



RESEARCH ARTICLE

SOL-GEL PREPARATION OF SULFATED TITANIA AS NICKEL SUPPORTING MATERIAL

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ABSTRACT

A series of sulfated titania xerogels impregnated with nickel were prepared by sol gel method with different methods of surfactant cetyltrimethyl ammonium bromide (CTAB) templating and characterized by X-Ray Diffraction, Nitrogen adsorption, Fourier Transformed-Infra Red, and Transmission Electron Microscopy. The XRD patterns of the sulfated titania, TS and TS-P, showed anatase phase of titania with TS-P sample having higher crystallinity. While, TS-P/N8 sample, sulfated titania impregnated with 8wt% of nickel showed higher crystallinity than both pure sulfated titania. The addition of nickel increased the crystallinity of the samples, which was consistent with the result observed by TEM measurement and texture assessment. The texture assessment by Nitrogen adsorption method showed that the specific surface areas, pore diameter and pore volume of the nickel supported on sulphated titania, TS-P/N8 were higher than that of TS/N8. Sulfate loading tend to increase the specific surface area. The largest specific surface area was obtained for the TS-P/N8 with 8 wt% of nickel and 10 wt% of sulfate. Reduction process of the samples decreased the specific surface area, pore diameter and pore volume. There is an impact from the reduction process which could be explained from the FTIR spectra.

Key words: Modified sol-gel, surfactant templating, impregnation, Nickel, Sulfated Titania

INTRODUCTION

Recently, non-polluting and efficient catalytic technologies are much required, considering that environmental restrictions on emissions are covered in several legislations throughout the world. Solid acids have begun to replace highly corrosive, hazardous and polluting liquid acids. The substitution of homogeneous liquid acids by heterogeneous solid superacids as catalysts is expected to ease their separation from reacting mixture, allowing continuous operation as well as regeneration and neutralization of the catalyst (Bokhimi *et al.*, 2004) and lowering the cost of process installation and maintenance (Lonyi *et al.*, 1996). The properties of catalysts and support materials strongly depend on the preparation procedures. The high porosity and the large specific surface area of materials prepared by the sol-gel method make them very attractive from a catalytic point of view. The sol-gel method not only allows good control of the characteristics of the support, but also offers the possibility of preparing oxide-supported metal catalysts from a homogenous solution containing both the catalytic metal precursor and the support precursor (Tursiloadi *et al.*, 2004). A metal alkoxide undergoes hydrolysis and subsequent condensation in an alcohol solvent, forming a polymer oxide network entraining the alcohol. For catalytic uses, the liquid solvent must be removed from the alcogel. In conventional drying, a liquid-vapor interface forms in the pores and the corresponding surface tension collapses the oxide network, thereby reducing the surface area (Ward *et al.*,

1994). To prevent the collapsing of the oxide network, most work usually apply the removal of solvents by supercritical drying. Another different approach during the removal of solvents is by using surfactants as a template to fabricate porous materials and to improve the alcogel properties (Weissman *et al.*, 1993). By immersing the *wet alcogels* in surfactant solution before drying, the oxide network will be prevented from collapsing.

Catalysts prepared using TiO₂ as supports are at least two or three times more active than the equivalent Al₂O₃ supported catalyst, measured on either a surface area, weight, or atomic basis. However, because of the typical low surface area of these supports, usually less than 50 m²/g, the volume activity is much lower than that of Al₂O₃ supports, which usually have surface areas of at least 200 m²/g (Weissman, J.G. *et al.*, 1993). Sulfated metal oxides have been tested as catalysts. The most studied sulfated oxides are ZrO₂ and TiO₂. Sulfated titania has been found to be efficient catalysts for isomerization, alkylation, Friedel-Crafts acylation, esterification, photocatalytic oxidation and reduction of NO_x (Bokhimi *et al.*, 2004; Lonyi *et al.*, 1996). Previous studies on sulfated oxides have shown that the surface of active oxides is modified by sulfate ions. There are different models proposing how sulfur and oxygen ions are linked to the oxide atoms (Bokhimi *et al.*, 2004). The problem of low surface area in TiO₂ supports, as mentioned above can be addressed through alternative preparation methods. Many studies on the preparation of mesoporous materials using self-assembled structures, such as surfactants or block copolymers, as a template have been reported. In this work, we apply the modified sol-gel method using surfactants to fabricate porous

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materials and to improve their surface area of the sulfated titania support material for nickel. Youn and coworkers (2010) have prepared Nickel catalysts supported on pure metal oxides (ZnO, MgO, ZrO₂, TiO₂, and Al₂O₃) with different acidity which were obtained by an incipient wetness impregnation method. These catalysts were applied to the hydrogen production by auto-thermal reforming of ethanol. Among various pure metal oxides, ZrO₂ and TiO₂ with an intermediate acidity were found to be efficient supporting materials for nickel catalysts in the auto-thermal reforming of ethanol (Youn *et al*, 2010).

The properties of alumina-supported Ni catalysts prepared by wet impregnation were also extensively studied by Huang and Schwarz. These authors prepared Ni/Al₂O₃ catalysts at various loadings with better metallic dispersion and improved resistance to deactivation by coke deposition, as compared to solids of the same composition obtained by impregnation to incipient wetness (Huang *et al*, 1987). On the other hand, Ni/TiO₂ is a typical system where the strong metal support interaction state (SMSI) is manifested after high reduction temperature, its magnitude depending mainly on the preparation method (Sankar *et al*, 1991) and metal loading (van de Loosdrecht *et al*, 1997). Rodríguez *et al* found an increase in the reducibility of nickel by titania addition in cogelled and impregnated 10 wt.% Ni in equimolar Al₂O₃-TiO₂. In this work, a modified sol-gel method to control pore sizes of sulfated TiO₂ (TiO₂-SO₄²⁻) powders with surfactant-templating has been investigated. The characterization of the catalyst samples were performed by means of X-Ray Diffraction (XRD), Nitrogen adsorption for texture assessment, Fourier Transform Infra Red (FTIR) and Transmission Electron Microscopy (TEM). The effect of immersing surfactant into titania sulfated gels and impregnation of nickel metal particle will be studied.

MATERIALS AND METHOD

Materials

All chemicals were of reagent grade purity and were used without any further treatment. Precursor titanium alkoxide employed in this study was titanium iso-propoxide, Ti(OC₃H₇)₄ from Sigma-Aldrich. Commercial cetyltrimethylammonium-bromide (CTAB), Ni(NO₃)₂·6H₂O powder used as source of Ni²⁺, *n*-Propanol, HNO₃, and H₂SO₄ are purchased from E-Merck.

Preparation of samples

The precursor employed in the preparation of the sol-gel catalyst was titanium *iso*-propoxide in *iso*-propanol. The sulfated titania modified xerogels were prepared by two different methods of surfactant templating, which will be compared in later discussion. The first sample series (TS) were prepared as follows: 3.0 mol of *iso*-propanol was put in a glass system at low temperature (0°C) with constant stirring. After, 0.5 mol of titanium iso-propoxide were dropwise added to the solution and then the pH was adjusted to 3.0 with HNO₃. At this temperature, 0.306 ml of concentrated sulfuric acid was dropped under constant stirring. The flask was put under reflux at 70°C and stirred for 5 h. Finally 3.3 mol of H₂O were added to the reaction system and the resulting suspension was maintained under reflux and constant stirring until gelling was achieved. The wet gel was

immersed overnight at room temperature in an *iso*-propanol solution of surfactant (cetyltrimethylammonium bromide, CTAB), decanted and then dried under vacuum for 24 h at 70°C. The second sample series (TS-P) were prepared using the same materials, *iso*-propanol, titanium iso-propoxide and HNO₃ with the same amount ratio 3.0, 0.5 and 3.0 mols, respectively. Concentrated sulphuric acid of 0.306 ml was dropped under constant stirring. Prior to adding 3.3 mol of H₂O to the reaction system, a sufficient amount of *iso*-propanol solution of surfactant CTAB was added. The system was then maintained under reflux (70°C) and constant stirring until gelling was achieved. The wet gel was further dried under vacuum for 24 h at 70°C. Calcination of wet gels of both samples were performed for 4 h at 500°C. Nickel supported on sulphated titania modified xerogel (8% Ni/TiO₂-SO₄) was obtained by wetness impregnation at 50°C, using Ni(NO₃)₂. The impregnated samples were dried for 3 h at 70°C, then calcined for 4 h at 500°C and reduced in H₂ for 2h at 350°C.

Characterization of samples

X-ray diffraction (XRD) analysis was carried out for crystallographic phases identification of the sulphated titania catalyst samples using a Phillip PW 1710 diffractometer, using Cu K α radiation at 40 kV and 30 mA, and a secondary graphite monochromator. The crystallite size was calculated using the Debye-Scherrer equation. The specific surface area and pore size of the particles was determined by the BET and BJH method using N₂ adsorption/desorption at 77 K (Quantasorb, Quantachrome, USA). Prior to each measurement all samples were degassed at 110 °C and 10⁻⁴ Torr pressure to evacuate the physisorbed moisture. Surface species were analysed by Fourier transform infrared spectroscopy (FTIR, Shimadzu). Samples were mixed with potassium bromide phase using FT-IR spectrometer (Parkin-Elmer, Paragon-500) attached to an automatic data acquisition center. The morphology and particle size was determined under a transmission electron microscope (Phillips CM120).

RESULTS

X-ray Diffraction

XRD patterns for pure sulfated titania prepared by different methods of surfactant templating followed by nickel impregnation are shown in Figure 1. All the titania based samples showed diffraction peaks ascribed to anatase phase of TiO₂ together with some other peaks. In the TiO₂ spectrum, the peak at 2 θ = 25.5 corresponds to the anatase crystalline phase. At the same time, small diffraction peaks from nickel titanate, NiTiO₃ was observed at 2 θ = 46. Nickel supported on sulfated titania shows the highest crystallinity. The addition of nickel increased the crystallinity in the order of: TS < TS-P < TS-P,N8. Also from Figure 1, the sharpness of the XRD peaks indicates the crystallinity of the particles. From the Debye-Scherrer equation the crystallite size for each sulfated samples TS, TS-P and TS-P,N8 were 16.71, 11.23 and 9.4 nm, respectively. The addition of nickel on the other hand, decreased the crystal size in the order of: TS > TS-P > TS-P,N8.

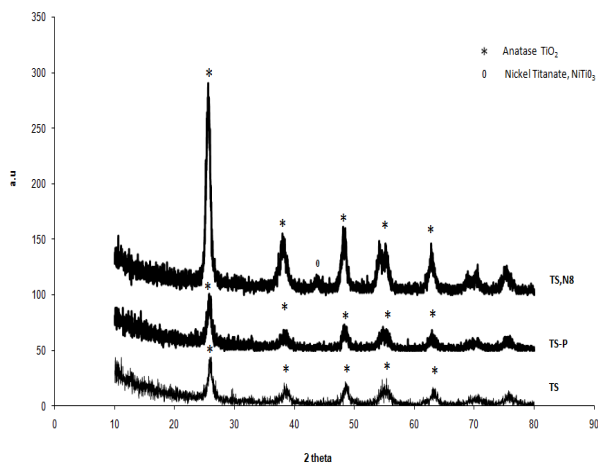


Fig 1. XRD pattern of catalyst samples before and after 8% Ni impregnation, calcinated at 500°C

Texture assessment by nitrogen adsorption isotherms

Specific surface area, pore diameter and pore volume were calculated by applying the Brunauer-Emmett-Teller (BET) and Barret-Joyner-Halenda (BJH) calculation method. The effect of sulfate loading into the supporting material of titania gels were observed. The optimum specific surface area was obtained at sulfate concentration of 10%, which was 95.64 m²/g (as shown in Table 2). Higher sulfate concentration of more than 10% reduced the surface area.

Table 1. List of catalyst samples and nomenclature

Supercacid catalyst samples	Sample Code	Preparation Method
TiO ₂ -SO ₄ ²⁻ , surfactant premix	TS-P	Sol-gel method, surfactant was added before gelation
TiO ₂ -SO ₄ ²⁻ , Surfactant immersed	TS	Sol-gel method, surfactant was immersed after gelation
Ni/ TiO ₂ -SO ₄ ²⁻ , Surfactant premix	TS-P,N8	Sol-gel method, surfactant was added before gelation, Ni impregnation 8%, calcination 500 °C
Ni/TiO ₂ -SO ₄ ²⁻ , Surfactant immersed	TS,N8	Sol-gel method, surfactant was immersed after gelation, Ni impregnation 8%, calcination 500 °C
Ni/TiO ₂ -SO ₄ ²⁻ , Surfactant immersed, reduced	TS,N8 _{red}	Sol-gel method, surfactant was immersed after gelation, Ni impregnation 8%, calcination 500 °C, reduction 350 °C

Table 2. Texture characteristics of the samples prior Ni-impregnation

Modified sulfated titania xerogels	Sulfate, SO ₄ ²⁻ (wt%)	Specific Surface Area (m ² /g)
TS0	0	4.71
TS5	5	70.27
TS10	10	95.64
TS25	25	85.06

The sample having the largest surface area, TS10 was then compared to those being impregnated with nickel, as shown in Table 3. The addition of nickel, TS,N8, tend to decrease the specific surface area. The following reduction process further reduced the surface area from 62.43 m²/g to 47.36 m²/g. There was an impact of reduction process towards surface area as observed in sample TS,N8_{red}.

Table 3. Texture characteristics of the Ni-impregnated samples

Modified sulfated titania xerogels	Sulfate, SO ₄ ²⁻ (wt%)	Surface Area (m ² /g)
TS10	10	95.64
TS,N8	10	62.43
TS,N8 _{red}	10	47.36

The different method of surfactant templating in this modified sol gel method, which were by immersed and pre-mixture were compared after being impregnated by nickel. Specific surface area, pore size and pore volume of TS-P,N8; TS,N8 and TS,N8_{red} are shown in Table 4. Nickel supported on TS resulted in higher specific surface area, pore size and pore volume than TS-P. However, the results for both samples, TS-P,N8 and TS,N8 were quite similar. Further reduction process showed more significant difference on the sample texture, where it decreased the surface area and pore volume, but at the same time increased the pore size nearly six times larger.

Table 4. Texture characteristics of the Ni-impregnated xerogel samples

Sample	Tcalc, °C	Specific surface area, m ² /g	Pore size, Nm	Pore Volume, cm ³ /g
TS-P,N8	500	61.76	14.00	0.22
TS,N8	500	62.43	14.85	0.23
TS,N8 _{red}	500	47.36	86.44	0.10

Fourier Transformed-Infra Red

Surface species were analyzed by Fourier Transform Infra Red spectroscopy (FT-IR, Shimadzu). The FT-IR spectra for the catalyst samples before and after Ni impregnation are shown in Figure 2. The below figure also shows the FTIR

of the Ni-impregnated catalyst samples after reduction at 350 °C. The spectra provides information on the surface functional groups. As can be seen from Figure 2, the Ni impregnated samples (TS-P,N8 and TS,N8) exhibit similar spectra but differ when compared to the unimpregnated (TS-P) and the impregnated and reduced (TS,N8_{red}) samples. The peaks over when 400-1250 cm⁻¹ are characteristic of the formation of O-Ti-O network. The peak centred at ~1630 cm⁻¹ corresponds to the O-H bond of adsorbed water molecules. The peak at ~1040 cm⁻¹ is due to SO₃H bond of sulfate in the titania alcogel. This peak did not appear in the TS,N8_{red} spectra. The band at 2900-3000 cm⁻¹ is due to C-H stretch from the persence of alkyl groups.

Transmission Electron Microscopy

Transmission electron micrographs of the prepared xerogels are shown in Figure 3. The morphologies and particle size of the xerogels were determined through TEM analysis. The morphology of the samples after Ni impregnation TS-P,N8; TS,N8 and TS,N8_{red} tend to form the same particle features (Figure 3), where one particle was larger than the other. This shows that NiO or Ni was impregnated homogeneously into the surface of the sulfated titania gels. For samples TS,N8

and TS,N8_{red}, the particle sizes ranged between 21 and 30 nm and in larger amount compared to the smaller particles of 18 nm size TS-P,N8 sample.

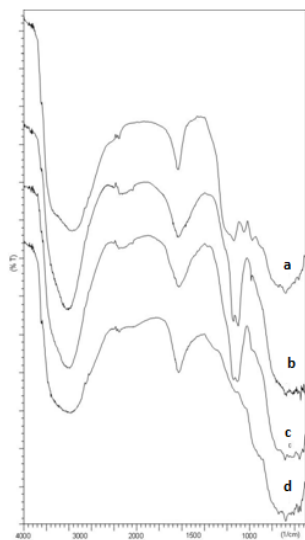


Fig 2. FTIR spectra of the catalyst samples (a) TS-P (b) TS,N8 (c) TS-P,N8 (d) TS,N8_{red}

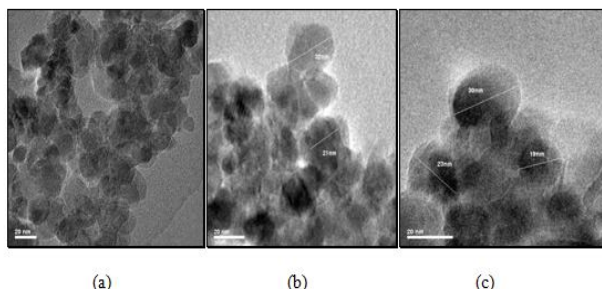


Fig 4. Transmission electron micrographs of the Ni impregnated catalyst samples (a) TS-P,N8 (b) TS,N8 (c) TS,N8_{red}

DISCUSSION

A detailed study of crystalline phases formed during the preparation process is of great importance, because the nature of the crystalline phase can affect the catalytic behaviour of the sample material. XRD patterns for calcinated samples at 500°C are shown in Figure 1. All the titania based samples show diffraction peaks ascribed to anatase phase of TiO₂ together with some other peaks. Small diffraction peaks from nickel titanate, NiTiO₃ observed at $2\theta = 46$. The formation of nickel titanate phase at this sample was similar to the results reported by Numata *et al* (2010). Nickel titanate would be formed by solid reaction on the surface of anatase with NiO. The different preparation method of surfactant templating resulted in the increasing of crystallinity of xerogel samples : TS < TS-P < TS-P,N8. Sample TS, prepared by sol gel method with surfactant immersed after gelation, showed the lowest crystallinity as surfactant was not distributed thoroughly into the entire microstructure of sulfated titania gels. Surfactant only interacts with the surface of sulfated titania. Sample TS-P, also prepared by sol-gel method with surfactant added before gelation, shows higher crystallinity than TS due to homogenous distribution of surfactant into the entire microstructure of sulfated titania gels. As for sample

TS-P,N8, which was the xerogels further impregnated with nickel 8wt% showed the highest crystallinity. The addition of nickel tend to increase the crystallinity of titania sulfated gels.

Nickel impregnated by wet impregnation was distributed well into microstructure of supporting material, TS-P contributing to a higher crystallinity of the whole material system (supporting material and impregnated nickel), TS-P,N8 than the initial supporting materials, TS-P and TS. Also from Figure 1, the sharpness of the XRD peaks indicates the crystallinity of the particles. The crystal size of each samples TS, TS-P and TS-P,N8 were calculated from the Debye-Scherrer equation which were 16.71, 11.23 and 9.4 nm respectively. In general, the broadening of XRD peaks indicate decrease of crystal size. The sulfated titania crystals, synthesized by both methods, premix (TS-P) and immerse (TS) surfactant have similar narrow XRD peaks. However, after impregnation the TiO₂ crystals have broader XRD peaks, indicating smaller crystal sizes, as stated above. Compared to the crystallinity, the crystal size of the samples tend to decrease in the order : TS > TSP > TS-P,N8, respectively. There was an inverse correlation between crystallinity and crystal size. Smaller crystal size resulted in higher crystallinity of the materials. The contribution of nickel as metal particles in sample TS-P,N8 tend to increase the crystallinity and decrease the crystal size. Nickel with particle size of 0.124 nm can be impregnated well into the micropore sulfated titania gels, TS-P,N8 which resulted having the lowest crystal size and highest crystallinity. From the XRD pattern, it can be concluded that preparation of materials by sol gel method, surfactant immersed before gelation (premix) resulted higher crystallinity than surfactant immersed after gelation.

Specific surface area, pore diameter and pore volume were calculated by applying the Brunauer-Emmett-Teller (BET) and Barret-Joyner-Halenda (BJH) calculation method. The effect of sulfate loading into the samples without Ni impregnation are studied. The sulfate loading tend to increase the surface area of the samples. The optimum surface area was obtained at sulfate concentration of 10%, which was 95.64 m²/g (as shown in Table 2). Sulfate concentration of more than 10% tend to reduce the surface area. The largest surface area of samples were compared by the ones impregnated with nickel (as shown in Table 3). Nickel impregnation decreased the specific surface area. Further reduction proses also reduced the surface area as observed in sample TS,N8_{red}. Specific surface area, pore size and pore volume of impregnated samples TS-P,N8; TS,N8 and TS,N8_{red} are shown in Table 4. These characteristics were affected by the preparation method. The addition of certain amount of nickel to TS-P and TS improved the specific surface area as well as the textural properties of the sample. The small particle size of nickel which is about 0.124 nm were distributed well into the titania gels of supporting material, both TS and TS-P. Impregnation of nickel resulted higher surface area, pore size and pore volume. Nickel was distributed well in both the surface and micropore of the supporting materials as NiO. Compared to the previous research, the results were similar to those reported by Numata *et al* (2010). It was found that impregnation nickel into titania resulted higher surface area, pore size and pore volume.

TS,N8_{red} samples showed that reduction process has great impact of reducing surface area, pore size and pore volume. Reduction process was conducted to obtain Ni²⁺ on the surface of sulphated titania. The presence of Ni species in the sulphated titania gel network affects the shrinkage. Nickel metal particles covered both surface and micropore channelled as agglomerate particles. The growth of anatase crystallites and the crystallization of NiTiO₃ (Numata *et al*, 2010) contributed to the decrease of surface area of TS,N8_{red} sample. Furthermore, the reduction process reduced the sulfate from supporting material, TS as can be seen on the FT-IR spectra. From the texture assessment, it can be concluded that supporting material TS resulted in better performance of surface area, pore size and pore volume than TS-P when impregnated by nickel. Surface species functional group were analyzed by Fourier Transformed Infra Red spectroscopy (FT-IR, Shimadzu). The FT-IR spectra for the catalyst samples before and after Ni impregnation are shown in Figure 2. The Ni impregnated samples (TS-P,N8 and TS,N8) exhibited similar spectra but differ when compared to the unimpregnated (TS-P) and the impregnated and reduced (TS,N8_{red}) samples. The characteristic peak at ~1040 cm⁻¹ which is due to SO₃H bond of sulfate in the titania alcogel did not appear in the TS,N8_{red} spectra. It can be explained that during the reduction process of the catalyst samples, sulfate was also reduced.

Figure 3 shows the transmission electron micrographs of the prepared xerogels. The morphologies and particle size of the xerogels are determined through TEM analysis. The morphology of the samples after Ni impregnation TS-P,N8; TS,N8 and TS,N8_{red} tend to form the same particle features (Figure 3), where one particle is larger than the other. This observation reveals that the particles are uniformly distributed over the entire solid materials of the sulfated titania gels. The nickel promoted samples also exhibited nanocrystalline particles. The TEM micrographs further showed that these samples are in more densely packed configuration and prone to crystallization, as the particles exhibit some sharp edges that were indicative of sintering to bigger crystallite formation. In relation to the morphology of impregnated materials, these samples seem to be configured by a stack of spherical particles. As for the TS,N8 and TS,N8_{red} sample, the particle sizes ranged between 21 and 30 nm and in larger quantities compared to the smaller particles of 18 nm of TS-P,N8 sample. Many randomly oriented nano-crystallites with sets of clearly resolved lattice fingers were observed. These results indicate that introduction of NiO can effectively inhibit the excessive crystal growth and stabilizes the porous structure.

Conclusion

In the preparation of sulfated titania impregnated with nickel by sol gel method with different surfactant cetyltrimethyl ammonium bromide (CTAC) templating, catalyst material with better properties were obtained. The XRD patterns of pure sulfated titania with different method of surfactant templating, TS-P, showed anatase phase of titania and higher crystallinity than the TS sample. The addition of nickel

caused the increasing of crystallinity, which was consistent with the result observed by TEM measurement and texture assessment. The texture assessment showed that specific surface areas, pore diameter and pore volume of the nickel supported on TS-P,N8 were higher than that of TS,N8. It was observed that the loading of sulfate also tend to increase specific surface area. The largest specific surface area was obtained for the TS-P,N8 with 8 wt% of nickel and 10 wt% of sulfate.

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