn/SiO_2 catalyst also catalysed the formation of methacrylonitrile from isobutane at 573 K, which contrasts with the negligible activity of Pt/SiO_2 as shown in Fig. 2. On the contrary, on Pt/SiO_2, acetonitrile was selectively produced in NO–ethene, while Sn rather suppressed production of acetonitrile. This may be due to the difference of the reaction intermediate between ethene and other hydrocarbons. Ethene is known to form ethylidine on a Pt metal surface,[11] which may be the intermediate for acetonitrile formation on Pt/SiO_2. Platinum multisites required for ethylidine formation are broken by the addition of Sn, with the Pt–Sn ensemble structure (Fig. 1) being less active for ethene activation. In the case of propene and isobutene, allyl intermediates can be formed on Pt.[12,13] Allyl species have been demonstrated to be the intermediates in the ammoxidation reaction of propene to form acrylonitrile on mixed metal oxide catalysts such as Bi–Mo–O and U–Sb–O.[14] In Pt–Sn/SiO_2, SnO_x ($x < 0.5$) is expected to play a role in stabilizing allyl intermediates. On the Pt–Sn bimetallic surface (Fig. 1) Pt ensembles are small enough to suppress C–C bond cracking, but large enough to dehydrogenate propene, isobutene and isobutane to form the corresponding allyl species. In this context crotononitrile formation is expected in the NO + but-2-ene reaction, but is flammable even at room temperature. It may decompose under the reaction conditions used and as a result no nitrile was detected in this reaction.

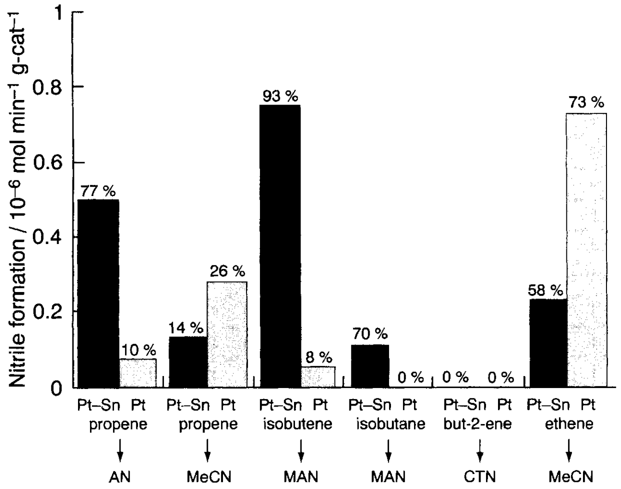

Fig. 2 Initial rates and selectivities for the formation of nitriles in NO + hydrocarbon reactions: Pt, Pt/SiO_2; Pt–Sn, Pt–Sn/SiO_2 (Sn/Pt = 0.17); AN, acrylonitrile; MAN, methacrylonitrile; CTN, crotononitrile. T = 573 K; NO = 1.3 kPa, hydrocarbon = 5.3 kPa.

In conclusion, we have found that the Pt–Sn/SiO_2 catalysts (characterized by EXAFS) selectively produce unsaturated nitriles in NO + propene, NO + isobutene and NO + isobutane reactions, where NO dissociation and allyl hydrogen abstraction are promoted on Pt–Sn bimetallic ensemble sites.

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References

1 duPont, *US Pat.*, 3,141,902, 1964.
2 F. Zidan, G. Pajonk, J. E. Germain and S. J. Teichner, *Bull. Soc. Chim. Fr.*, 1977, 1021.
3 A. Sayari, A. Ghorbel, G. Pajonk and S. J. Teichner, *Bull. Soc. Chim. Fr. I*, 1982, 220.
4 duPont, *Br. Pat.*, 729,013, 1955.
5 K. Tomishige, K. Asakura and Y. Iwasawa, *J. Chem. Soc., Chem. Commun.*, 1993, 184.
6 K. Tomishige, K. Asakura and Y. Iwasawa, *J. Catal.*, 1994, **149**, 70.
7 J. P. Candy, O. A. Ferretti, G. Mablion, J. P. Bournonville, A. El Mansour, J. M. Basset and G. Martino, *J. Catal.*, 1988, **112**, 210.
8 C. Nedez, A. Theolier, F. Lefebvre, A. Choplin, J. M. Basset and J. F. Joly, *J. Am. Chem. Soc.*, 1993, **115**, 722.
9 T. Inoue, K. Tomishige and Y. Iwasawa, unpublished work.
10 J. J. Rehr, J. M. Leon, S. I. Zabinsky and R. C. Albers, *J. Am. Chem. Soc.*, 1991, **113**, 5135.
11 N. Sheppard, *Ann. Rev. Phys. Chem.*, 1988, **39**, 589.
12 S. Naito and M. Tanimoto, *Shokubai (Catalyst)*, 1985, **27**, 356.
13 J. M. Griffiths, A. T. Bell and J. A. Reimer, *J. Phys. Chem.*, 1994, **98**, 1918.
14 R. K. Grasselli and J. D. Burrington, *Adv. Catal.*, 1981, **30**, 133.