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Visible Light Absorption Ability and Photocatalytic Oxidation Activity of Co-Doped TiO_2 on Active Carbon for Degradation of Toluene

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N, Zn, Fe-doped TiO_2 was developed to enable photocatalytic reactions using the visible range of the solar spectrum. This work reports on the synthesis, characteristic and kinetic study of interstitial N, Zn, Fe-doped TiO_2 on active carbon prepared by the sol-gel method using urea, zinc nitrate and iron nitrate as N, Zn, Fe-dopants, respectively. X-ray diffraction, fourier transform infrared spectroscopy and UV-visible spectroscopy were used to analyze the titania. Different factors affecting catalyst activity were also discussed. The results show that the photocatalyst has an average diameter of 16 nm and under optimum conditions where the mol ratio of N, Fe, Zn and TiO_2 were 0.4:0.1: 0.005:1 and calcination time was 2 h at 773 K. The degradation rate of toluene on photocatalyst doped with N, Zn, Fe was up to 98 % under irradiation of visible light. And degradation rate accords with first order and its L-H value is also obtained.

Keywords: TiO_2, N,Zn,Fe co-doped, Sol-gel dip-coating technique, Photocatalysis, Gas phase toluene.

INTRODUCTION

Titanium dioxide has a band gap of 3 eV for the rutile phase and 3.2 eV for the anatase phase. These values require ultraviolet (UV) radiation to activate. Recently, many attempts have been made to make TiO_2 highly reactive under visible light excitation to allow utilization of the solar spectrum[1].

Many groups have been involved in depositing transition metal ions such as Fe, Au, Ag, V, Cr and Ni onto the surface of TiO_2 to improve the separation of electrons and holes[2-28]. Among these elements, Fe is very cost-effective and can contribute to shifting the absorption edge of TiO_2 into visible light range because the radius of Fe^{3+} (0.79 Å) is similar to that of Ti^{4+} (0.75 Å), so that Fe^{3+} can be easily incorporated into the crystal lattice of TiO_2[2-7]. The band gap energies of ZnO and TiO_2 are similar to each other (approximately 3.2 eV). And the combination of TiO_2 and ZnO can further separate the charge and increase the lifetime of the charge carriers[3,4,28]. Zinc oxide has also been conceived as a significant candidate that was reportedly known to be more efficient than TiO_2 in photooxidation of organic compound. Some anionic species such as nitrogen, carbon and sulfur were also identified to potentially form new impurity levels closest to the UV band. Many previous works indicated that doping of TiO_2 with nitrogen is one of the most effective approaches in improving properties and photocatalytic activity of TiO_2 in visible light regions[9-15]. The improvement observed in photocatalytic activity has been described by either mixing of nitrogen 2p states with oxygen 2p states on the top of the valance band or a creation of N-induced mid-gap level[11]. So it is well accepted that the wide band gap semiconductors generate a high photo voltage but exhibit low photocurrent whereas smaller band gap semiconductors can utilize a larger fraction of the incident photons but generate lower photo voltage[3,4]. Therefore, a device having multiple band gap energy layers can cover broad range of solar spectrum. Elements co-doped TiO_2 may have a better performance than that of single element doped and most of these studies are focused on two elements co-doping. However, most of these catalysts do not show long-term stability or do not have sufficiently high photocatalytic activities for a wide range of applications[19,23,20,28]. In this study, N, Zn, Fe were chosen to make co-doped TiO_2 and its catalyst ability was tested.

Nevertheless, these modified photocatalysts can not be easily retrieved after the reaction on account of their nanometer scales, which restricts their industrial application. These problems have motivated the development of supported photocatalysts, wherein TiO_2 is immobilized on the materials that facilitate phase separation. Among these supports, activated carbon (AC) was made excellent alternative because it could concentrate pollutants through adsorption around the loaded TiO_2 leading to an increase in the degradation of the pollutants[24]. Activated carbon was chosen as support media in this study.

The doping method of elements in the titania matrix and coating of catalyst onto surface of a support are impregnation, metal organic chemical vapor deposition and sol-gel techniques. Among these methods, sol-gel method has the superiority of low-cost, low-temperature processing and good shaping ability and was chosen in this paper for the preparation of TiO_2/AC composites. So this study aims at characterizing the properties of this novel catalyst and test its photocatalytic oxidation activity for degradation of toluene.

EXPERIMENTAL

Materials and catalyst synthesis: All reagents used were of analytical grade and employed as received. Tetrabutyl titanate, urea were purchased from Sino-pharm Chemical Reagent Co. Ltd. Anhydrous ethanol, glacial acetic acid, zinc nitrate, iron nitrate and granular activated carbon were obtained from Tianjin Chemical Reagent Co. Ltd. 18 MΩ deionized water (H_2O) was used to prepare the solutions.

Synthesis of catalyst: 200 g granular activated carbon was washed with water, then soaked in 10 % dilute nitric acid for several hours, placed in ultrasonic cleaning machine washed 2 times to neutral for 0.5 h, dried for 2 h in oven. At room temperature, 17 mL (0.05 mol) of tetrabutyl titanate was added to 30 mL of anhydrous ethanol, magnetic stirred for 0.5 h to be uniform to a yellow solution a; 28.32 mL of anhydrous ethanol, 20 mL of glacial acetic acid, 7.2 mL of distilled water, and certain amount of urea, zinc nitrate, iron nitrate were mixed to form a solution b, which was reserved in a separatory funnel. Stirred by magnetic, the solution b was added to the solution a slowly, a transparent sol was obtained. Then 30 g granular activated carbon were added to the sol to be loaded. After aging for 10 h in the electric oven, calcined at 773 K for 2 h, then the catalyst was obtained.

In step (3), the molar ratios of N to Ti were set as 1:0, 1:0.2, 1:0.3, 1:0.4 and other steps were unchanged to find the best N to Ti ratio as 1:4; then the molar ratios of N:Zn:Ti as 1:0.4:0.001, 1:0.4:0.005, 1:0.4:0.1 and other steps were unchanged to find the best N:Zn:Ti as 1:0.4:0.005, then the best N:Zn:Fe:Ti as 1:0.4:0.0015:0.01, 1:0.4:0.005:0.05, 1:0.4:0.05:0.1 and other steps were unchanged to find the best N:Zn:Fe:Ti as 1 :0.4:0.005:0.1.

Characterization of photocatalysts: X-ray diffraction was used to determine the phase composition of the samples, weight fractions of each phase and crystallite size. The crystalline phase was identified by X-ray diffraction (D/max2500PC, Japan) using CuK_α as radiation ($\lambda = 0.15406$ nm) with a voltage of 36 kV and current of 100 mA. The crystalline size was calculated from half maximum (FWHM) of XRD measurement by applying the Scherrer's formula. Fourier transform infrared spectroscopy (FT-IR) was used for the infrared analysis of membranes, operating conditions were: spectrometer resolution of 4 cm^{-1}, scan times of 32, measurement range 4000-400 cm^{-1}, DTGS detector (Deute-rated sulfuric acid three glycoside peptide). Optical absorption spectra of samples were measured in UV-visible spectrophotometer at the wavelength of 250-700 nm by using diffuse scattering method.

Photochemical reaction: In the photocatalytic activity studies, 2.5 mg/m^3 catalysts was put in a glass cube reactor (a volume of 1.5 m^3) with an initial toluene concentration of 26 mg/m^3 for 2 h. Concentration of toluene was determined by acetylacetone spectrophotometric method (GB/T15516-1995).

RESULTS AND DISCUSSION

Characteristics of investigated N-doped TiO_2: Fig. 1 shows the XRD patterns of pure TiO_2 and N, Zn, Fe-TiO_2. As displayed in the graph, the XRD peak of crystal plane (101) for anatase appeared at 25.48 (2θ) and crystal plane (110) for rutile appeared at 27.58 (2θ), which is in agreement with the literature report. The mass fraction of anatase in the samples were calculated from eqn. (1),

$$X_A = \frac{1}{1 + \frac{I_R}{I_A K_2}} \qquad (1)$$

where X_A is the mass fraction of anatase in the samples, I_A and I_R are the X-ray integrated intensities of (101) peak of the anatase and (110) peak of rutile, respectively. The crystalline size was calculated from half maximum (FWHM) of XRD measurement by applying the Scherrer's formula as followed:

$$L = \frac{K_\lambda}{\beta_{1/2} \cos\theta} \qquad (2)$$

where K is a constant (shape factor, about 0.89), λ is the X-ray wave length (2.1883 nm), $\beta_{1/2}$ is the FWHM of the diffraction line (0.1332) and θ is the diffraction angle (2θ = 48°).

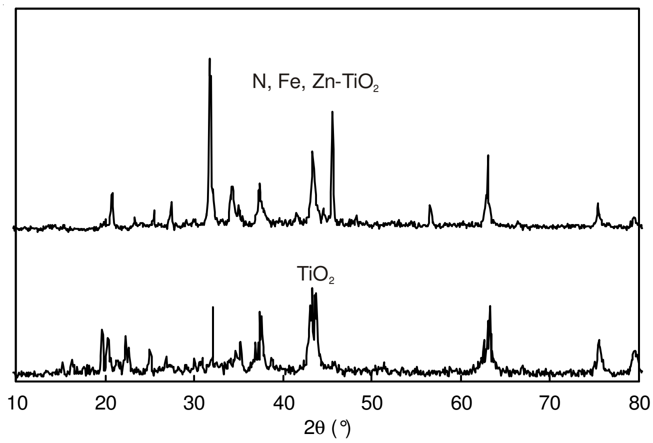

Fig. 1. XRD atlas of activated carbon load N, Fe, Zn-TiO_2 composite film

In this study, the content of anatase in N, Zn, Fe-doped TiO_2/AC is 90.3 %, that of anatase: rutile = 9:1, which shows the TiO_2 photocatalytic with high efficiency. Calculated from eqn. (2), the average grain size of TiO_2, N, Zn, Fe-TiO_2 are 20.18 and 16.02 nm, respectively. Compared with the XRD patterns of TiO_2 the catalyst has a strong peaks of TiO_2 near 25.3°, but its diffraction peak intensity is weak, this is because that the N, Zn, Fe incorporation inhibits the growth of grain, promotes the increasing of surface area rapidly, thus enhances the absorption of substrate and catalytic reaction. As the doping ions are embedded or replaced into the TiO_2, they formed homogeneous solid material, so there is no strong peaks of N, Zn, Fe seen in the Fig. 1.

In Fig. 2, the optical absorption spectra of the catalyst samples are compared with pure TiO_2. Pure TiO_2 of a single phase of anatase shows a clear absorption edge at around 320 nm, as reported by previous workers on anatase samples and no absorption in visible light region above 380 nm is observed. For nano-TiO_2 samples, some absorption of visible light is observed due to N, Zn, Fe support. That is to say, there is a red shift in the band gap transition of the doped TiO_2 samples, which resulted in more photogenerated electrons and holes participating in the photocatalytic reactions under visible light.

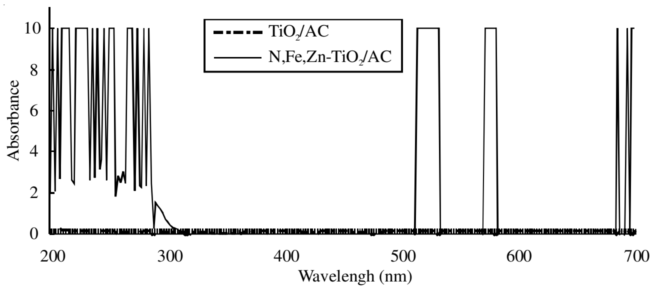

Fig. 2. UV-visible spectral chart of activated carbon load N, Zn, Fe-TiO_2 composite film

Fig. 3 showed that there are absorption peaks around 3400 and 1600 cm^{-1} on the surface of N, Zn, Fe-TiO_2, which means there are stronger stretching vibrations of surface physical absorbed water O-H and absorbed water O-H, respectively, which enhance catalytic reaction rate. Therefore, more O-H radicals were produced in the photocatalytic oxidation reaction and more toluene was degraded.

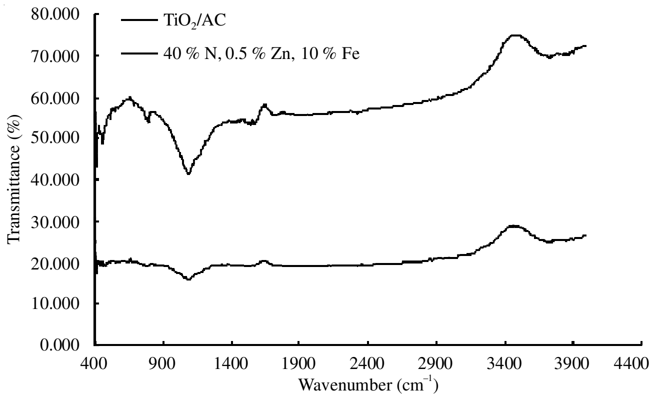

Fig. 3. FT-IR spectra of activated carbon load N,Fe,Zn composite film

Factors affecting catalyst activity: The effect of catalyst concentration on catalyst activity with an initial toluene concentration of 0.84 mg/m^3 under 40 W visible light is shown in Fig. 4.

It can be found that the degradation rate of the catalyst increases with the increasing of catalyst concentration. For a catalyst concentration of 0.84 mg/m^3, the 2 h degradation rate is only 59.5 %. When the catalyst concentration is 2.5 mg/m^3, within 2 h degradation rate can grow up to 92.2 %. When the catalyst concentration is 4.2 mg/m^3, the degradation rate can reach 98.96 % in 2 h. The degradation rate increases slower when the catalyst concentration is more than 2.5 mg/m^3.

The effect of initial formaldehyde concentration on catalyst activity of 2.5 mg/m^3 under 60 W visible light catalyst is shown in Fig. 5.

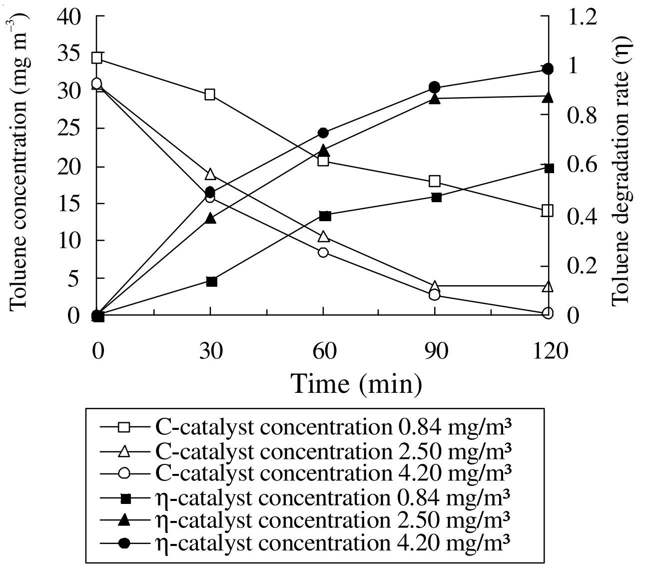

Fig. 4. Effect of initial catalyst concentration on catalyst activity

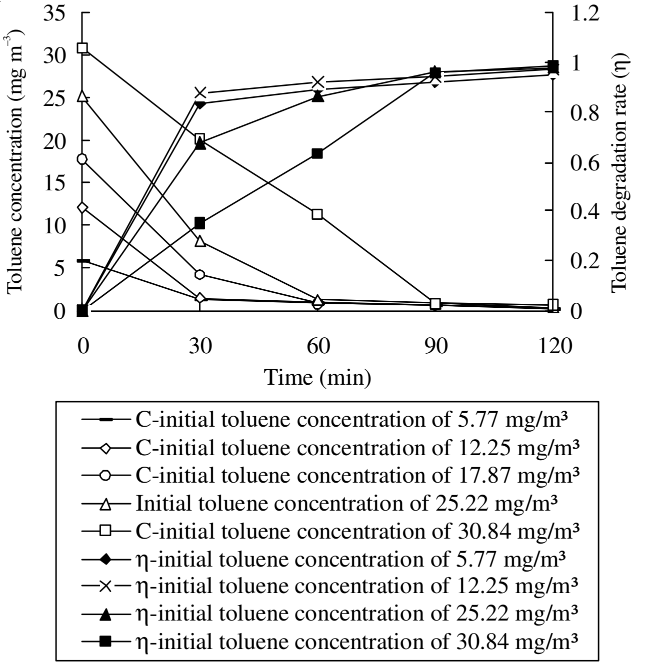

Fig. 5. Effect of initial toluene concentration on catalyst activity

It can be found that for an initial toluene concentration of no more than 30.84 mg/m^3, formaldehyde can be completely degraded (98.20 %) in 2 h. For a concentration of no more than 10.5 mg/m^3, formaldehyde can be completely degraded more than 90 % in 0.5 h.

The effect of light intensity of 2.5 mg/m^3 catalyst activity on toluene is shown in Fig. 6.

It can be found that without light, the degradation of the catalyst can only be 20.26 % after 2 h. Its catalyst activity can be enhanced with increasing of light intensity. Under 60 W visible light. Its degradation efficiency can be 99.48 % after 2 h, which can be easily achieved in our everyday life.

After dried at 293K in oven, the N, Zn, Fe-TiO_2/AC photocatalysts ability was reused for 2 times with a catalyst concentration of 2.5 mg/m^3 under 60 W visible light. The results are shown in Fig. 7.

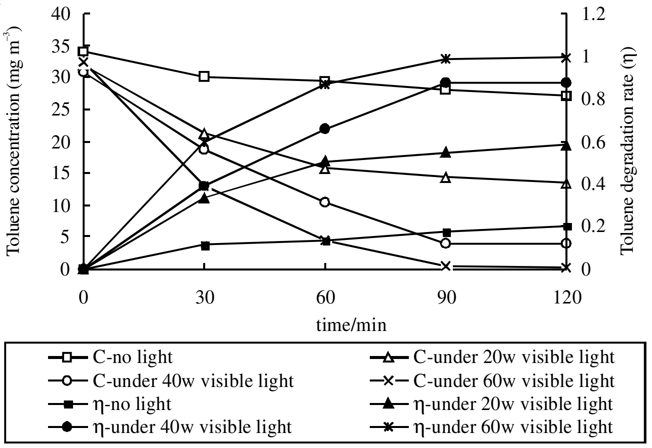

Fig. 6. Effects of light intensity on catalyst activity

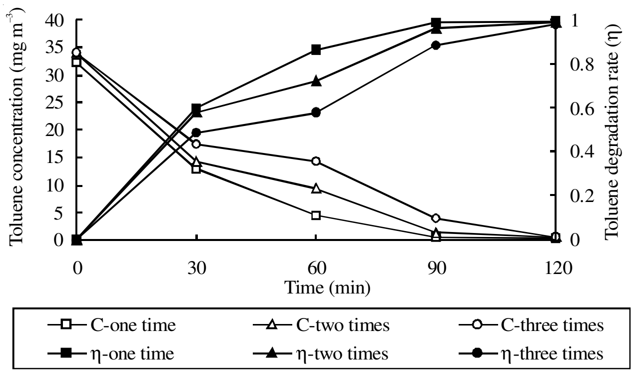

Fig. 7. Retrievability of photocatalysts

It can be seen that a degradation rate with a slight decrease but still over 99 % is observed in comparison with the 1st time, which means that the photocatalyst can be reused for times without large degradation rate decreasing.

Kinetics study of toluene removal using co-doped TiO_2: To investigate the ability of interstitial co-doped catalyst to remove a hazardous pollutant from gas, synthesized TiO_2 was used in the photocatalysis process of toluene degradation in gas phase.

The photocatalytic reactivity of various types of co-doped catalyst was represented by the ratio of residual concentration to initial concentration of toluene, C/C_0, as a function of irradiation time (Fig. 8).

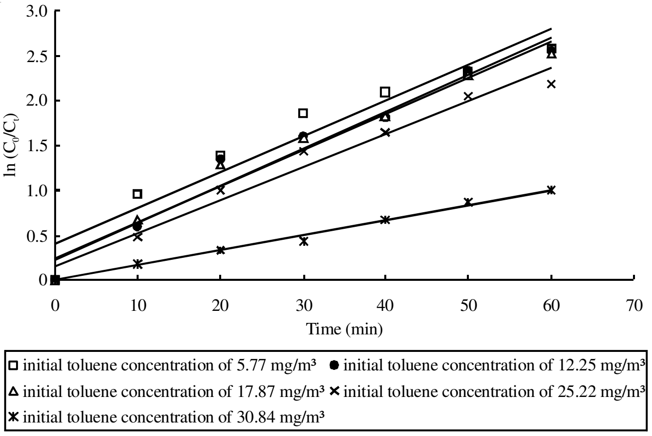

Fig. 8. $\ln(C/C_0)$ *versus* reaction time for toluene

Previous kinetic studies on photocatalytic reactions of N-doped TiO_2, the reaction can be well explained by a pseudo-first-order pattern, with the following equation demonstrating the relationship of C and t:

$$\ln\frac{C}{C_0} = -kt \tag{3}$$

where k is the apparent reaction rate constant, t the reaction time, C_0 the initial concentration of toluene in aqueous solution and C is the residual concentration of toluene at time t. The value of k was determined from the slope of the graph plotted between $-\ln(C/C_0)$ and the reaction time (Fig. 8). The R^2 value for linear regression was calculated to exhibit the tendency of the reaction, which followed the pseudo-first-order reaction. Values of initial rate, r, kinetic constant, k and the half-life of toluene, $t^{1/2}$, calculated from the pseudo-first-order equations are shown in Table-1.

TABLE-1
REGRESSION EQUATION UNDER VARIOUS TOLUENE CONCENTRATION

Initial toluene concentration (mg/m^3)	Regression equation	R^2	Apparent reaction rate constant (K_0)
5.77	$\ln C_0/C_t) = 0.0397t + 0.4018$	0.9271	0.0397
12.25	$\ln (C_0/C_t) = 0.0414t + 0.2188$	0.9626	0.0414
17.87	$\ln (C_0/C_t) = 0.0404t + 0.2391$	0.9674	0.0404
25.22	$\ln (C_0/C_t) = 0.0369t + 0.1494$	0.9733	0.0369
30.84	$\ln (C_0/C_t) = 0.0168t - 0.0074$	0.9925	0.0168

It can seen that the R^2 of the regression equation are no less than 0.9271, so the N, Zn, Fe-doped TiO_2 can also be accord with a pseudo-first, order reaction.

Heterogeneous photocatalytic reaction rate: Heterogeneous photocatalytic reaction can be explained by the (L-H) equation as follows:

$$\frac{\ln\left(\frac{C_0}{C}\right)}{C_0 - C} = kK\,\frac{t}{C_0 - C} - K \tag{4}$$

where k is the photocatalytic reaction rate constant and K is the Langmuir adsorption constant. Using Langmuir- Hinshelwoo equation, the plot between $\frac{\ln\left(\frac{C_0}{C}\right)}{C_0 - C}$ *versus* $\frac{t}{C_0 - C}$ show the linear relation with different initial toluene concentrations. Value of K, k are shown in Table-2.

TABLE-2
(L-H) EQUATION VALUE FOR TOLUENE

Initial toluene concentration (mg/m^3)	k (mg m^{-3} min)	K (m^3 mg^{-1})	kK (min^{-1})	R^2
5.77	0.4029	0.0958	0.0386	0.8706
12.25	1.5358	0.0265	0.0407	0.9337
17.87	1.9701	0.0201	0.0396	0.932
25.22	3.9782	0.0092	0.0366	0.9521
30.84	17.889	0.0009	0.0161	0.9701

It can be seen in Table-2 that under the initial toluene concentration of 5.77-30.84 mg/m^3, the k increases and K decreases with the increasing on initial toluene concentration. It can be explained that under lower toluene concentration, the toluene adsorbed into catalyst can be quickly degraded and then more toluene should be adsorbed for forthcoming degradation, so the value of K is large and k is small. While under higher toluene concentration, the toluene complementary access decreases, so k dereases and K increases.

Conclusion

N, Zn, Fe-doped TiO_2 was developed to enable photocatalytic reactions using the visible light. Results show that N, Zn, Fe-TiO_2/AC is the mixed crystal of anatase and rutile, the photocatalyst has an average diameter of 16 nm and its band gap was reduced to 2.9 eV and its absorption of light from the 320nm wavelength range extended to 500-700 nm and at 320 nm, the absorption increases a slight. After N, Zn, Fe ions doping, in the visible condition, TiO_2 showed excellent catalytic ability of gas phase toluene degradation more thoroughly. For an initial toluene concentration of no more than 30.84 mg/m^3, toluene can be completely degraded (98.20 %) in 2 h. And degradation rate accords with first order and its L-H equation value is also got.

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