

# Impacts of SiO<sub>2</sub> Shell Structure of Ni@SiO<sub>2</sub> Nanocatalysts on Their Performance for Catalytic Decomposition of Ammonia

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Abstract Various core-shell structured Ni@SiO<sub>2</sub> nanocatalysts were prepared to provide an insight into the intrinsic effects of shell structures on the ammonia decomposition activity. The thickness of silica shell structure can be fine tuned in the range of 5–20 nm. With the increase in shell thickness, it was found that the catalytic activity did not decrease obviously, even though the reducibility determined by H<sub>2</sub>-TPR exhibited a noticeable changes. As for the porosity of the shell, the SP-1 sample with a well-developed pore structure showed better catalytic performance than the SP-0 sample with a less-developed pore structure. It can be concluded that diffusion limitations would be greatly influenced by shell porosity nor shell thickness to some extent.

**Graphical Abstract** Various core-shell structured Ni@  $SiO_2$  nanocatalysts were prepared to provide an insight into the intrinsic effects of shell structures on the ammonia decomposition activity. The thickness and porosity of silica shell structure were fine tuned. It was concluded that diffusion limitations would be probably greatly influenced by shell porosity nor shell thickness to some extent.

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## **1** Introduction

Recently, core–shell structured materials have attracted great attentions for their unique structural feature and physicochemical properties [1–4]. They consist of a nanosized catalytic active core that is coated by a porous, thermally stable support. The shell materials not only hinder the aggregation of neighboring particles, even under harsh reaction conditions, but also provide channels for reactants accessible to cores.

Based on this concept, a series of core-shell structured catalysts have already been developed for catalytic application. Most of the investigated systems consist of Au or Pt nanoparticles in a metal oxide shell, such as silica [5, 6], zirconia [7], tin oxide [8], carbon [9], or cobalt oxide [10]. However, all of these reactions are

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performed far below 400 °C, although the presented shell materials can principally be used for reactions at higher temperatures, in which sintering processes play a more crucial role [8]. Some core–shell structured nanocatalysts are also developed for high temperature reaction, for examples, Ni@SiO<sub>2</sub> [11, 21] and NiCo@SiO<sub>2</sub> [12] and their modified catalysts [13] for partial oxidation of methane reactions, Ni@Al<sub>2</sub>O<sub>3</sub>, Ru@SiO<sub>2</sub> and Ni@MgO, Ce-doped Ni@SiO<sub>2</sub> for NH<sub>3</sub> decomposition reactions [14–16] and Pd@CeO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> [17] for methane combustion reactions. Consequently, the shell can prevent the core from aggregating or sintering into lager particles, which keeps a long time stability under high temperature conditions.

Besides the protection function of core-shell structural catalysts, this novel structure, including shell thickness and porosity, as well as the core particle size, also greatly influence the catalytic performance. As wellknown, adsorption of reactants on the surface of the active phase of the catalyst is necessary for reactions to take place, engineering the porosity of shell materials makes it possible to control the diffusion of reactant species and the reaction kinetics. However, up to date, there are few studies on the relationship between the shell structure and catalytic performance [18–22]. An understanding of the parameters that affect the diffusion of molecules through the shells of these structures may give rise to the design and synthesis of new catalysts.

Ammonia decomposition is an important reaction in at least two different fields related to energy and environmental science: it can be used to provide CO<sub>x</sub>-free hydrogen for fuel cells, and to remove ammonia from the reformate of internal gasification combined cycle (IGCC) power plants which might be widely deployed in the future as a  $CO_2$ -removal technology [23, 24]. For hydrogen production, ammonia decomposition requires temperature above 400 °C for thermodynamic reasons. As it is reported that complete conversion of ammonia take place at around 500 °C for Ru-based catalysts [26-32], at around 700 °C for other metals, such as Ni, Co or Fe, etc. [33–40] Therefore, highly active catalysts at low temperatures are required, but the high-temperature stability and long lifetime of the catalysts applied is a more crucial issue.

Herein, on the basis of the high temperature stability of core-shell structured nanocatalysts, we give a new insights into the correlations between shell structure (including shell thickness and porosity) and ammonia decomposition activity. The occurrence of diffusion limitations and their consequences in connection with the shell structure are illustrated through some physical and chemical characterizations.

#### **2** Experimental Section

## 2.1 Catalyst Preparation

#### 2.1.1 Preparation of NiO Nanoparticles (NPs)

Typically, 2.9 g of Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O was dissolved in 40 mL of deionized water, and the solution was added dropwise into a solution that contained 100 mL of deionized water and 330 mg of polyethylene glycol (PEG) (average MW = 20,000, Fluka) and 1.0 g NaOH. The resulting solution was stirred for 1 h at room temperature (RT). The collected material was then washed several times with deionized water and ethanol, dried at 50 °C for 24 h, and calcined in air at 400 °C for 3 h.

## 2.1.2 Preparation of NiO@SiO<sub>2</sub> Core–Shell Structured Catalyst

The core-shell structured NiO@SiO<sub>2</sub> samples were prepared by a modified Stöber method [11]. Typically, 0.1 g of NiO NPs was added to a poly-(vinylpyrrolidone) (PVP, K30, 1.0 g) ethanol solution of 100 mL. After the solution was stirred for 12 h, NH<sub>3</sub>·H<sub>2</sub>O (25 wt%) of 10 mL was added, and then the suspension was sonicated for 30 min in an ultrasound cleaner (KQ-100DE, 40 kHz, 100 W). Subsequently, an ethanol solution (5 mL) of tetraethyl orthosilicate (TEOS, P99%, Aldrich) of 0.1 mL was injected into the suspension. One hour later, the product was collected by centrifugation, washed twice with distilled water and ethanol, and dried at 80 °C in air for 6 h. Then the coreshell samples were further calcined at 550°C for 3h for removing surfactant. For comparison, the core-shell structured NiO@SiO<sub>2</sub> samples were prepared with two kinds of surfactants (mass ratio of PVP/CTAB = 1/4, Hexadecyl trimethyl ammonium Bromide). And they were labeled as SP-0 and SP-1 for distinguishing the porosity of the shell respectively. Similar to above preparation process, the shell thickness was controlled by tuning the amount of TEOS. The samples were denoted as ST-x, where x represented the mean shell thickness (5-20 nm)as determined by TEM images.

## 2.2 Catalyst Characterization

 $N_2$  sorption measurement was performed on a NOVA-2020 material physical structure determinator. Before measurement, the sample was degassed at 300 °C for 3 h. The BET surface area was calculated from a multipoint BET analysis of the nitrogen adsorption isotherms. The X-ray powder diffraction (XRD) patterns were recorded on a Philips X'Pert MPD Pro X-ray diffractometer with graphite-monochromatized Cu Karadiation (K $\alpha$ =0.1541 nm).

The TEM images were taken over a JEOL JEM-2000EX instrument operated at 100 kV. The HRTEM images were obtained with a Philips Tecnai G220 operated at 200 kV. Hydrogen temperature programmed reduction (H<sub>2</sub>-TPR) was carried out using a TP-5080 multi-purpose automatic adsorption instrument. In typical runs, 30 mg of NiO@ SiO<sub>2</sub> was heated to 120 °C at 10 °C/min under Ar flow of 50 mL/min and kept at this temperature for 1 h to remove adsorbed water. After the sample cooled down to RT and was switched to a 10% H<sub>2</sub>/N<sub>2</sub> (v/v, 50 mL/min) mixture, the sample temperature was programmed to 650 °C at 10 °C/min.

## 2.3 Catalytic Activity

Catalytic activity was evaluated in a continuous-flow quartz reactor. In a standard experiment, 25 mg of powder catalyst was placed on quartz wool in the reactor with an inner diameter of 6 mm. Before reaction, the catalyst was reduced in situ in a 25% H<sub>2</sub>/Ar flow at 550 °C for 2 h, then purged with a flow of pure Ar. Subsequently, the temperature was decreased to 350 °C and the gas flow was switched to pure NH<sub>3</sub>. For temperature-dependent conversion measurements of NH<sub>3</sub>, the NH<sub>3</sub> flow was fixed at 30,000 mL/ g<sub>cat</sub>/h, and the temperature was varied between 400 and 700 °C in 50 °C steps. For each temperature, four values were recorded within 30 min under steady-state conditions using an on-line gas chromatograph (GC9860). The GC is equipped with a thermal conductivity detector (TCD) and Poropak Q column to detect NH<sub>3</sub> in a carrier gas flow of H<sub>2</sub>. NH<sub>3</sub> conversion in a blank reactor was <1.0% at 600°C.

## **3** Results and Discussion

## 3.1 XRD Characterization

Figure 1 shows the XRD patterns of the typical prepared core–shell structured NiO@SiO<sub>2</sub> and reduced Ni@SiO<sub>2</sub> nanocatalysts. The original nickel oxides nanoparticles were obtained by calcining amorphous nickel hydroxide at 400 °C for 3 h. Then, NiO NPs were coated with silica through the modified stöber method. The corresponding samples show only the fcc-NiO phase (JCPDS No. 78-0429) with typical reflections of the (111), (200), and (220) planes at  $2\theta = 37^{\circ}$ ,  $43^{\circ}$  and  $64^{\circ}$ , respectively. After in-situ reduction, the NiO entities were completely transformed into elemental Ni<sup>0</sup>, as revealed by the reflections of the (111), (200), and (220) planes at  $2\theta = 44^{\circ}$ ,  $52^{\circ}$  and  $76^{\circ}$  (JCPDS No. 04-0850). In addition, no peaks of SiO<sub>2</sub> crystalline phases can be identified, suggesting the SiO<sub>2</sub> shells are essentially amorphous. It can be observed that a

(111)Intensity (a.u.) (200)After Reduced (220)(200)(111)(220)As synthesized (311)10  $\dot{20}$ 30 40 50 60 70 80 **2θ/°** 

Fig. 1 XRD patterns of typical NiO@SiO $_2$  (SP-1) sample: As synthesized and after reduced

weak drum peak occurs at around 23°. Through calculation from the Scherrer equation, the crystallite size of NiO NPs is 9.2 nm based on the NiO (200) reflection peaks. When calculation has been done according to other three diffraction peaks, the crystallite size of NiO NPs is 10.2m, 9.2 and 9.7 nm respectively. Therefore, the mean size of NiO NPs is ca.10 nm. After in-situ reduction, core-shell structured Ni@SiO<sub>2</sub> catalysts are obtained with a crystallite size of 13.2 nm, which is calculated from the Ni (111) reflection peak. According to our previous research [11], due to the dispersion of NiO NPs in ethanol solution, it is hard to realize 100% single-particle encapsulation, and there is a certain degree of multiparticles encapsulation. Thus, compared with the mean size of original NiO NPs, the mean size of Ni NPs enwrapped in silica shell becomes large after in-situ reduction.

#### 3.2 TEM Characterization

TEM images of the non-reduced catalysts with various silica shells are presented in Fig. 2. As core materials, NiO NPs exhibit a nearly homogeneous and monodisperse, with a mean size of  $9.1 \pm 1.6$  nm (Fig. 2a, b). When calculation has been done from their special surface area, the mean size of NiO NPs is 10.7 nm (Table 1). This is consistent with the mean size of NiO NPs obtained by XRD and TEM characterization. The encapsulation of the NiO with silica was achieved by means of the base-catalyzed hydrolysis of tetraethylorthosilicate (TEOS) in an ethanol/water mixture. Seen from Fig. 2c–f, all catalysts show the core–shell morphologies with NiO well encapsulated by the silica shells. As well-known, the preparation of well defined core–shell structures is only possible if a homogenous distribution of the colloids via the classic Stöber process. However, the



Fig. 2 TEM images a, b NiO nanoparticles and their size distribution; c ST-5 sample; d ST-10 sample; e ST-20 sample (or SP-0); f SP-1 sample

as-prepared NiO NPs would precipitate under the reaction conditions before the coating step, so their surfaces needed to be modified with polyvinylpyrrolidone (PVP). Owing to the assistant of amphiphilic and nonionic PVP polymer, colloidal particles are easily coated with homogeneous silica shells [41]. And the remaining PVP in silica shell can be removed by calcination, resulting a high surface area, which are further verified by BET characterization.

As for the thickness of silica shell, it is well tuned by changing the amount of TEOS. It is observed that the silica shell thickness increases obviously with the increased dosage of TEOS (Fig. 2c–e). By precisely controlling the amount of TEOS and its hydrolysis time, the thickness can be tuned from ca.5 to ca.10 and ca.20 nm, corresponding to ST-5, ST-10 and ST-20. The mean thickness size is roughly counted by TEM image. In addition, the porosity of silica shell is tuned by introducing another surfactant. CTAB as a cationic surfactant, which is different from PVP, was added together with PVP during the synthesized process. Note that when the CTAB surfactant is introduced,  
 Table 1
 Characteristics of NiO@SiO2 samples with different shell structure

Samples	Si/Ni molar ratio (nominal)	Metal loading (wt%) <sup>a</sup>	$S_{BET} (m^2/g)$	Pore volume (cm <sup>3</sup> /g)	Shell thickness (nm) <sup>b</sup>
NiO	_	100	84.2	_	_
ST-5	0.17	82.2	52.3	0.08	5.0
ST-10	0.34	67.6	80.6	0.10	10.0
ST-20 (SP-0)	0.67	50.1	104.5	0.13	20.0
SP-1	0.67	52.8	341.3	0.18	20.0

<sup>a</sup>Measured by H<sub>2</sub>-TPR, calculation based on the quantity of NiO NPs sample

<sup>b</sup>The approximate mean shell thickness was determined by TEM images

the core–shell structure keeps well for SP-1 sample. And the mean thickness size of  $SiO_2$  shell is ca.20 nm, which is similar to ST-20 (SP-0) sample (Fig. 2e). It indicates that the silica shell thickness is affected little by this kind of surfactant under the same preparation condition. In fact, compared with SP-0 sample, the SP-1 sample has a high surface area after the use of CTAB surfactant, which is further verified by BET results.

## 3.3 N<sub>2</sub> Sorption Characterization

Figure 3 presents the  $N_2$  adsorption–desorption isotherms and the corresponding pore size distribution curves of core–shell structured NiO@SiO<sub>2</sub> catalysts with different shell structure. Seen from the adsorption–desorption isotherms, it shows that no matter SP-0 or SP-1 sample exhibits a typical type-IV isotherms with a hysteresis loop and the capillary condensation occurred at values around P/  $P_0 = 0.4$ . Note that the pore structure of SP-0 and SP-1 sample is different. For SP-1 sample, besides of mesopores, a rapid increase of sorption occurs at a relatively lower pressure, indicating that some micropores exist in silica shell. As for SP-0 sample, the N2 adsorption-desorption isotherms show two hysteresis loops, especially at a relatively higher pressure. This means that the pore structure in shell is irregular. Moreover, the mesoporous silica shell had a narrow pore size distribution centered at 2.1 and 5.0 nm for SP-1 and SP-0 samples, respectively (Right, Fig. 3). Previous studies suggested that a certain number of mesopores would be formed during coating process with an assistant of PVP surfactant [11, 42]. It is well known that the strong interaction between PVP and CTA<sup>+</sup> is very effective for the subsequent mesoporous silica shell formation [43]. More mesopores and larger surface area can be obtained with an addition of CTAB [44, 45]. And their textural properties are placed in Table 1. It is observed that the surface area





raises from 52.3 to 104.5  $m^2/g$  with an increase on silica shell thickness. Compared with the SP-0 sample, the SP-1 sample shows a larger surface area of 341.3  $m^2/g$ , indicating a well-developed porosity.

#### 3.4 H<sub>2</sub>-TPR Experiments

In order to characterize the reducibility of NiO NPs and the possible metal–support interactions,  $H_2$ -TPR experiments were carried out. Figure 4 illustrates the  $H_2$ -TPR profiles of various NiO@SiO<sub>2</sub> samples. For a quantitative analysis of the content of Ni over various catalysts, the pure NiO sample was chose as a target reference. The Ni contents of corresponding sample are determined by comparing the  $H_2$  reduction peak areas. And the calculation results are placed in Table 1. No doubt that the sample with a thin silica shell shows a high Ni content. The Ni contents of SP-0 sample is similar to that of SP-1 sample.

Seen from Fig. 4, the tested pure NiO sample exhibits a broad reduction peak in the range of 200-400 °C. Obviously, all core-shell structured samples present a higher reduction temperature than pure NiO sample. Due to silica shell protection, the rate of H<sub>2</sub> diffusion becomes slow. Compared to the supported catalysts, the coreshell structured catalysts were difficult to be reduced, as a result of the stronger core-shell interaction [44, 46]. Thus, a possible core-shell interaction might exist in our studied catalyst. Note that there is no reduction peak at around 600 °C, indicating the absence of nickel silicate species. This is consistent with above XRD characterization. Moreover, we also observed that there is a continuous peak shift towards higher temperature as the shell thickness increased, which may be resulted from the rate of hydrogen diffusion. For SP-1 sample, the shell with a

highly developed porous structure, shows a broader and lower reduction temperature than SP-0 sample. It suggests that highly developed porous structure facilitate small molecular diffusion to the core part.

## 3.5 Catalytic Performance of NH<sub>3</sub> Decomposition

The catalytic activities of the prepared core–shell structured Ni@SiO<sub>2</sub> catalysts for NH<sub>3</sub> decomposition as a function of reaction temperature are presented in Fig. 5. The results show a similar behavior that the ammonia conversions increased with the increase of the catalytic reaction temperature measured in the catalyst bed for all the catalysts, indicating faster decomposition at higher temperature. The approximately complete conversion is achieved over all catalysts at the temperature of 700 °C and GHSV of 30,000 mL/h/g.

Figure 5 shows that the catalytic activities of various core-shell structured Ni@SiO<sub>2</sub> catalysts at temperature ranging from 400 to 700 °C. It is observed that increasing the shell thickness leads to a slight decrease in the catalytic activity, especially at 550 and 600 °C (insert diagram of Fig. 5). The reasons might be attributed to varied Ni loading and diffusion effects resulted from shell thickness. Zeng et al. [20] found that the shell thickness did not significantly weaken the accessibility of the reactants to the active sites, which was attributed to the highly porous nature of the silica shell. Therefore, higher porosity of silica shell can be tuned by adopting CTAB as another surfactant component, which is confirmed by the BET results (Fig. 3; Table 1). Indeed, it is observed that the activity of SP-1 catalyst is better than that of



Fig. 4 H<sub>2</sub>-TPR profiles for various samples



Fig. 5 The activities of the core-shell structured Ni@ SiO<sub>2</sub> catalysts with different shell structure (reaction conditions: T = 400-700 °C; GHSV = 30,000 mL/h/g; mcat = 25 mg)

SP-0 catalyst, though they have a similar Ni loading. Previous studies also pointed out that the higher porosity of silica shell indeed enhance catalytic performance [14, 20, 22], indicating that diffusion effects played an important role during reaction process. Zhang et al. [22] described a "surface-protected etching" approach that conveniently converts dense coatings into porous shells so that chemical species can reach the core material to participate in reactions. The results indicated that the reaction rate could be controlled by varying shell porosity. However, direct characterization of diffusion processes in these system is difficult, and only a few examples have been reported of such studies to date, mostly in gas phase [18, 21] but also in liquids [19]. FTIR spectroscopy had been used to monitor the transport of CO to the cores of yolkshell nanostructures [21]. It was found that the mechanism of diffusion through the oxide shells was dominated by transport at the grain boundaries rather than at the pores.

The typical data of ammonia conversion and H<sub>2</sub> production are shown in Table 2. It is observed that the NH<sub>3</sub> decomposition activity decreases with an increase of shell thickness. However, the H<sub>2</sub> production over per gram of Ni increases with an increase of shell thickness,

suggesting that a lower utilization of Ni active phase and un-notable diffusion limitations. Owing to the internal diffusion effects, the conversion and H<sub>2</sub> production of SP-1 sample are higher than that of SP-0 sample. For comparison, Table 3 summarizes the catalytic performance of typical Ni@SiO<sub>2</sub> catalyst (SP-1) and other typical Ni-based catalysts reported previously for ammonia decomposition. Compared with other supported Ni catalysts reported in the literature under the same conditions, our prepared catalyst (SP-1) shows good catalytic performance. In terms of SP-1 catalyst, the stability in ammonia decomposition was tested at 600 °C for a period of 50 h. As shown in Fig. 6, ammonia conversion is almost constant, indicating a very stable catalytic performance at a high temperature. As mentioned in the introduction section, lots of core-shell structured nanocatalysts reported in the literature have a high-temperature stability.

In addition, the apparent activation energy of ammonia decomposition reaction  $(E_a)$  were obtained from the Arrhenius relationship between the rate constant (k) and the temperature (T), which can be described by the equation:  $\ln(k) = -E_{0}/RT + \text{constant}$ , and the results are listed in Table 2. It can be seen that the value of  $E_a$  is in the range from 77 to 82 kJ/mol for different catalysts. This result is

Table 2         The catalytic activities           of various catalysts	Samples	Conversion <sup>a</sup> (%)	H <sub>2</sub> production <sup>a</sup> (mmol/min/g <sub>cat</sub> )	H <sub>2</sub> production <sup>a</sup> (mmol/min/g <sub>Ni</sub> )	TOF <sup>a,b</sup> (mmol <sub>NH3</sub> /h/ mol <sub>Ni</sub> )	E <sup>a,c</sup> (kJ/mol)
	ST-5	72.0	24.2	27.6	62.0	82.3
	ST-10	69.2	23.1	31.0	69.7	82.1
	ST-20 (SP-0)	66.3	22.2	36.2	81.4	79.6
	SP-1	78.9	26.4	43.1	96.9	77.2

<sup>a</sup>The data were measured at 600 °C under pure NH<sub>3</sub> flow of 12.5 mL/min

<sup>b</sup>TOF units as reported for the literature data for a flow of 3 dm<sup>3</sup>/h [15, 52]; if calculated for NH<sub>3</sub> (data in text), TOF = V $\alpha$  / n, where V is the molar flow rate of NH<sub>3</sub>,  $\alpha$  is the conversion degree and n is the moles of Me NPs (Me<sub>NP</sub>)

<sup>c</sup>The apparent activation energy was measured under pure NH<sub>3</sub> flow at 400–500 <sup>°</sup>C

Samples	Temperature (°C)	Conversion (%)	H <sub>2</sub> production rate (mmol/min/g <sub>cat</sub> )	References
10% Ni/SiO <sub>2</sub>	600	36.4	11.4	[48]
65% Ni/SiO <sub>2</sub> -Al <sub>2</sub> O <sub>3</sub>	600	79.5	24.9	[48]
Ni/MCM-41 (TIE)	600	71.6	24.0	[49]
5% Ni/CNTs	500	_	2.9	[26]
Ni/Al <sub>2</sub> O <sub>3</sub>	600	_	32.6	[33]
Ni/CNFs	650	90.5	36.4	[50]
15% Ni/MRM	700	97.9	32.8	[51]
Ce10-NiO-SiO <sub>2</sub> -350	600	86.9	29.09	[47]
71%Nano-Ni@SiO <sub>2</sub>	600	_	25.6	[15]
Ni@SiO <sub>2</sub> (SP-1)	600	78.9	26.4	This study

Table 3 Comparison of the catalytic performance of Ni@SiO2 with several typical Ni-based ammonia decomposition catalysts at  $GHSV = 30\ 000\ mL/h/g_{cal}$ 





Fig. 6 Time course of ammonia decomposition at 600 °C using SP-1 as a catalyst. GHSV =  $30\ 000\ mL/h/g_{cat}$ 

comparable to the reported values of core–shell structured catalysts [14, 47]. Obviously, the SP-1 sample shows the lowest activation energy among all samples. It indicates that a weak difference over  $E_a$  values would be attributed to the difference of shell structure.

## 4 Conclusions

In summary, core–shell structured Ni@SiO<sub>2</sub> nanocatalysts with well tuned structure (shell thickness/porosity) were prepared, characterized and applied to catalytic ammonia decomposition. With increasing shell thickness, the NH<sub>3</sub> decomposition activity decreased slightly. While a distinct difference in activity was observed by tuning the porosity of silica shell. No matter the NH<sub>3</sub> conversion or H<sub>2</sub> production, the SP-1 sample with more developed pore structure showed better performance than the SP-0 sample. It was concluded that diffusion limitations would be probably greatly influenced by the shell porosity nor the shell thickness to some extent. An understanding of the parameters that affect the diffusion of molecules through the shells of these structures may give rise to the design and synthesis of new catalysts.

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