Sintering behavior of Pt metal particles supported on silica-coated alumina surface

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The sintering behavior of Pt metal particles was studied by supporting them on silica-coated alumina. Silica coating was found to be effective for the retention of a large surface area of alumina even after calcination at elevated temperatures. Before sintering, the size of Pt metal particles on all the silica-coated aluminas, including the uncoated alumina, was identical, while the particle size was larger on silica than on alumina. After sintering the Pt catalyst at 1073 K, the particle size increased on uncoated alumina as well as on alumina coated with thicker silica layers, especially on the supports previously calcined at >1473 K. On the other hand, the size of Pt metal particles did not increase much on alumina coated with monolayer silica. The observed suppression of sintering of Pt metal particles resulted from the retention of a large surface area of alumina with a thinner silica layer. In the case of a thicker silica layer, although a large surface area was maintained after calcination at elevated temperatures, the existence of a bulk silica-like property of the support did not favor the suppression of sintering of Pt metal particles.

KEY WORDS: sintering; supported Pt catalyst; metal particle size; silica-coated alumina; phase transformation

1. Introduction

Sintering is a serious mode of deactivation in a metal catalyst. In order to suppress the sintering of metal particles, a metal catalyst is usually used in a way of supporting it on a refractory material. A large surface area is an important requirement for a support material, on which metal particles are highly dispersed for the purpose of suppressing their sintering. Owing to their large surface area, transition aluminas are most widely used as a catalyst support. However, they readily transform to α-phase alumina upon heating at temperatures >1423 K, accompanying a drastic decrease in surface area to <10 m^2 g^{-1}. Although silica is also a large surface area material, it has the disadvantage that metal particles grow more easily on it than on alumina [1,2].

It was found that coating an alumina surface with a thin film of silica was effective for the retention of a large surface area upon heating at elevated temperatures [3,4]. This finding leads us to expect that the sintering of metal particles will be suppressed by supporting them on silica-coated alumina, because its large surface area is maintained even after heating at elevated temperatures. However, silica coating would not be effective if particle growth readily occurs on silica-coated alumina just as on silica. The purpose of the present study is, therefore, to clarify in which fashion silica-coated alumina behaves toward the sintering of supported Pt metal particles, like silica or like alumina.

2. Experimental

The alumina used was a commercially obtainable θ-phase alumina (TM-100, Taimei Chemicals Co.), which was synthesized by decomposing $Al(NH_4)CO_3(OH)_2$. This alumina was coated with a thin film of silica in a manner such that $Si(OC_2H_5)_4$ (TEOS; Kanto Chemical Co., Ltd.), previously hydrolyzed with 1 N HNO_3 (Wako Pure Chemical Industries, Ltd.), was added to an aqueous suspension of the alumina powders, followed by the evaporation of water. The resultant mixture was calcined at 1073 K for 1 h. The amount of TEOS added was varied so that the alumina surface was covered with a single, double, and triple layer of silica. All the samples were further calcined at 1373, 1473, 1573, and 1673 K for 1 h. Uncoated TM-100 and fumed silica (SIGMA Chemical Co.) were also used as a reference catalyst support.

Pt metal catalysts were prepared by impregnating a support material with an aqueous solution of H_2PtCl_6 (Wako Pure Chemical Industries), followed by the evaporation of water and subsequent heating at 723 K for 3 h in flowing helium. Metal loading was 1 wt%. The catalyst was sintered by further heating at 1073 K for 6 h in flowing helium. In this paper, in order to avoid any confusion, the heating of catalyst supports and the Pt metal catalysts were referred to as calcination/calcine and sintering/sinter, respectively.

XRD spectra were taken by using an MXP powder diffractometer with a Cu Kα radiation (MAC Science Inc.), which was operated at 40 kV and 20 mA. BET surface area was measured with a Flowsorp II adsorption apparatus (Simadzu Inc.). The coverage of the alumina surface with a thin film of silica was estimated by a benzaldehyde–

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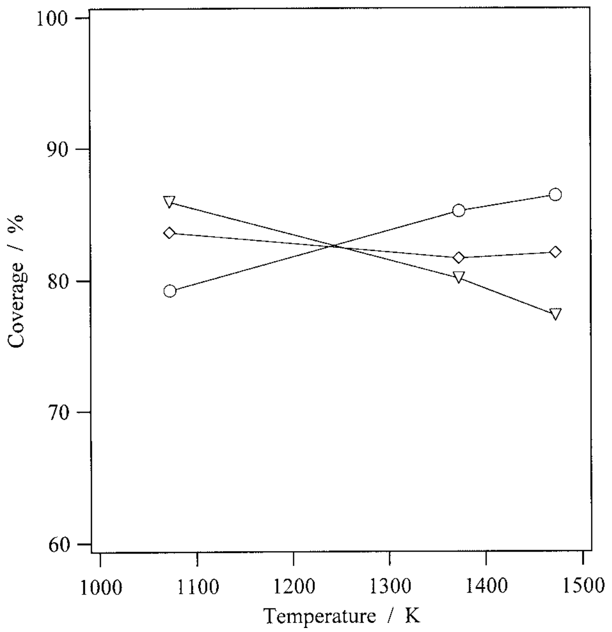


Figure 1. Extent of the alumina surface covered with a thin layer of silica. Amount of silica coating: 11.6 (○), 20.8 (◇), and 29.2 wt% (▽).

ammonia titration method: NH_3 was pulsed onto a catalyst, on which benzaldehyde was previously adsorbed, followed by determining the amount of benzonitrile produced [5]. For the determination of the average size of Pt metal particles, the amount of CO adsorbed on the catalyst was measured by using a flow-type pulse adsorption apparatus. For the direct measurement of the particle size, TEM observation was carried out using a Joel JEM-3010 electron microscope at an acceleration voltage of 300 V.

3. Results and discussion

Since benzaldehyde is irreversibly adsorbed only on the alumina surface, not on the silica surface, the extent of coverage with silica coating can be estimated from the amount of benzonitrile produced from reaction of adsorbed benzaldehyde with pulsed NH_3 [5]. Figure 1 illustrates the result. Regardless of the amount of added silica, about 80% of the alumina surface was covered with silica. This observation leads us to conclude that as designed, most of the alumina surface was covered with a single, double, and triple silica monolayer by adding 11.6, 20.8, and 29.2 wt% silica, respectively.

Figure 2 shows XRD patterns for uncoated alumina after calcination at 1073, 1373, and 1473 K. While the starting θ-phase alumina was observed at a temperature <1373 K, transformation to α-phase alumina was completed after calcination at 1473 K. Figure 3 shows XRD patterns for silica-coated alumina after calcination at various temperatures. In this case, the amount of silica coating was 11.6 wt%. As shown, no α-phase alumina was observed even after calcination at 1473 K. The phase transformation was still incomplete and mullite ($3Al_2O_3 \cdot 2SiO_2$) was formed after calcination at >1573 K. It is described that irrespective of the calcination temperature, no Si-containing crystalline phases

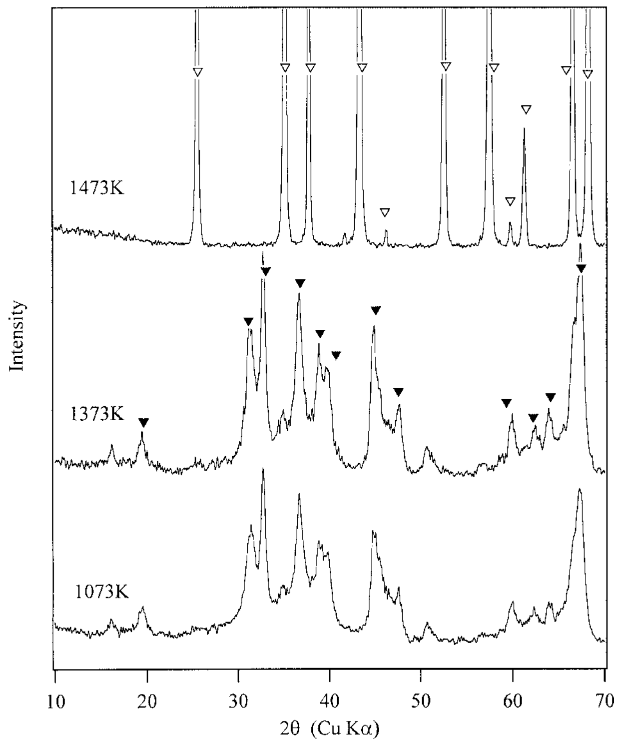


Figure 2. XRD patterns of uncoated alumina after calcination at various temperatures: (▼) θ-Al_2O_3 and (▽) α-Al_2O_3.

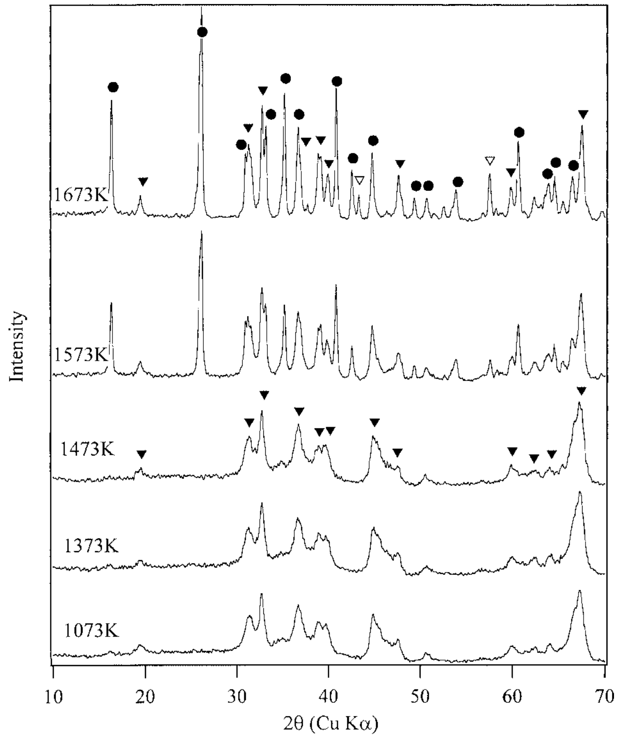


Figure 3. XRD patterns of silica-coated alumina after calcination at various temperatures. Amount of silica coating: 11.6 (▼) θ-Al_2O_3, (▽) α-Al_2O_3, and (●) mullite.

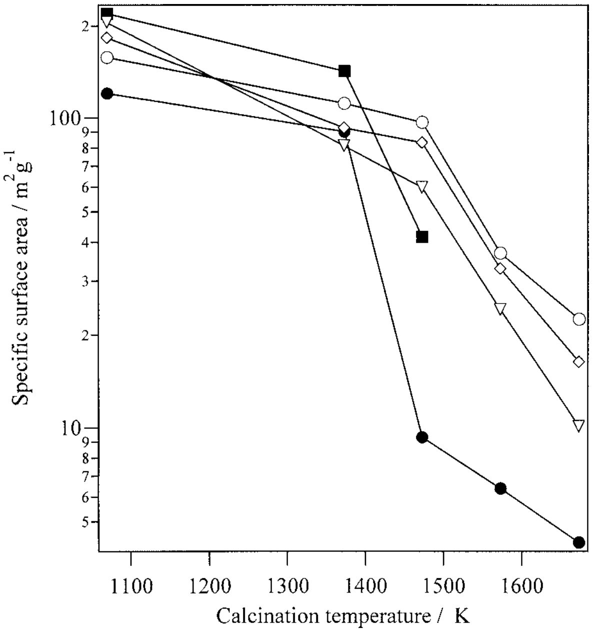


Figure 4. BET surface area of samples after calcination at elevated temperatures. Closed symbols are for uncoated alumina (●) and for fumed silica (■). Open symbols are for alumina coated with 11.6 (○), 20.8 (◇), and 29.2 wt% silica (▽).

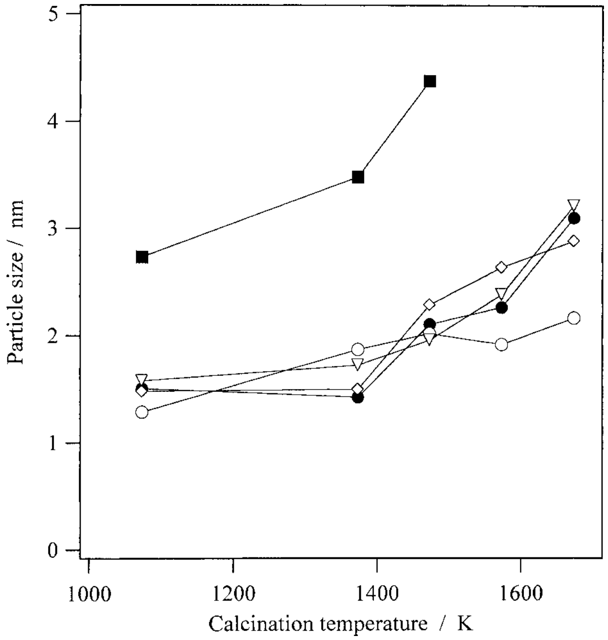


Figure 5. Mean diameter of supported Pt metal particles before sintering. Closed symbols are for uncoated alumina (●) and for fumed silica (■). Open symbols are for alumina coated with 11.6 (○), 20.8 (◇), and 29.2 wt% silica (▽).

other than mullite were detected in the silica-coated alumina. Very similar results were also obtained for the larger amount of silica coating. It was, therefore, confirmed again that silica coating considerably suppresses phase transformation to α-alumina. These findings support the validity of the conclusion derived from benzaldehyde–ammonia titration that the alumina surface is covered with a thin layer of silica.

For uncoated and silica-coated aluminas, BET surface area is plotted in figure 4 as a function of the calcination temperature. As a result of the suppression of phase transformation, silica-coated aluminas exhibited quite a large surface area even after calcination at elevated temperatures. The surface area was 60–97 m^2 g^{-1} at 1473 K and it remains 24–37 m^2 g^{-1} at 1573 K. Without coating, on the other hand, the surface area was as small as 9 m^2 g^{-1} at 1473 K and 6 m^2 g^{-1} at 1573 K.

The size of supported Pt metal particles was determined from CO chemisorption. Figure 5 illustrates the results before sintering. The mean diameter increased for all the supports with the elevation of their calcination temperature, resulting from the decrease in their surface area. In agreement with the literature [1], the diameter was always much larger on silica than on uncoated alumina. It was also seen that silica coating hardly affected the size of deposited Pt metal particles. Figure 6 shows the particle size after sintering the Pt catalyst at 1073 K for 6 h. A considerable increase in the diameter of Pt metal particles was observed on all the supports. Such an increase was marked on silica and on uncoated alumina, especially on those previously calcined at >1473 K. The observed increase in the diameter was due to the decrease in the surface area of these supports. As on uncoated alumina, the diameter of Pt metal particles increased with increasing calcination temperature on alumina coated with 29.2 wt% silica. It is interesting to note that the particle size on this support is very similar to that on uncoated alumina except for the sample calcined at 1073 K, although surface area markedly differs from each other after calcination

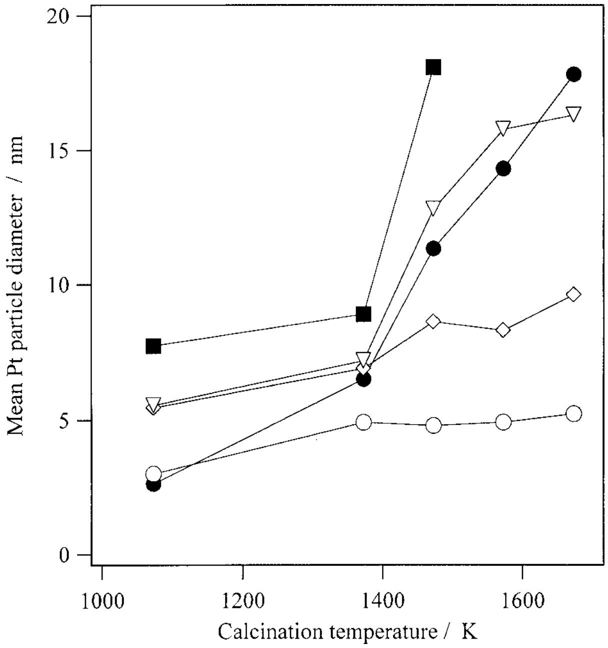
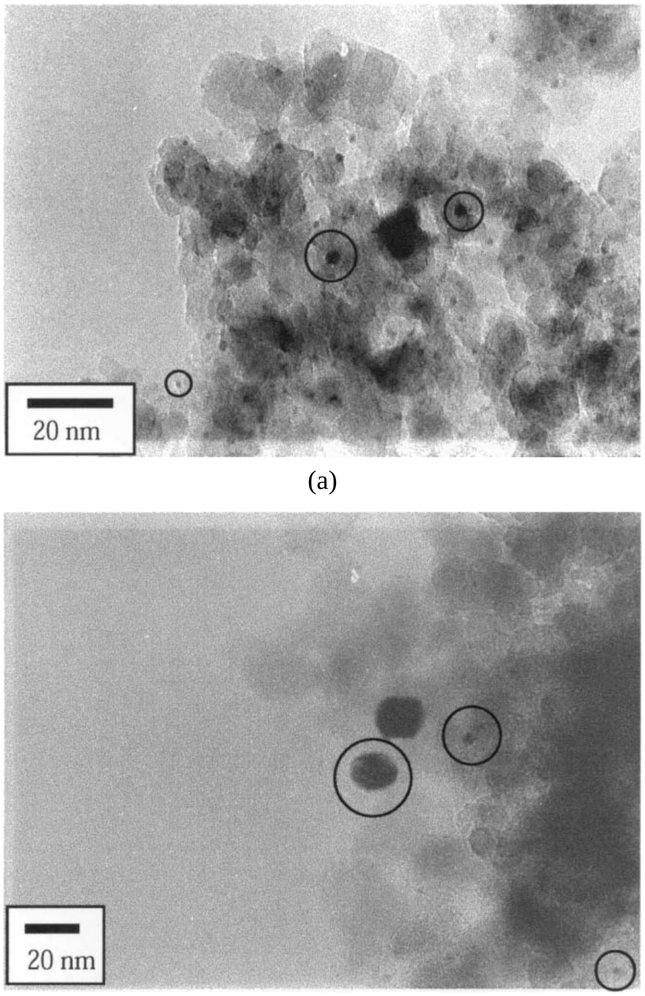


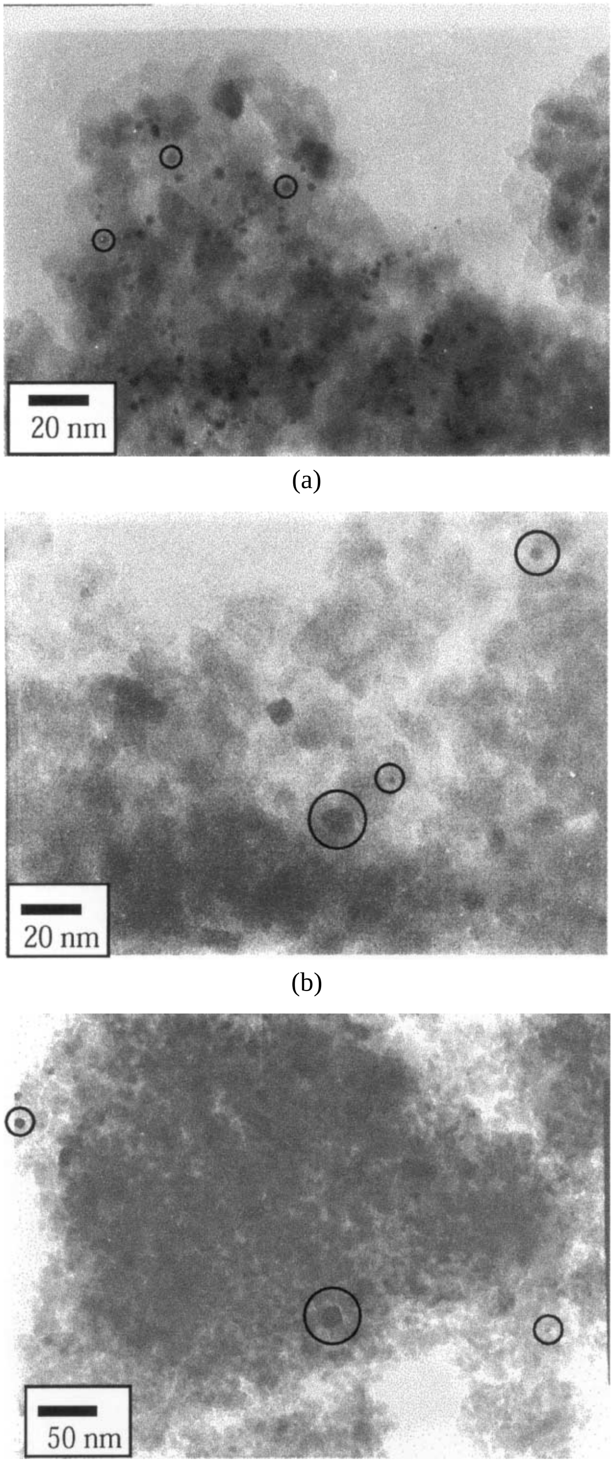
Figure 6. Mean diameter of supported Pt metal particles after sintering. Closed symbols are for uncoated alumina (●) and for fumed silica (■). Open symbols are for alumina coated with 11.6 (○), 20.8 (◇), and 29.2 wt% silica (▽).



(a)

(b)

Figure 7. TEM images for Pt metal particles on uncoated alumina (a) and on fumed silica (b) after sintering at 1073 K for 6 h. The dark spot in the circle indicates a Pt metal particle.



(a)

(b)

(c)

Figure 8. TEM images for Pt metal particles on alumina with different amounts of silica after sintering at 1073 K for 6 h. The amounts of silica coats are 11.6 (a), 20.8 (b), and 29.2 wt% (c). The dark spot in the circle indicates a Pt metal particle.

at >1473 K. Since silica films with the thickness of a triple monolayer are formed on alumina containing 29.2 wt% silica, high-temperature heating is expected to produce a bulk silica-like character in this support, and as a result the diameter of Pt metal particles increases.

For coating with 11.6 wt% silica, with which a monolayer silica covered the alumina surface, the increase in the diameter of supported Pt metal particles was markedly suppressed to almost the same level irrespective of the calcination temperature of the support. It can, therefore, be concluded that bulk silica-like character does not appear for such a thin silica layer, and this provides a favorable condition in the support for the suppression of the sintering of Pt metal particles on it. It is mentioned that mullite plays no role in sintering of Pt metal particles, because mullite was formed in all the silica-coated aluminas examined after calcination at >1573 K.

The sintering behavior was confirmed by TEM observation for supported Pt metal catalysts. Fine particles with a relatively uniform distribution are observed on uncoated alumina previously calcined at 1073 K: the size being 2–4 nm (figure 7(a)). Compared with this, Pt metal particles with inhomogeneous distribution, the size of which varies from 3 to 18 nm, are observed on silica for the same calcination temperature (figure 7(b)). Figure 8 is for sintered Pt catalyst supported on silica-coated aluminas previously calcined at 1473 K. In the case of 11.6 wt% silica coating, fine Pt metal particles of 3–5 nm are distributed (figure 8(a)), while well-grown particles of 7–20 nm are observed on alumina coated with 29.2 wt% silica (figure 8(c)). On alumina coated with 20.8 wt% silica, Pt metal particles with an intermediate size, namely 3–13 nm, are observed (figure 8(b)). These observations are in line with the result from CO chemisorption.

It was reported that the direct contact between platinum and alumina produced the $Pt{\cdot}Al_2O_{3-x}$ surface compound or Pt–Al alloy, both of which did not chemisorb hydrogen [6–8]. One of the authors also reported the possible reduction of alumina deposited on Pt clusters to AlO_x moieties [9]. Since it is considered that the $Pt{\cdot}Al_2O_{3-x}$ surface compound or Pt–Al alloy does not chemisorb CO, the precise size of Pt metal particles may not be determined from the amount of CO chemisorption. However, it is expected that no such compounds are produced in our supported Pt catalyst system, because silica coating excludes direct contact between platinum and alumina. Such an expectation was supported by the fact that the result of CO chemisorption was in line with TEM observations.

4. Conclusions

Sintering of Pt metal particles was studied by supporting them on silica-coated alumina. At the same calcination temperature of the support, the particle size was much smaller on uncoated alumina than on silica before and after sintering the catalyst at 1073 K. The increase in the size of Pt metal particles was highly suppressed by supporting them on alumina coated with monolayer silica because of the retention of a large surface area of the support even after high-temperature calcination. Although a large surface area was also maintained by coating with a thicker layer of silica, namely triple monolayer, the sintering of Pt metal particles was not suppressed, and this was attributed to the existence of a bulk silica-like character of the support.

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