Hydrodechlorination of 1,2-Dichloroethane over Differently Reduced Pd/SiO₂ Catalysts

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Samples of 5 wt.% Pd/SiO₂ catalyst reduced at moderate (400°C) and high temperature (600°C) were investigated in the reaction of 1,2-dichloroethane hydrodechlorination (HDC). The highly reduced catalyst exhibited a higher selectivity towards ethylene, approaching 70% at 300°C, whereas the catalyst reduced at 400°C gave mainly ethane ($S_{C_2H_6}$ ~90% at 300°C). Reduction of Pd/SiO₂ at 600°C leads to the formation of palladium silicide. In consequence, incorporation of Si in Pd surface lowers the hydrogenating strength of palladium, contributing to a higher ethylene selectivity. Such a behaviour resembles an analogous situation with Pd modified by Ag. It was shown that the catalysts deactivated rapidly at temperatures between 200 and 300°C. After reaction, much larger amounts of carbon were found in the sample reduced at 400°C. X-ray diffraction studies showed that a considerable part of this carbon was located in the bulk of palladium phase, *i.e.* forming a PdC_x solution.

Key words: 1,2-dichloroethane (DCE), hydrodechlorinaton (HDC), Pd/SiO₂ catalyst; palladium silicide, deactivation, ethylene selectivity, temperature programmed hydrogenation (TPH)

Spent chlorinated solvents (*e.g*. trichloroethane, methylene chloride, tetrachloroethylene) and waste streams from the manufacture of viable chemicals (*e.g*. from vinyl chloride production) often contain high concentrations of chloroalkanes and chlorinated olefins. Catalytic hydrodechlorination (HDC) is an environmentally and economically attractive route for the remediation of chlorinated wastes [1–11]. Its potential advantage compared to other pollution abatement methods (thermal incineration or catalytic oxidation) includes a minimal production of detrimental byproducts, such as dioxins, chlorine or phosgene. A major concern in development of catalytic hydrodechlorination is the rapid deactivation of catalyst (*e.g*. palladium or platinum-based) [8,10,11]. Therefore, search for more efficient and, especially stable HDC catalysts is desirable.

In this paper we examine silica-supported palladium catalysts, which were subjected to different reduction procedures. Highly reduced (at ≥ 450°C) Pd/SiO₂ undergoes transformation to palladium silicide [13–17], which would exhibit interesting

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properties in hydrodechlorination. It has been recently found that in the HDC of 1,2-dichloroethane the modification of Pd (or Pt) by addition of a group IB metal, such as Cu [3,4] or Ag [5–7] has a strong positive effect on the selectivity towards ethylene (desired product). It was thought that incorporation of silicon into palladium surface (realized by high temperature reduction) would also lead to similar positive variations.

EXPERIMENTAL

The 5 wt.% Pd/SiO$_2$ catalyst was prepared by incipient wetness impregnation of silica (Davison Grade 62, 340 m^2/g, pore volume 1.15 cm^3/g, 75–120 mesh, acid washed and dried) with an aqueous solution of PdCl$_2$ (analytical reagent from POCh Gliwice, Poland). After impregnation the material was dried overnight at 120°C. Next, this catalyst precursor was precalcined in flowing air at 700°C for 4 h.

The catalytic conversion of 1,2-dichloroethane (HPLC grade, 99.8% pure from Sigma-Aldrich, Germany) was performed in a flow glass reactor at atmospheric pressure. The flows of all gases, except 1,2-dichloroethane (DCE), were fixed by using Bronkhorst Hi-Tec mass flow controllers. After reduction, the catalysts were contacted with the reaction mixture, *i.e.* with a flow of hydrogen + argon at 41.2 cm^3/min and 1,2-dichloroethane, provided from a saturator kept at 0°C (to give the partial pressure of 1,2-dichloroethane of 2.9 kPa). The partial pressure ratio P$_{H_2}$/P$_{DCE}$ was 1:1. The mass of catalysts used was ~200 mg, to keep the conversion level (at steady state) below 10%. Prior to the reaction, the catalysts were subjected to reduction at different temperatures. One portion of 5 wt.% Pd/SiO$_2$ was reduced at 400°C in a flow of Ar (22.5 cm^3/min) and H$_2$ (2.5 cm^3/min), ramping the temperature (at 8°C/min) from 20 to 400°C and kept at 400°C for 3 h. Alternatively, more drastically pretreated catalysts were reduced at 600°C for 17 h at high flow reducing mixture (39 cm^3/min of H$_2$ and 100 cm^3/min of Ar). After reduction, the catalysts were cooled to the lowest temperature of reaction, *i.e.* 200°C. The reaction protocol was similar as in [5], *i.e.* after a short catalyst's screening at 200°C, the reaction temperature was successively adjusted at 230, 250 and 300°C. The reaction was followed by gas chromatography (HP 5890 series II with FID, a 5% Fluorcol/Carbopack B column (10 ft) from Supelco). The results of GC analysis were elaborated using HP Chemstation. In all kinetic runs, the activities of most catalysts declined with time-on-stream. A typical run lasted ~24 hours. Blank experiments with silica showed negligible activity in the temperature range used for screening Pd/SiO$_2$ catalysts, *i.e.* ≤300°C. Samples of Pd/SiO$_2$ catalyst after reaction were investigated by temperature programmed hydrogenation (TPH), using a mass spectrometer (M200 from Dycor-Ametek, Pittsburgh, PA) for identification of gaseous species liberated during the TPH run. To this aim, a silica-fused U-tube reactor was loaded with a spent catalyst sample and mounted in a specially designed glass flow system. During TPH runs (in a flow of 10% H$_2$/He mixture, 25 cm^3/min) the temperature of catalyst was ramped at 10°C/min. Special attention was focused at evolution of three masses: m/z = 15, m/z = 36 and m/z = 2. The first mass was showing the quantity of deposited carbon, removable as methane during TPH. The second mass revealed HCl liberation, while monitoring the third mass served as indication of palladium hydride decomposition.

The X-ray diffraction (XRD) patterns of the samples were obtained with a standard Rigaku-Denki diffractometer, using a standard Ni-filtered CuK$_\alpha$ radiation source. Differently reduced samples of 5 wt.% Pd/SiO$_2$ catalyst were scanned by a step-by-step scanning technique at 2Θ intervals of 0.05° and a recording time of 10 s for each step. Obtained XRD patterns served for phase identification in catalysts subjected to reaction and subsequent carbon removal by TPH. In addition, for differently pretreated samples, the crystallite size was calculated with the Scherrer equation using the (111) and (200) reflections. For the catalyst reduced at 400°C, the particle size of Pd was ~14 nm. Reduction at 600°C only slightly increased the crystallite size, up to ~17 nm.

RESULTS AND DISCUSSION

All results of this work are presented graphically in Figures 1–6. The first two figures concern catalytic behaviour of differently reduced 5 wt.% Pd/SiO_2 in hydrodechlorination of 1,2-dichloroethane. Because identical catalyst weights were used in each case, one can directly compare the catalytic activity (per g_{Pd}) of different samples.

Fig. 1 shows the time-on-stream behaviour of the 5 wt.% Pd/SiO_2, which has been subjected to reduction at 400°C. It is seen that a serious deactivation proceeds at each temperature. The most serious activity decline was observed at 300°C, which was the highest temperature of screening. Ethane was the dominant product, its selectivity was 80–90%, depending on temperature. Ethylene (desired product) and ethyl chloride were minor products at selectivities below 10%. Such a catalytic behaviour (serious deactivation, low ethylene selectivity) of Pd/SiO_2 is consistent with earlier reports [5].

Fig. 2 presents the corresponding catalytic data for the 5 wt.% Pd/SiO_2 prereduced at 600°C. A severe catalyst deactivation is also seen in this case. However, now we observe a remarkable increase of ethylene selectivity at 300°C. During 1000 min, the selectivity for ethylene increases from < 20 to ~70%, while ethane constitutes
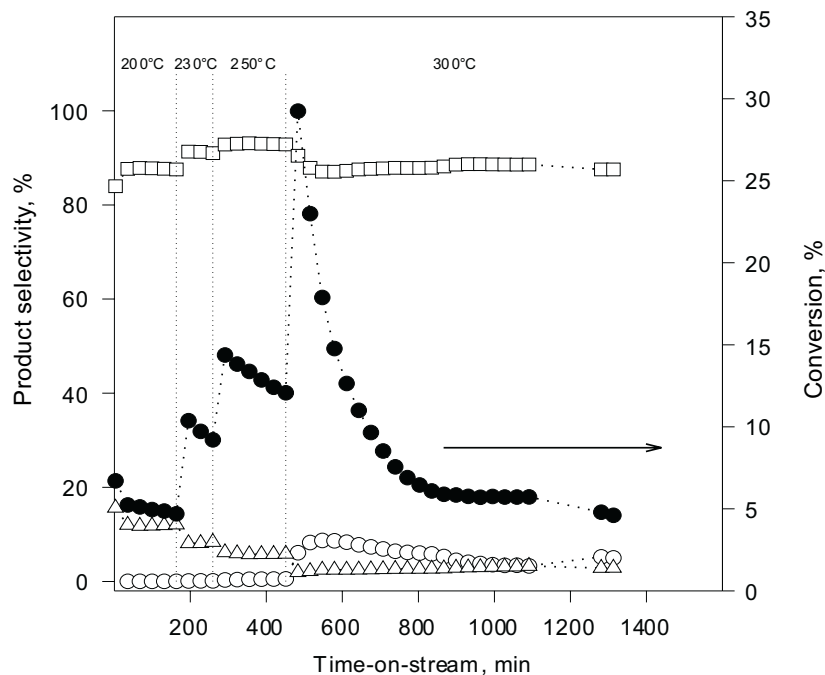

Figure 1. Time-on-stream behaviour of 5 wt.% Pd/SiO_2 catalyst reduced at 400°C in hydrodechlorination of 1,2-dichloroethane at 200, 230, 250 and 300°C. Product selectivities to: ethylene (white circles), ethane (squares) and ethyl chloride (triangles). Overall conversion – black circles.
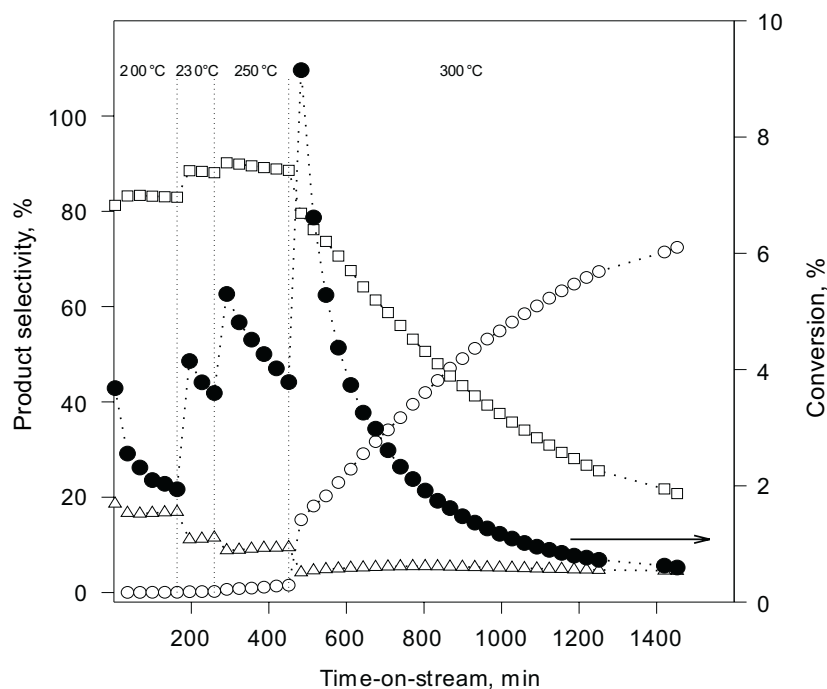
Figure 2. Time-on-stream behaviour of 5 wt.% Pd/SiO$_2$ catalyst reduced at 600°C in hydrodechlori-
nation of 1,2-dichloroethane at 200, 230, 250 and 300°C. Product selectivities to: ethylene
(white circles), ethane (squares) and ethyl chloride (triangles). Overall conversion – black cir-
cles).

~25% of products. The difference in the catalytic behaviour of Pd/SiO$_2$ reduced at
400 and 600°C is explained in terms of great morphological changes generated by
high temperature reduction at 600°C. Indeed, reduction of silica-supported palladium
in hydrogen at 500–600°C leads to a catalyst transformation to palladium silicide
[13,14], with a considerable effect on the behaviour in several reactions [15–17]. Ap-
parently, also in the case of HDC of 1,2-dichloroethane incorporation of silicon in
palladium surface induces large changes in the catalytic performance. We assume
that the disruption of the contiguity of palladium atoms by added silicon must lead to
a weaker bonding of dechlorinated hydrocarbon species, *i.e.* of ethylene, which de-
sorbs to the gas phase before being hydrogenated to ethane. In this way, the rate of
side reaction leading to ethane is suppressed. Similar results were obtained by Hein-
richs *et al.* [5–7] in their study of Pd-Ag/SiO$_2$ catalysts in HDC of 1,2-dichloroetha-
ne. Apparently, dilution of palladium surface species by Si and Ag has similar
catalytic consequencies. As in the case of Pd-Ag/SiO$_2$, the overall activity of mono-
metallic Pd/SiO$_2$ is higher than that of Si-modified catalyst (compare Fig. 2 with Fig. 1).

Characterisation of the Pd/SiO$_2$ catalysts comprised the samples after reaction.
Two problems were addressed.

First, it seemed important to check if the presence of palladium silicide in highly
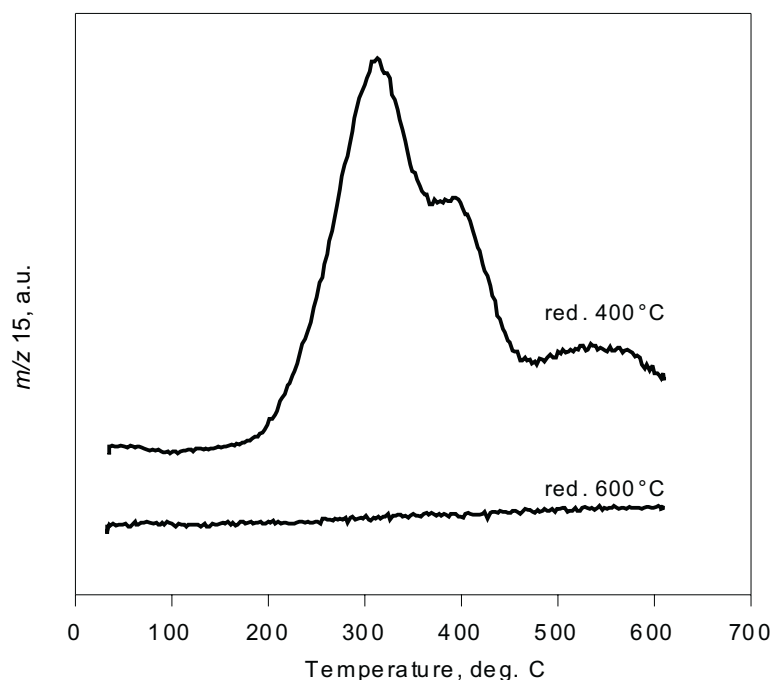reduced Pd/SiO$_2$ catalyst is preserved in the entire catalytic run. One can suspect that

Figure 3. Evolution of m/z 15 (methane liberation) during TPH runs on spent Pd/SiO$_2$ catalysts reduced at 400 (upper trace) and 600°C (lower trace).

Pd$_4$Si and/or Pd$_3$Si species unambiguously formed in effect of reduction of Pd/SiO$_2$ catalysts at 500–600°C [15,16], would be decomposed during hydrodechlorination by HCl, which is an unavoidable reaction product. In spite of this, the XRD study of the highly reduced Pd/SiO$_2$ catalyst after reaction shows a distinct presence of Pd$_4$Si in it (Fig. 6).

Second, it was also interesting to look into the source of the rapid deactivation of Pd/SiO$_2$ catalysts, the main hindrance which makes the commercialization of HDC difficult. Earlier studies suggest that deposited coke (not HCl) is the principal cause of deactivation [11]. The temperature programmed hydrogenation (TPH) runs confirmed the previous speculations. Only very small amounts of HCl (as m/z = 36) were liberated from the spent catalysts (spectra not shown). On the other hand, Fig. 3 shows large amounts of liberated methane, which is a measure of deposited carbon in catalysts after reaction. However, this carbon is well detected only in the Pd/SiO$_2$ catalyst, which was subjected to reduction at 400°C. The spent Pd/SiO$_2$ reduced at 600°C shows negligible amounts of carbon, compared to the previous sample (Fig. 3). This significant difference in the behaviour of both samples is understandable after inspecting the XRD spectra (Fig. 5 and 6). Fig. 5 shows the presence of PdC$_x$ solution in the sample of spent 5 wt.% Pd/SiO$_2$ catalyst prereduced at 400°C. The carbon in palladium necessarily originates from DCE molecule and is being entirely removed during TPH (as shown by the upper XRD profile in Fig. 5). Therefore, huge amounts of liberated methane during TPH reflect a high content of carbon in the Pd phase. Similar
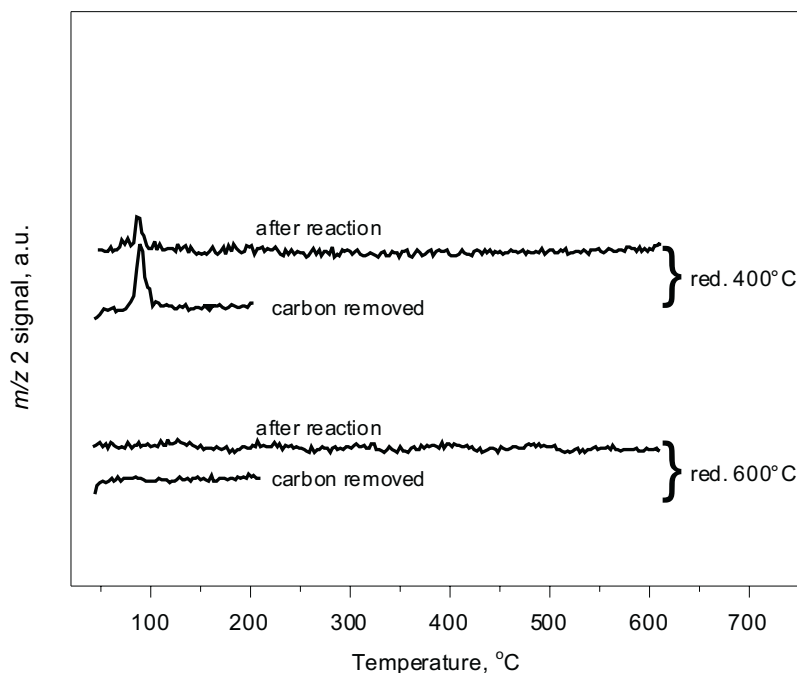
Figure 4. Evolution of m/z 2 (hydrogen liberation) during TPH runs on spent Pd/SiO$_2$ catalysts reduced at 400 and 600°C. Profiles after reaction (first TPH runs) and after carbon removal (second TPH runs).

dissolution of carbon in palladium catalysts was found by us in CCl_2F_2 hydrodechlorination [18,19]. On the other hand, a silicon-containing palladium phase (in highly reduced catalyst) does not practically dissolve much carbon, in line with our recent data [16]. Therefore, deactivation of this sample is only associated with surface deposition of coke.

Fig. 4 shows the evolution of mass m/z = 2. Hydrogen liberation seen as small maxima at ~90°C points to palladium hydride decomposition only from the spent sample of Pd/SiO$_2$ prereduced at 400°C (upper traces). However, smaller quantities of hydrogen enter the palladium phase of spent catalyst, compared to the situation after removing all carbon. The presence of carbon, as well as silicon in palladium, suppresses the bulk hydride formation. Palladium silicide does not form hydrides at the conditions of TPH runs (lower traces), in line with [20].

CONCLUSIONS

The highly reduced (at 600°C) 5 wt.% Pd/SiO$_2$ catalyst shows interesting properties in hydrodechlorination of 1,2-dichloroethane. The selectivity towards ethylene, which is the desired product, is close to 70% at 300°C, whereas the same catalyst prereduced at 400°C gives mainly ethane (~90% at 300°C). This great difference in catalytic behaviour is related to the different state of catalyst surface in both samples.
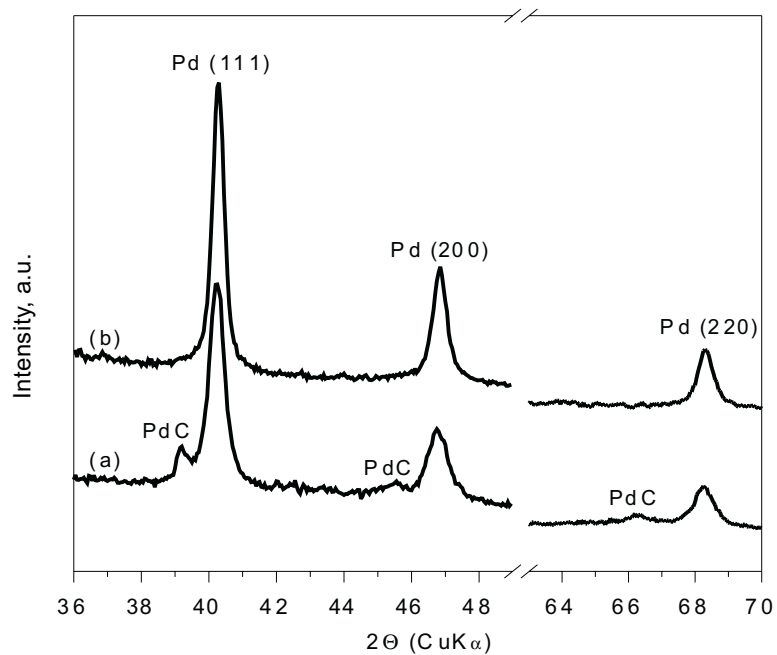
Figure 5. X-ray diffraction profiles of 5 wt.% Pd/SiO$_2$ reduced at 400°C: (a) after reaction, (b) after TPH of used catalyst.
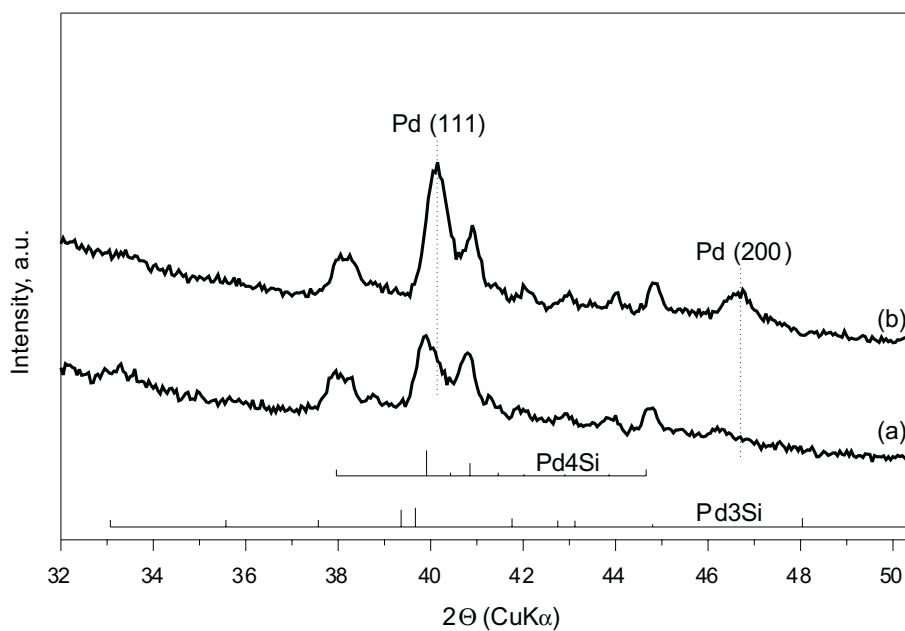

Figure 6. X-ray diffraction profiles of 5 wt.% Pd/SiO$_2$ reduced at 600°C: (a) after reaction, (b) after TPH of used catalyst.

Reduction of Pd/SiO_2 at 600°C leads to the formation of palladium silicide. It is assumed that incorporation of silicon decreases the hydrogenating strength of nearby palladium species, contributing to a higher ethylene selectivity. Serious deactivation of Pd/SiO_2 catalysts is caused by deposition of considerable amounts of coke. Furthermore, the sample reduced at 400℃, in contrast to the sample reduced at 600℃, accumulates larger amounts of carbon dissolved in bulk of the Pd phase.

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