Catalyst poisoning by methyl groups

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Received (in Cambridge, UK) 23rd June 1999, Accepted 12th July 1999

Palladium catalysts which showed premature deactivation under technical conditions were studied by means of inelastic incoherent neutron scattering (INS) spectroscopy revealing the cause of the poisoning to be a surface-bound methyl group.

During investigations on deactivation phenomena on catalysts from various industrial applications, macroscopic samples (many kilograms each) of spent palladium catalysts were isolated because of their peculiar behaviour. These catalysts were used for the partial hydrogenation of C=C structures in the ring systems of aromatic and polyaromatic molecules and for the hydrogenation of C=O groups to C–OH groups of functionalized aromatic and polyaromatic systems.† Conventional analytical methods for catalyst characterisation did not give any clear evidence for the presence of coke, inorganic contaminants or chemical poisons (carbon monoxide, sulfidic species) which are the most common causes of premature deactivation. Hydrogen absorption/desorption isotherms did not reveal anomalous properties or atypical hysteresis effects compared to literature data,[1,2] nor did electron microscopy studies show any unusual particle growth or sintering effects. When comparing the compositions of active and deactivated catalysts by elemental analysis, there was no correlation between the total amount of residual carbonaceous species and the catalytic activity. Surface spectroscopy by means of energy dispersive X-ray microanalysis, time-of-flight secondary ion mass spectrometry, and X-ray photoelectron spectroscopy did not result in the identification of any critical surface contamination involved. The signals of residual amounts of adsorbed solvent molecules were observed predominantly.

Vibrational spectroscopy has been extensively used for the characterisation of surface species on metal single crystal surfaces[3] and supported metal catalysts.[4] However, finely divided metal particles of catalysts absorb electromagnetic radiation from the infrared through the visible. As a result, Raman spectroscopy, using either visible or near-infrared excitation, and infrared spectroscopy were both unsuccessful. This problem could uniquely be circumvented by the use of inelastic neutron scattering spectroscopy. For neutrons the scattering is determined by the total scattering cross-section and the amplitude of vibration. For palladium the large mass (106.4 u) and small cross-section (4.48 barns, 1 barn $= 1 \times 10^{-28}$ m^2) mean that the palladium is largely transparent to neutrons. In contrast, the incoherent scattering cross-section for hydrogen is huge (79.90 barns) and together with its light mass (1.007 u) has the result that the scattering is dominated by hydrogenous motions.

The normalized INS spectra‡ of a deactivated catalyst before and after extraction with acetone (24 h, afterwards dried *in vacuo*) are shown in Fig. 1 together with the spectrum of the corresponding active catalyst after extraction with acetone under exactly the same conditions. In its original condition—as obtained from the technical application—the catalyst surface is still covered by a variety of adsorbed species consisting of polyaromatic molecules which are mainly residual amounts of solvent molecules [Fig. 1(a)]. After extraction, the broad background due to these solvent molecules or other adsorbed organic species is removed from the spectrum but a series of strong, sharp peaks remain [Fig. 1(b)] which are completely absent on the corresponding active catalyst [Fig. 1(c)]. Note that the same peaks are present in the "as-received" sample before clean-up.

The most striking feature of the spectrum is its simplicity: there are remarkably few bands. This implies either a highly symmetric structure with many degenerate modes or a small molecule. The intense 302 cm^{-1} feature suggested a methyl torsion, so a model consisting of a methyl group in an on-top site (see inset in Fig. 2) was used as the basis for a CLIMAX[5] analysis of the spectrum. The excellent fit shown in Fig. 2 was obtained. The quality of the fit is not dependent on the precise geometry of the model; small changes in bond angles or distances do not make any significant difference. The critical factors are the number of atoms and their spatial arrangement, thus a surface methylene group gives a different pattern. The only modification necessary was to increase the mass of the outer Pd atoms by a factor of 10 (*i.e.* to 1060 u) to mimic the

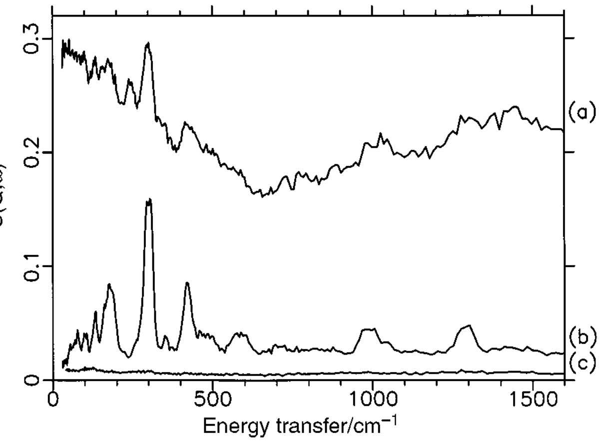

Fig. 1 INS spectra of palladium catalysts. Deactivated catalyst before (a) and after (b) extraction. Active catalyst after extraction (c).

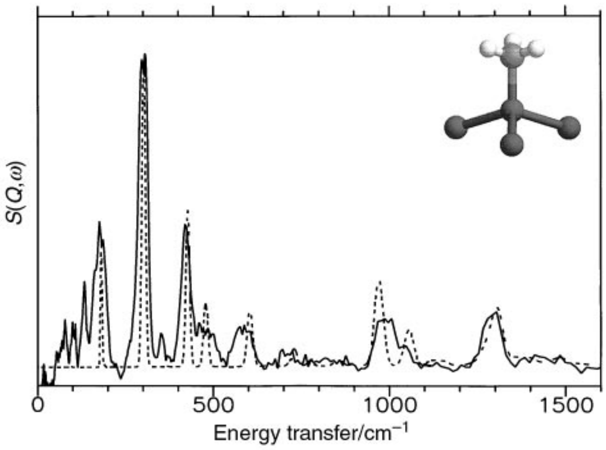

Fig. 2 Comparison of the INS spectrum of the deactivated catalyst (solid line) and the results from the CLIMAX analysis of the spectrum (dashed line).

Table 1 Observed bands (cm^{-1}) and assignments for MCH_3 in C_{3v} symmetry

Literature					
Typical[6]	$CH_3Mn(CO)_5$[7,8]	$CH_3Ni(111)$[9]	$CH_3Pt(111)$[10]	Present work	Assignment
				74w	Bulk Pd phonon
				100w	νPd–Pd (A_1)
				133w	Bulk Pd phonon
				179s	νPd–Pd (E)
				265sh	Bulk Pd phonon
				301vs	CH_3 torsion (A_2)
				353w	2 × νPd–Pd (E)
				420s	δPd–C (E)
400–700	420	370	520	484w	νM–CH_3 (A_1)
				580m	2 × CH_3 torsion (A_2)
				699w	CH_3 torsion (A_2) + δPd–C (E)
700–950	783		820	973m	CH_3 rock (E)
1100–1300	1184	1220	1180	1013sh	δCH_3 (A_1)
1350–1400	1420	1360	1410	1287m	δCH_3 (E)

ν = stretch, δ = bend, s = strong, m = medium, w = weak, v = very, br = broad, sh = shoulder

inertia of the catalyst surface. Only the band at 179 cm^{-1} was affected by this procedure. Table 1 lists all the observed bands and their assignments as well as some literature comparisons.[6–10] The assignments for the fundamentals are taken from the literature. It should be noted that the frequencies for the methyl vibrations differ significantly from those typical of organic molecules, this is well documented. The assignments for the overtones and combinations come from the CLIMAX fit. The assignment to surface bound methyl groups is also supported by a recent density functional calculation[11] that indicated CH_3 on Pd(111) was stable to dehydrogenation and preferentially adsorbed in the on-top site, as observed here. Additional computer simulation experiments on the spectral features of ethyl, methylidyne, methylene and ethylidyne groups revealed that the only fit with reasonable quality and chemically reasonable frequencies was obtained for a surface methyl group.

The sharpness of the peaks suggests that the methyl groups are bound to the topmost atomic layer of the catalyst and the intensities suggest that macroscopic amounts of CH_3–Pd species are present. Comparing the normalized intensities of the CH_3–Pd signals for several deactivated samples showed an excellent correlation of these intensities with the degree of catalyst deactivation. The large quantity of bound methyl groups presumably caused a modified surface polarity by their sp^3 centres inhibiting the adsorption of sp^2 type reactants on the catalyst surface and, therefore, significantly lowered the catalyst performance by a surface blocking effect. The CH_3–Pd species at the surfaces of the deactivated catalysts were observed to be quite stable in air and quite resistant to repeated solvent extraction or hydrogenation/dehydrogenation experiments under ambient conditions.

It seems remarkable that on the surfaces of finely divided, deactivated catalysts from large scale technical applications very well defined, simple molecular structures can reproducibly be found at a macroscopic scale which hitherto have only been detected in surface science experiments on metal single crystals. This example illustrates that the gap[12] between surface science and technical catalysis, which is considered to complicate the translation of results from experiments on low surface area materials at low pressures on the one hand into the field of applied catalysis on high surface area materials at ambient or high pressures on the other, may, in some cases, not be as large as is believed.

We would like to express our gratitude to the Rutherford Appleton Laboratory for access to the neutron beam facilities of ISIS. Degussa-Hüls AG is thanked for support of the measurements.

Notes and references

† The hydrogenation reactions were carried out in conventional gas/liquid reactor systems with suspended catalyst and internal recycle at temperatures between 60 °C and 90 °C, hydrogenation pressures between 1.5 and 3 bar. At reactant concentrations of 10–15% the degree of hydrogenation was adjusted to 60–70% yielding product concentrations of about 7–10% of hydrogenated products for further processing. The spent catalyst samples exhibited less than 10% of their regular hydrogenation activity. Usually they show excellent activity over extended times of use under varying conditions.

‡ 25 g samples of the palladium catalysts were put into thin walled aluminium cans which were evacuated to 10^{-6} mbar to remove volatile adsorbed species. INS spectra were recorded at 20 K using the INS spectrometer TFXA (Time Focused Crystal Analyzer) at the ISIS pulsed neutron scattering facility (Rutherford Appleton Laboratory, Chilton, UK).

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Communication 9/05034E