

DETERMINATION OF THE METAL PARTICLE SIZE OF SUPPORTED Pt, Rh, AND Ir CATALYSTS. A CALIBRATION OF HYDROGEN CHEMISORPTION BY EXAFS

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Abstract - Hydrogen chemisorption measurements of highly dispersed Pt, Rh, and Ir catalysts yielded H/M values exceeding unity. These results cannot be used straightforwardly to determine the average metal particle size, because the H/M stoichiometry on the surface is unknown. EXAFS measurements were performed to determine the metal particle size and thereby, to calibrate the hydrogen chemisorption results. The high hydrogen chemisorption values can be explained best by assuming H/M surface stoichiometries exceeding unity. The adsorption stoichiometry differs among Pt, Rh, and Ir in the order $H/Pt < H/Rh < H/Ir$, analogous to the order in stability of the corresponding metal polyhydride complexes.

I. INTRODUCTION

Hydrogen chemisorption is extensively used to estimate the dispersion of group VIII metal catalysts (1). In the calculations, often a hydrogen-to-metal stoichiometry of one is assumed. However, H/M_{total} values exceeding unity have been obtained for supported Pt, Rh, and Ir systems (2-8). In these cases the dispersions cannot be calculated straightforwardly, because of the uncertainty in the adsorption stoichiometry. Therefore we used the EXAFS (Extended X-ray Absorption Fine Structure) technique to determine the average metal-metal coordination number in the metal particles, which is related to the particle size.

II. EXPERIMENTAL

The catalysts were prepared from $RhCl_3$ and $IrCl_3$ via the incipient wetness technique (5,6,8), from $Pt(NH_3)_4(OH)_2$ and $Rh(NO_3)_3$ via the ionexchange technique (7,9), and from $IrCl_3$ via the urea method (8). $\gamma-Al_2O_3$ and SiO_2 were used as supports. Metal loadings were in the range of 0.5 - 7.0 wt%.

Volumetric hydrogen chemisorption measurements were performed in a conventional glass system at 298 K. After reduction and evacuation at the reduction temperature, hydrogen was admitted at 473 K ($p(H_2) = 93$ kPa). Desorption isotherms were measured at room temperature. The total amount of chemisorbed H atoms was obtained by extrapolating the linear high pressure part (20 kPa $< P < 80$ kPa) of the isotherm to zero pressure (1).

For the EXAFS measurements catalyst samples were pressed as thin self-supporting wafers. After in-situ reduction the samples were measured in H_2 at liquid nitrogen temperature. Rh and Pt measurements were performed on beamline I-5 at the Stanford Synchrotron Radiation Laboratory in Stanford, U. S. A. (3 GeV, 40 - 80 mA, Si(220) monochromator) at the Rh K-edge (23220 eV) and the Pt L_{III} -edge (11564 eV), respectively. Ir measurements were performed on Wiggler station 9.2 at the Synchrotron Radiation Source in Daresbury, U. K. (2 GeV, 80 - 250 mA, Si(220) monochromator) at the Ir L_{III} -edge (11215 eV).

The data were analyzed using reference compounds (10-12). In the case of the Rh catalysts, Rh foil and Rh_2O_3 were used. For the Pt and Ir data, Pt foil and $Na_2Pt(OH)_6$ were used. Both theoretically (13) and experimentally (14) the choice of Pt references for the analysis of Ir data can be justified. The results of the analysis of the Rh data have been published before (10-12), as well as the results for the Pt catalyst with $H/M_{total} = 1.14$ (7). The metal-metal coordination parameters of the Ir and other Pt catalysts were determined as follows. A k^3 Fourier transform ($\Delta k = 2.7 - 15 \text{ \AA}^{-1}$) was applied to the EXAFS data. In the resulting spectrum in R space, the peak representing the first M-M shell (but also including M-O_{support} contributions) was back transformed ($\Delta R = 1.9 - 3.5 \text{ \AA}$) to k space. In the resulting spectrum the M-O_{support} contributions are only significant below $k = 8 \text{ \AA}^{-1}$, because a low Z element like oxygen doesn't scatter very much at high k values. Therefore, the M-M coordination parameters were determined by fitting the data between $k \sim 8 - 13.5 \text{ \AA}^{-1}$, in such a way that a good agreement was obtained in k and in R space.

III. RESULTS

Details about the data analysis used for the Rh data, and the data for the Pt catalyst with $H/M_{total} = 1.14$ have been reported earlier (7,10-12). For the Ir and other Pt data the fit obtained for the first M-M shell in the EXAFS data was always good. As an example, in Fig. 1 the results are shown for the 4.2 wt% Pt/ Al_2O_3 sample with $H/M_{total} = 0.77$. In all samples first M-M coordination distances were found to contract less than 0.03 \AA , while Debye-Waller factors up to 0.004 \AA^2 larger were observed with respect to the reference foil. The average numbers of neighbour metal atoms N obtained from the EXAFS analysis are presented in Fig. 2.

Several supports and a variety of preparation methods were used. However, if any of these parameters has an effect on the hydrogen-to-metal stoichiometry, it can only be a minor one since the metal-metal coordination number versus H/M_{total} relationship can be described by a single straight line for each metal. Rather unexpectedly there is a large difference between the three metals. This difference is very marked and experimentally significant above $H/M_{total} = 1$, but still exists at lower H/M_{total} values. For a given particle size (equal M-M coordination number) the H/M_{total} values increase in the sequence $H/Pt < H/Rh < H/Ir$.

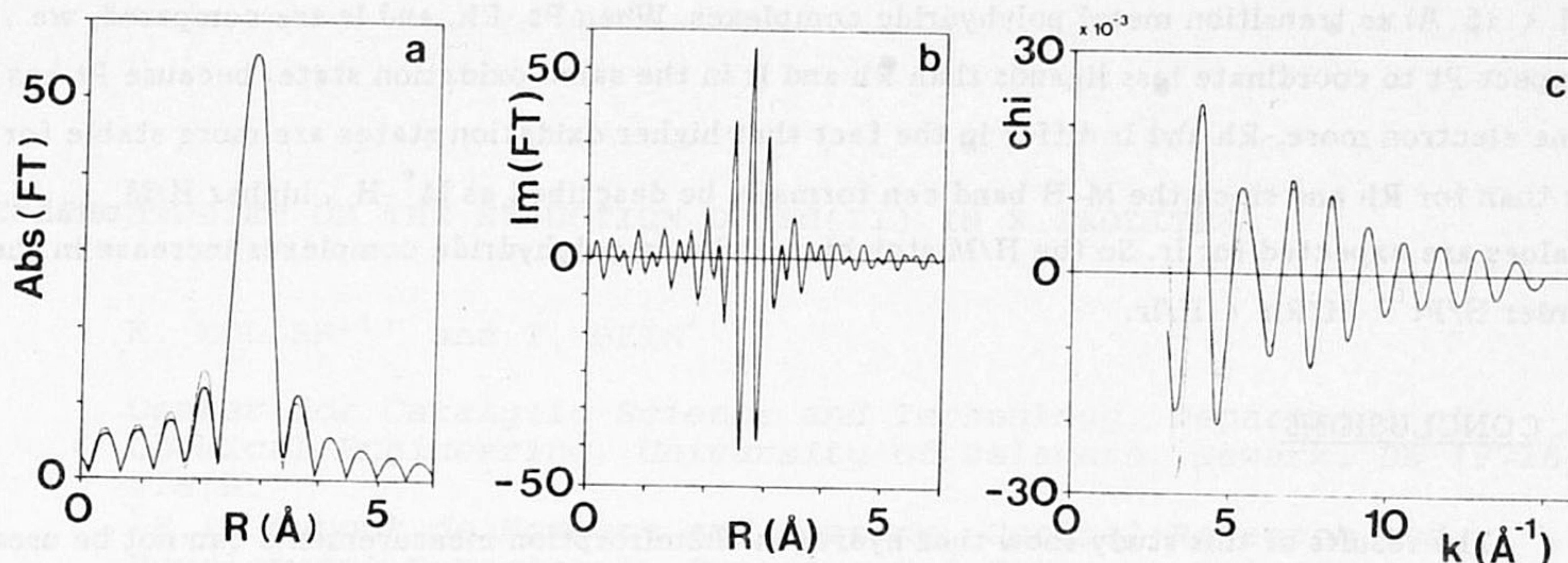


Fig. 1 - Example of the fit obtained for 4.2 wt% Pt/Al₂O₃ ($H/M_{\text{total}} = 0.77$): $N = 7.6$, $R = 2.75 \text{ \AA}$, $\Delta\sigma^2 = 0.004 \text{ \AA}^2$; (a) magnitude, (b) imaginary part in R space after k^3 Fourier transformation ($\Delta k = 7.9 - 13.8 \text{ \AA}^{-1}$, Pt-Pt phase and amplitude corrected), and (c) in k space; (—) back transformed shell, (...) spectrum calculated on the basis of the M-M fit parameters

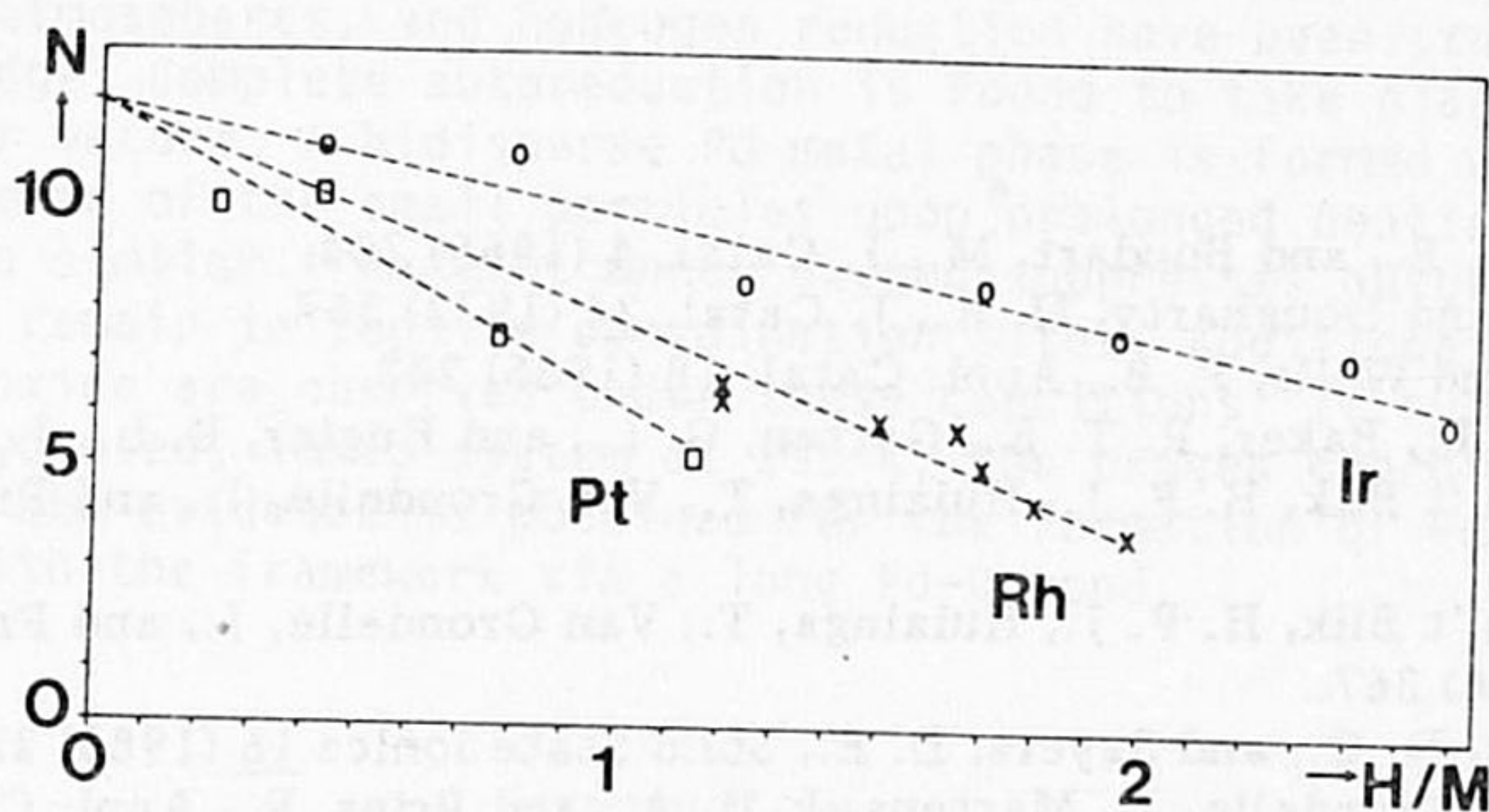


Fig. 2 - H/M_{total} versus coordination number N results for Pt (\square), Rh (\times), and Ir (\circ) catalysts

IV. DISCUSSION

Several explanations have been proposed for high H/M_{total} values. A common explanation is that part of the hydrogen is supposed to be adsorbed by the support through hydrogen spillover from the metal particles (15). Since in the case of spillover differences are expected between the supports used, and not between the metals used, spillover can not explain our observations. Our results have to be explained by an adsorption stoichiometry larger than one. Subsurface hydrogen (16) seems to provide an opportunity for high stoichiometries. However, subsurface adsorption can not explain H/M_{total} values higher than one either, because subsurface adsorption sites need subsurface metal atoms in order to exist. Therefore multiple adsorption on exposed metal atoms, especially at edge or corner positions (2,4), must be the main reason for the observed high H/M_{total} values. To explain the observed differences in adsorption stoichiometry for Pt, Rh, and Ir, we have considered the small metal particles

($d < 15 \text{ \AA}$) as transition metal polyhydride complexes. When Pt, Rh, and Ir are compared, we expect Pt to coordinate less ligands than Rh and Ir in the same oxidation state, because Pt has one electron more. Rh and Ir differ in the fact that higher oxidation states are more stable for Ir than for Rh and since the M-H band can formally be described as $M^+ - H^-$, higher H/M_{total} values are expected for Ir. So the H/M stoichiometries in polyhydride complexes increase in the order $H/Pt < H/Rh < H/Ir$.

V. CONCLUSIONS

The results of this study show that hydrogen chemisorption measurements can not be used directly to determine particle sizes in highly dispersed catalysts because the hydrogen-to-metal stoichiometry differs from unity. By means of the EXAFS technique the H/M_{total} values can be quantitatively related to the percentage of exposed metal atoms. The observed differences in adsorption stoichiometry for Pt, Rh, and Ir are analogous to the differences in stability of their polyhydride complexes.

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