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The effect of water on the performance of TiO_2 in photocatalytic selective alkane oxidation

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ABSTRACT

Deactivation of TiO_2 is hampering practical implementation of photocatalytic alternatives for energetically intensive selective oxidation processes. In the present study, humidification of the air stream is demonstrated to be a solution to this problem for well-defined photocatalysts, such as Solaronix TiO_2, in selective oxidation of cyclohexane. Water establishes enhanced product desorption and stimulates decomposition of deactivating surface carboxylate species, as clearly demonstrated by ATR-FTIR spectroscopy. For high surface area TiO_2, such as Hombikat UV100, water molecules adsorb too strongly, and addition of water vapor to the air stream is detrimental to catalyst performance.

1. Introduction

Photocatalysis studies focus mainly on environmental and solar energy-related applications [1–7]. Relatively few studies discuss the application of photocatalysis for selective oxidation. Although product yields are only in the micro- to milli-molar level, the possibility to operate under mild conditions and the high selectivities that can be achieved are quite attractive [8–11]. For example, a high selectivity in photocatalytic cyclohexane oxidation was first reported by Giannotti et al. [12]. To increase the low conversion levels, different solvents, oxygen pressures, modes of light activation (i.e. wavelength and intensity), and catalyst modifications were used [13–23].

A major issue that has not been very well addressed, and has frustrated practical application of photo-activated TiO_2 in selective oxidation, is catalyst deactivation. The formation of surface-bound carbonates and carboxylates by consecutive oxidation of surface adsorbed products is likely the cause of this catalyst deactivation [18]. We have followed various strategies to stimulate desorption of the product of cyclohexane oxidation, i.e. cyclohexanone, including surface modification of TiO_2 by surface silylation, and optimization of the crystal structure and morphology [24–26]. At the same time, particle size and crystal structure have a significant influence on photoefficiency. In particular, we observed that upon increasing the crystallite size, productivity (g^{-1} catalyst) decreases, while (i) the TOF (moles of cyclohexanone formed per minute per OH-site), (ii) the rate of cyclohexanone desorption, (iii) catalytic site stability, and (iv) the cyclohexanol/cyclohexanone ratio increase. While catalyst performance and regenerability have been improved by these strategies, further improvement in process operation is needed, in particular when one aims for a continuous process.

Several reports on photocatalytic air cleaning technology mention an effect of humidity on photocatalytic activity. In commercial applications of photocatalysis, this is an important issue since most contaminated air streams are also partially (1–2% water vapor) humidified. The influence of 10,000–20,000 ppm water is dependent on the nature of the contaminant [26]. The presence of water is reported to enhance toluene and benzene conversion rates over TiO_2, explained by an increase in concentration of OH-radicals, which induce the decomposition to CO_2 and H_2O [27–29]. Negative effects of water have also been reported, e.g. in the case of acetone oxidation, explained by inhibition of reactant adsorption on the catalyst surface [30]. Overall, optimization of the water concentration appears necessary to optimize photocatalytic activity in these applications [31,32].

To the best of our knowledge, the effect of adding water to the oxygen (air) feed on catalyst performance in photocatalytic selective oxidation has not been previously addressed and is the topic of the study described herein. Particularly, we focus on humidification of air to lower the rate of deactivation of two commercially available catalysts, Hombikat UV100 (H) and the Solaronix T-series, pretreated at 450 °C (S450). These catalysts were chosen, since these allow the comparison of a rather amorphous high surface area anatase TiO_2 (Hombikat), to a better defined

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crystalline anatase catalyst (Solaronix) [34]. Besides comparison of performance in a slurry reactor, the surface chemistry of the catalysts was also evaluated in dry and humidified conditions, making use of *in-situ* ATR-FTIR spectroscopy. Again cyclohexane oxidation was chosen as the model reaction to evaluate selective photocatalysis in a broader context, since (i) the reaction is highly selective (e.g. alkenes give a range of products), (ii) the reaction is easy to handle in the lab (e.g. benzene derivates are highly carcinogenic and require special precautions), (iii) products are relatively easily analytically identified (in particular by ATR spectroscopy), and (iv) the reaction is of industrial relevance.

2. Experimental

Hombikat UV100 was obtained from Sachtleben™ (H). A TiO_2 paste used for solar cell applications, i.e. Ti nanoxide T-series, was purchased from Solaronix™ in a suspension in butanol [33], and calcined for 15 min at 450 °C with a high heating rate of 10 K min^{-1}, before use. After calcination of the paste, the crystals obtained are well defined with truncated faces with polygonal shapes and particle sizes of ~20 nm [34]. We will refer to this catalyst as S450 throughout this paper.

To evaluate catalyst performance in the selective oxidation of cyclohexane, reactions were carried out in a top illuminated slurry reactor (TIR). In a typical experiment, 100 mL of cyclohexane containing 1 g L^{-1} of catalyst was used. The catalysts were dried for 1 h at 120 °C to remove adsorbed water and impurities. The solution was illuminated from the top of the reactor through a Pyrex window that cuts off highly energetic UV radiation [19]. A high pressure mercury lamp of 50 W was used (HBO50 W from ZEISS). The light intensity of the lamp used in the wavelength absorption range of TiO_2 (275–388 nm) is 55 mW cm^{-2}, which corresponds to 2×10^{-7} Einstein cm^{-2} s^{-1}. This value was obtained by using the following equation:

$$I'' = \frac{E\lambda}{chN_A}$$

where I'' is the photon flux (Einst m^{-2} s^{-1}), E the radiant flux (W m^{-2}), λ the wavelength (m), c the speed of light (3.0×10^8 m s^{-1}), h Planck's constant (6.63×10^{-34} J s), and N_A Avogadro's number (6.02×10^{23} mol^{-1}).

Air presaturated with cyclohexane, dried over Molsieve 3 Å, (Acros Organics), was bubbled through the TiO_2 suspension at a rate of 30 mL min^{-1}. The same experiments were conducted with air presaturated with water (~4% STP conditions). During the reactions, liquid was withdrawn and analyzed by GC [34]. The performance was also evaluated with an ATR-FTIR *in situ* system, reported previously [33,34]. An approximately 1-μm-thick coating on a Ge crystal was applied for the analysis. A volume of 50 mL of cyclohexane (99.0% from J.T. Baker) was used. A spectrum of adsorbed cyclohexane on TiO_2 was collected as background for the photo-oxidation experiments. A mirror velocity of 0.6329 cm s^{-1} and a resolution of 4 cm^{-1} were used for all measurements. UV-induced oxidation of cyclohexane was initiated and continued for 5 h, taking a spectrum every minute. The same experiments were performed using humid air (~4% STP conditions) achieved by passing the air through a water saturator before bubbling through cyclohexane. The light was provided by an assembly of 7 UV LEDs (Roithner Lasertechnik) placed on the top of the cell, emitting 375 nm light with an incident photon flux of 9×10^{-9} Einstein cm^{-2} s^{-1} at the surface of the catalyst coating. The background and the sample spectra were averaged from 64 and 32 spectra, respectively.

3. Results and discussion

Fig. 1 shows the changes in performance in a slurry type reactor when water is added to the air feed. In the case of H, Fig. 1a, adding water decreases the initial rate of cyclohexanone formation as well as the total production, whereas cyclohexanol production increases slightly. In the case of S450, Fig. 1b, adding water does not change the initial rate of cyclohexanone formation but increases the final amount of cyclohexanone produced. The photonic efficiencies of Hombikat and Solaronix were quite similar and calculated in dry conditions to be in the order of 0.5%.

Furthermore, cyclohexanol formation is found to also increase when water is present in the feed, although this remains a minor product. The different behavior of the two TiO_2 samples is striking and can be explained as follows. First, agglomeration of H particles, i.e. deterioration of the slurry suspension, is visually observed, whereas S450 remained nicely suspended after the air feed was humidified. The agglomeration behavior of TiO_2 particles is very likely a strong function of the OH-group population and associated surface-bound water. Quantities of these surface groups vary significantly for different TiO_2 samples, as we have demonstrated recently by DRIFT spectroscopy and NH_3 TPD analyses. A decreasing surface water content and higher specificity for particular OH-groups are apparent for better defined and relatively larger TiO_2 crystals [24]. Besides these surface properties, the potential of the catalyst to convert surface adsorbed water and hydroxyl groups in hydroxyl radicals is also affected by particle morphology. The latter is related to the hole availability [24]. The surface hole concentration is known to be significantly larger for S450 than for H [34], and hence for S450, there is an efficient turnover of OH-groups adsorbed on the catalyst surface. In the case of H, this turnover is not as efficient [24], and adsorbed water accumulates on the outer surface of the catalyst particles, leading to agglomeration. The differences in catalyst behavior upon air humidification

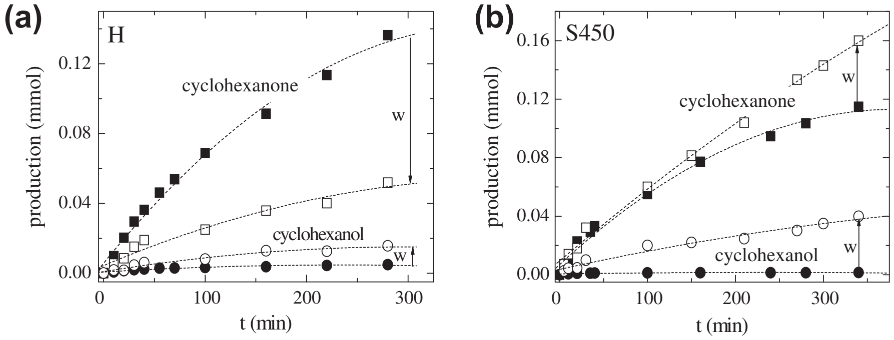

Fig. 1. Production of cyclohexanone and cyclohexanol in the slurry reactor using dry and humid (denoted by *w*) air for (a) Hombicat UV 1000 (H) and (b) Solaronix T (S450) as catalyst.

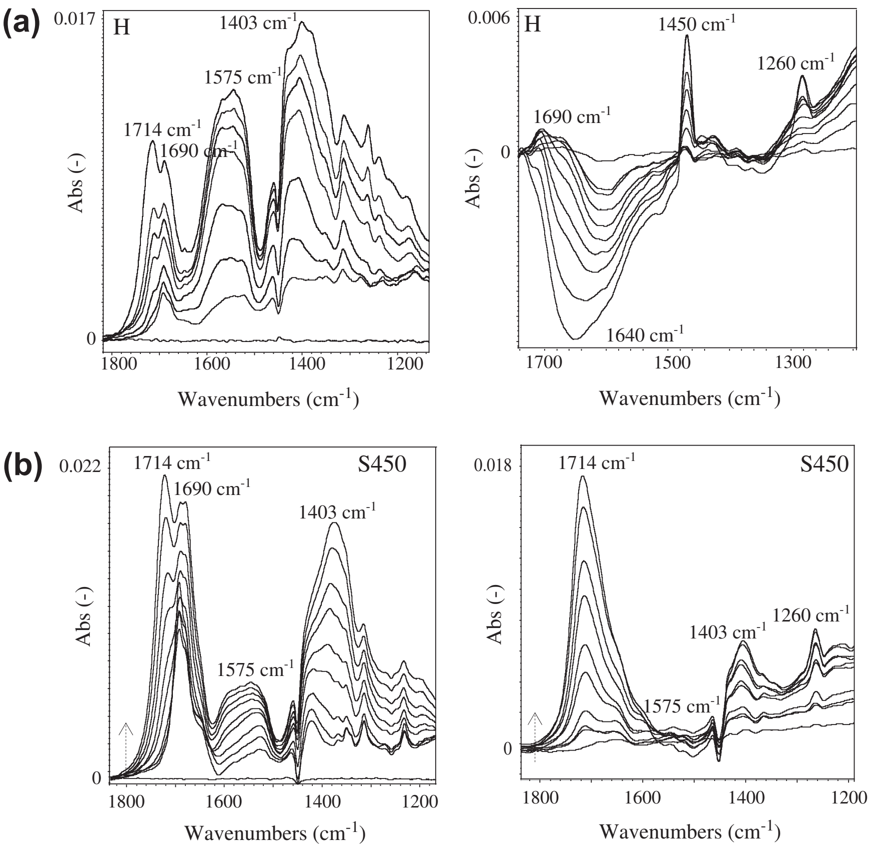

Fig. 2. ATR-FTIR spectra of cyclohexane photocatalytic oxidation on (a) H and (b) S450 coated on a Ge crystal. Spectra recorded at different reaction times until 240 min. The pictures in the left correspond to the reaction using dry air and in the right using humid air (~4% humidity, NPT).

are confirmed by the *in situ* ATR-FTIR data presented in Fig. 2. The spectral development for H using dry air, Fig. 2a left, is in agreement with that reported previously [24]. A broad range of infrared absorptions develops in time, consisting of several overlapping bands. The formation of cyclohexanone can be identified by the band at 1714 cm^{-1} corresponding to the C=O stretching vibration of bulk cyclohexanone (i.e. dissolved in cyclohexane) and a shouldered band at 1690 cm^{-1}, assigned to the C=O stretching vibration of the corresponding adsorbed cyclohexanone [24]. It is our assumption that the formation of cyclohexanone essentially occurs on the surface of the TiO_2 rather than in solution, which would imply that observed intensities in ATR spectra of surface adsorbed species are simply the result of the efficiency of polar product adsorption. In a previous study [18], we have clearly demonstrated that at the wavelengths applied here (above 350 nm) the presence of TiO_2 is essential for the selective formation of cyclohexanone, whereas photochemistry induced by exposing cyclohexane/oxygen mixtures to wavelengths below 300 nm will lead to radical chemistry and cyclohexanol as a significant product [18]. Furthermore, studies on the formation of hydroxyl radicals on metal oxide surfaces clearly show that desorption of these radicals into an organic solvent is highly unlikely and that the very high selectivity obtained is the result of surface reactions [35,36]. We have evidence from recent infrared studies using a reference mixture supplied by DSM that cyclohexylhydroperoxide is formed on the catalyst surface. We are currently establishing if this is truly an intermediate for cyclohexanone formation, or mainly a spectator species and/or precursor of the formation of carboxylates and carbonates.

The band at 1575 cm^{-1} is assigned to C=O stretching vibrations of adsorbed carboxylates [37,38], and adsorbed carbonates give rise to the broad feature centered at 1403 cm^{-1} [38,39]. The carboxylates are likely a mixture of species ranging from C_1 to C_6 (hexanoate to formate), which in view of the multitude of overlapping absorption bands can unfortunately not be resolved. When humid air was used, Fig. 2a right, the product distribution at the catalyst surface changed completely. In the early stages of the reaction, cyclohexanone can be detected at the catalyst surface, but the band intensity is very small. A band corresponding to physisorbed water, at 1640 cm^{-1}, decreases with reaction time, while bands assigned to carboxylates and carbonates are absent. The 1450 cm^{-1} and 1260 cm^{-1} bands are assigned to the CH_2 bending vibrations of (adsorbing) cyclohexane. Fig. 2b, left, shows that the relative intensity growth of cyclohexanone over carboxylates is higher for S450 when compared to H, indicating that S450 is more selective toward the ketone.

Comparing Fig. 2b right with the S450 spectra recorded in dry air, Fig. 2b left, carboxylate formation is absent, and only a small contribution of a carbonate band at 1403 cm^{-1} is apparent. Furthermore, the amount of bulk cyclohexanone compared to adsorbed is significantly higher in the case of using humid air. In order to visualize the development of the quantities of dissolved and adsorbed cyclohexanone better, peak deconvolution was applied. For the profiles obtained with dry air, Fig. 3a, a fast increase of the amount of adsorbed cyclohexanone is accompanied by a much smaller rate of formation of bulk cyclohexanone. Regarding the profiles obtained with humid air, Fig. 3b, in the beginning of the reaction (until 5 min), the rate of formation of adsorbed cyclohexanone is suppressed, whereas the rate of bulk cyclohexanone formation is enhanced. The rate of formation of bulk cyclohexanone increases continuously, whereas adsorbed cyclohexanone reaches a *plateau* after 20 min.

From the ATR-FTIR spectra, it is clearly visible that water prevents the surface reaction in the case of H: almost no cyclohexanone formation was detected, Fig. 2a. The negative band observed

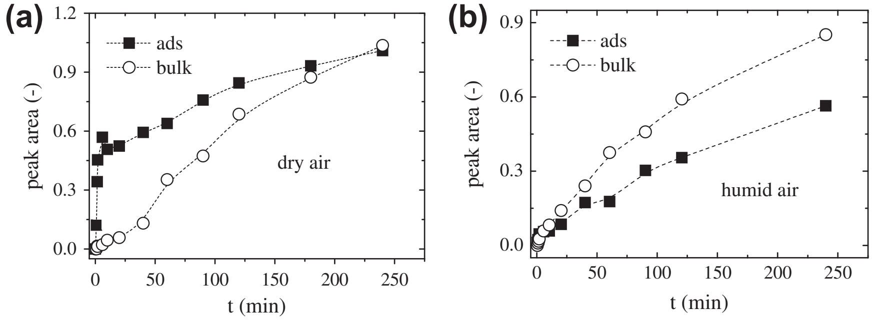

Fig. 3. Bulk (1714 cm^{-1}) and adsorbed (1690 cm^{-1}) cyclohexanone formation time profiles obtained from peak deconvolution until 240 min using (a) dry air and (b) humid air on S450.

at 1640 cm^{-1} corresponds to water displacement from the catalyst surface, in agreement with growing quantities of adsorbed cyclohexane. The role of water during reaction at the surface of S450 is completely different and extraordinary. When water is present, Fig. 2b right, there is (i) no formation of carboxylates, (ii) the formation of carbonates is much lower, and (iii) cyclohexanone desorption is enhanced, visualized in Fig. 3b.

With the objective of analyzing the effect of water on the desorption rate of surface adsorbed products, the following experiment was conducted with S450. First, the catalyst was exposed to 10 min of reaction in dry air, Fig. 4a, followed by exposure of the deactivated catalyst to humid air for 90 min in the dark, Fig. 4b, and finally to humid air for 90 min under light illumination, Fig. 4c. Results show that after 10 min, bulk (1714 cm^{-1}) and adsorbed (1690 cm^{-1}) cyclohexanone are already formed at the catalyst surface, as well as carboxylate and carbonate species. When exposing the catalyst to humid air in the dark, the adsorbed cyclohexanone disappears from the surface (relatively small band at 1690 cm^{-1}) and water (1640 cm^{-1}) starts to accumulate. The carbonate and carboxylate species are not removed. When the light is switched on, the reaction starts with the formation of adsorbed and bulk cyclohexanone, while carboxylate intensities decrease, suggesting consecutive oxidation to CO_2 and H_2O. Carboxylates might undergo decarboxylation via the photo-Kolbe reaction as indicated by Bard and coworker [40]. Clearly the properties of S450 are much more favorable than of H to allow a high stability in the reaction. The fact that cyclohexanone displacement by water is fast suggests that the surface of S450 is more hydrophilic than of H. The water-induced desorption of cyclohexanone limits consecutive oxidation to deactivating species. At the same time, the

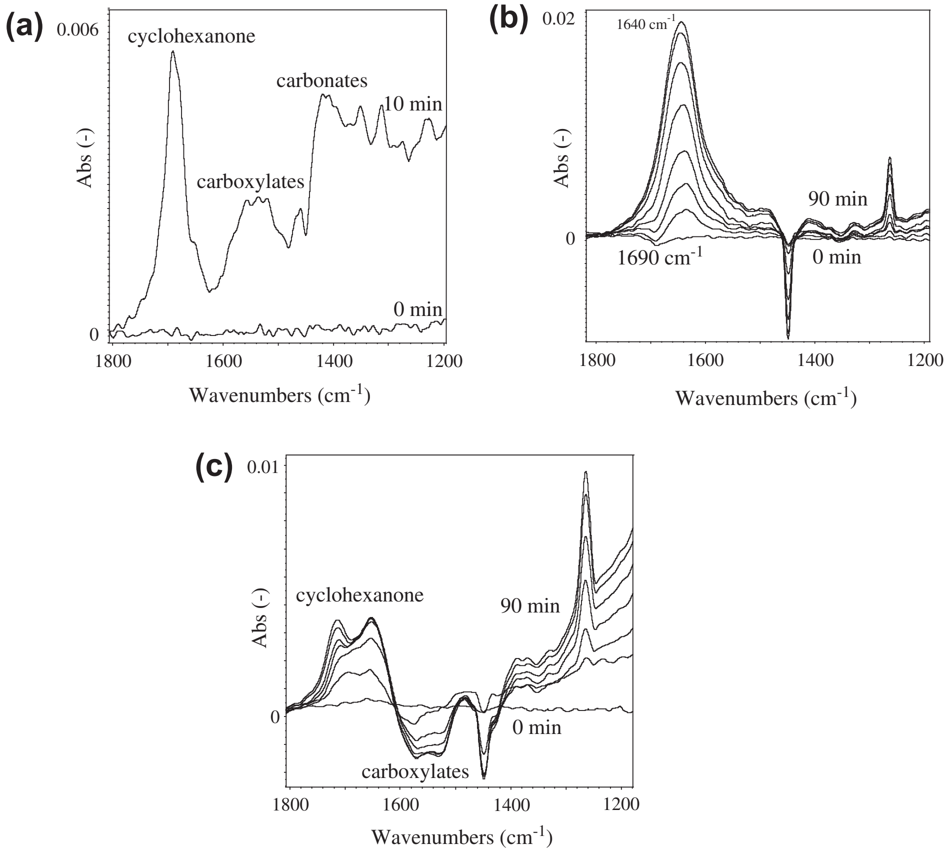

Fig. 4. Effect of the presence of water in the feed on the desorption rate of cyclohexanone for S450. ATR-FTIR spectra were recorded: (a) 10 min under reaction conditions with dry air, (b) 90 min in the dark with humid air, and (c) 90 min under reaction conditions with humid air.

previously mentioned opto-electronic properties are such that if formed carboxylates oxidize (to CO_2), regenerating active OH-sites. It is already known for gas-phase processes that the surface hydroxyl groups consumed in the photoreaction are regenerated in the presence of humidified air [27,28,41–43], which leads to a stable catalytic cycle. Cho et al. [44] showed that not only the particle size is important but also the presence of well-defined and faceted crystals, which have a higher capacity to adopt hydroxyl ions. This resulted in the reported higher photocatalytic activity for this type of materials in chloroform decomposition in water. Clearly, the morphology of S450 confirms to that of the TiO_2 used by Cho et al., and the present study demonstrates that for stable performance in liquid-phase selective oxidation processes this is also of high importance [45]. It should be mentioned that the S450 surface structure also induces a lower thermal stability of deactivating species, when compared to H [34]. The enhanced cyclohexanol production obtained when humid air is used, Fig. 1, is explained by the higher effective hydroxyl radical concentration which leads to a higher concentration of cyclohexylhydroxy radicals. This increases the probability of cyclohexanol formation as discussed elsewhere [24,34].

The results of the present study clearly demonstrate that one issue hampering practical application of photocatalysis for selective oxidation, i.e. catalyst deactivation, can be resolved. Other issues remain, including improvement of the photoefficiency of the process, i.e. the chemical conversion per unit of energy. While some advances have been reported, including particle size optimization and consequently crystal morphology [24], and operational conditions such as light intensity and slurry density, the photocatalytic community has not been successful in dramatically reducing the recombination rate of the holes and electrons formed upon photoactivation. Adding metal particles, such as Pt or Au, as electron acceptors have been demonstrated an improvement and certainly leaves room for further development.

Based on the data shown in the present study, a continuous process can be foreseen where a multiphase application in the Taylor flow regime [46] in monolith catalyst carriers could be useful. Enhanced mass transfer characteristics could further stimulate cyclohexanone desorption, as well as the rate of regeneration, since the liquid slug of cyclohexane is well mixed, and the humidified air bubble (i.e. regenerative phase) separated from the catalyst surface only by a relatively thin cyclohexane liquid film. The benefits of such reactor configuration are currently evaluated.

4. Conclusions

In dry conditions, anatase TiO_2 suffers from fast deactivation in selective photo-oxidation reactions as a result of the formation of carbonates and carboxylates that decrease the quantity of active OH-sites on the surface. The accumulation of these deactivating species can be largely reduced by applying TiO_2 with favorable surface chemical properties and by tuning the humidity of the oxygen feed. By using a highly crystalline TiO_2 catalyst, particle agglomeration is prevented, water-induced cyclohexanone desorption stimulated, and surface regeneration continuous. The latter is most likely the result of "surface cleaning" by conversion of carboxylates and carbonates to CO_2.

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