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NO reduction by CO over TiO_2 - γ - Al_2O_3 supported In/Ag catalyst under lean burn conditions

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ABSTRACT

$\text{TiO}_2/\gamma\text{-Al}_2\text{O}_3$ supported In/Ag catalysts were prepared by impregnation method, and investigated for NO reduction with CO as the reducing agent under lean burn conditions. The microscopic structure and surface properties of the catalysts were studied by N_2 adsorption-desorption, X-ray diffraction, transmission electron microscopy, X-ray photoelectron spectroscopy, ultraviolet-visible spectroscopy, H_2 temperature-programmed reduction and Fourier transform infrared spectroscopy. $\text{TiO}_2/\gamma\text{-Al}_2\text{O}_3$ supported In/Ag is a good catalyst for the reduction of NO to N_2 . It displayed high dispersion, large amounts of surface active components and high NO adsorption capacity, which gave good catalytic performance and stability for the reduction of NO with CO under lean burn conditions. The silver species stabilized and improved the dispersion of the indium species. The introduction of TiO_2 into the $\gamma\text{-Al}_2\text{O}_3$ support promoted NO adsorption and improved the dispersion of the indium species and silver species.

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1. Introduction

NO_x emission from automobiles leads to acid rain, photochemical smog and ozone depletion. Various reductants such as ammonia, urea, CO, CH_4 and other light hydrocarbons can be applied for the reduction of NO [1]. By considering that CO exists in car exhaust, it should be a very promising and economic agent for NO_x reduction [2]. Noble metals such as Ir [3], Pt [4], Pd [5] and Rh [6] show good activity for NO reduction by CO under lean burn conditions, with Ir [2] as the most active metal.

However, these noble metals are scarce in the Earth's crust and costly. Among non-noble metals, an Al_2O_3 supported Cu catalyst was reported to be effective for the reduction of NO with CO, but the activity was not very high [7]. As a replacement, an indium catalyst is considered a better candidate. Although indium is a rare metal at a worldwide scope, it is an available metal resource of China. The development of value-added rare metal catalysts (such as indium) is of great importance in China. Patel et al. [8] revealed that the metal-oxygen bond strength played an important role in a catalyst for the reduction of NO with CO.

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In₂O₃ would be a good catalyst due to its low In–O bond strength (180 kJ/mol) [9]. In addition, supported indium catalysts have shown significant activity in the reduction of NO_x under lean burn conditions [10–14].

Compared to single metal catalysts, bimetallic catalysts are often more efficient. Richter et al. [15] tested a series of Al₂O₃ supported catalysts comprising all the combinations of Ag, Co, Cu and In elements for the reduction of NO_x by propane under lean burn conditions. The results indicated that a synergistic effect existed between the silver and indium species. Moreover, Tanaka et al. [16] found that Ag and TiO₂ could be well dispersed at the nano scale on a TiO₂/Al₂O₃ support, thus it can be applied as a NO_x trapping material to improve the low temperature removal of NO_x from lean burn automobile exhaust. The reduction of NO by CO over a TiO₂/γ-Al₂O₃ supported In/Ag catalyst has not been studied previously. In this work, a TiO₂/γ-Al₂O₃ supported In/Ag catalyst was prepared by impregnation and its catalytic performance for the reduction of NO with CO under lean burn conditions was studied.

2. Experimental

2.1. Catalyst preparation

Commercial pseudo-boehmite powder was dried and calcined at 550 °C for 6 h to obtain γ-Al₂O₃. The TiO₂/γ-Al₂O₃ carrier was prepared according to a published procedure [17]. An amount of titanium isopropoxide was added to 20 mL of isopropyl alcohol solution followed by the addition of γ-Al₂O₃. Subsequently, the mixture was stirred for 8 h, dried at 120 °C and calcined at 550 °C for 6 h. The TiO₂ loading in the carrier was 15 wt%. The sample was denoted as TA, where T referred to TiO₂ and A referred to γ-Al₂O₃.

The TA supported In/Ag catalyst was synthesized by incipient wetness impregnation. The carrier material TA was impregnated with silver nitrate and indium nitrate solution and stirred for 2 h, then dried at 120 °C and calcined at 600 °C for 6 h. The contents of indium and silver of the catalyst were 8 wt%. The sample was denoted as InAg/TA. For comparison, γ-Al₂O₃ supported In/Ag (InAg/Al), TA supported In (In/TA), and TA supported Ag (Ag/TA) catalysts were prepared using the same method. The content of In or Ag of the catalysts was 8 wt%.

2.2. Catalyst characterization

The specific surface area was calculated by the BET equation using N₂ adsorption-desorption isotherms obtained with a Micromeritics ASAP 2020 apparatus. X-ray diffraction (XRD) measurements were carried out with a D/max-RB system using Cu K_α radiation. Electron microscope images of the samples were obtained by transmission electron microscopy (TEM) with a Japan JEOL microscope at 200 kV. X-ray photoelectron spectroscopy (XPS) was obtained using an Axis Ultra DLD electron spectrometer from VG Scientific using 300 W Al K_α radiation. Ultraviolet-visible spectra (UV-vis) were recorded using a Perkin Elmer Lambda 650 spectrometer in the diffuse reflectance mode. H₂ temperature-programmed reduction (H₂-TPR)

was performed on a Micromeritics Autochem 2920 equipment with a thermal conductivity detector (TCD) from room temperature to 700 °C. Fourier transform infrared spectroscopy (FTIR) measurements were performed using a Nicolet NEXUS-6700 with a MCT detector. The catalyst samples were pretreated in situ for 1 h at 400 °C in He flow, then cooled to 30 °C. A background spectra was recorded and subtracted from the sample spectra. The spectra were measured in flowing NO/He with a heating rate of 10 °C/min.

2.3. Catalytic activity measurements

The catalytic activity was tested in a fixed bed quartz reactor. Reactant gas consisting of 0.72% NO, 2.1% CO, 1.0% O₂, and He as balance at a GHSV = 7000 h⁻¹ was introduced into the reactor. The catalyst was left to stabilize for 30 min after each change of temperature. The gas composition was analyzed by a Varian CP-3800 gas chromatograph (GC) equipped with a TCD and a 5 Å molecular sieve column (2 m × 3 mm). The NO conversion was calculated by $2[\text{N}_2]_{\text{outlet}}/[\text{NO}]_{\text{inlet}} \times 100\%$, where $[\text{N}_2]_{\text{outlet}}$ and $[\text{NO}]_{\text{inlet}}$ were the concentrations of outlet N₂ and inlet NO, respectively. The CO conversion was expressed as $([\text{CO}]_{\text{inlet}} - [\text{CO}]_{\text{outlet}})/[\text{CO}]_{\text{inlet}} \times 100\%$, where $[\text{CO}]_{\text{inlet}}$ and $[\text{CO}]_{\text{outlet}}$ were the concentrations of inlet and outlet CO, respectively.

3. Results and discussion

3.1. Catalytic activity evaluation

In/TA, Ag/TA, InAg/Al, and InAg/TA were applied as catalysts for the reduction of NO with CO under lean burn conditions. Fig. 1(a) reflects the catalytic activity of the different samples for the reduction of NO to N₂ at different temperatures. In the case of In/TA, the onset temperature was about 400 °C, and a rapid increase of the N₂ yield was observed above 400 °C. Ag/TA displayed a lower onset temperature (300 °C) as compared to In/TA. Obviously, the silver species significantly lowered the onset temperature for the reduction of NO with CO under lean burn conditions. For InAg/TA and InAg/Al, the onset temperature was 250 and 300 °C, respectively, similar to that of Ag/TA and lower than In/TA. The data also reflected that the activities of the single metal catalysts were lower than that of the bimetallic catalyst (Fig. 1(a)). Liu et al. [14] have reported the catalytic performance of a Co-In/Al₂O₃ catalyst for the selective reduction of NO by propene and found that the Co significantly improved the activity. Duane et al. [18] found that the silver species of a Ag-Pd/Al₂O₃ catalyst also played an important role in improving NO conversion for the NO-CO reaction. Our observations were in good accord with these published results. InAg/TA showed the highest catalytic activity measured as N₂ yield among the different catalysts (> 60% at 550–600 °C). The selective catalytic reduction of NO_x using either methane or butane as the reducing agent over In/Fe-zeolite has been reported by Serra et al. [19]. However, only < 55% N₂ yield was achieved at 300–600 °C. Erkkfeldt et al. [10] also reported an alumina-supported In₂O₃ catalyzed NO_x

Fig. 1. Catalytic activity over the different catalysts.

reduction with DME under lean burn conditions, where only 47% NO_x conversion was observed at 250–550 °C. InAg/TA was more efficient than InAg/Al, indicating that the introduction of TiO₂ significantly improved the catalyst activity. Macleod et al. [20] described that TiO₂ was critical for the formation of the intermediates, which would promote the reduction of NO_x over the Pd/TiO₂/Al₂O₃-catalysed H₂/CO/NO/O₂ reaction.

As can be seen in Fig. 1(b), the conversion of CO to CO₂ decreased in the order of InAg/TA > InAg/Al > Ag/TA > In/Ta in the temperature range of 50–600 °C. InAg/TA showed the highest activity with more than 71% conversion of CO at 200 °C and almost 100% above 400 °C.

3.2. Textural properties

The BET surface area, total pore volume and average pore size of the different catalysts are summarized in Table 1. All the samples showed a high surface area and large pore volume. Although InAg/TA gave the highest catalyst activity, the BET surface area, pore volume and pore size of InAg/TA were lower than that of In/Ta, Ag/TA and InAg/Al. Thus, these parameters would not be responsible for the good catalytic performance of InAg/TA. The influences of other factors such as dispersion and interaction of metal active species on catalytic performance were further studied.

The XRD patterns of the different samples are shown in Fig. 2. The characteristic diffraction peaks of In₂O₃ were observed for In/Ta and InAg/Al at $2\theta = 30.60^\circ$, 35.46° and 51.02° [14]. The XRD pattern exhibited a wide and weak amorphous peak between 25° and 40° for InAg/TA. The disappearance of In₂O₃ crystalline diffraction peaks may be due to the increased dis-

persion of the indium species on the carrier surface of InAg/TA, which would thus contribute to the activity [21].

TEM images and particle size distributions are shown in Fig. 3. The black particles observed in the TEM images for Ag/TA, In/Ta and InAg/Al were identified as indium or silver species. The TEM images and particle size distribution showed a non-uniform particle size of the Ag/TA catalyst. However, the diffraction peaks of silver species were not observed in the XRD pattern, possibly because the large particles did not consist of one single crystal but of many small crystal grains [22]. The average particle size of the In/Ta catalyst was 12.73 nm (Fig. 3(f)), which exhibited obvious characteristic diffraction peaks in XRD, indicating agglomeration and poor dispersion of the indium species on TA carrier. Compared to In/Ta, Ag/TA and InAg/Al, the average particle size of InAg/TA was smaller and showed a more uniform distribution. No obvious indium or silver particles was observed in the TEM image of InAg/TA, and the particle size was in the range of 1–5 nm (Fig. 3(h)). These results revealed that the silver species helped to improve the dispersion of the indium species, and the indium species was also useful for improving the dispersion of the silver species, and the TiO₂ and γ -Al₂O₃ composite support TA was beneficial for the uniform dispersion of the indium species and silver

Fig. 2. XRD patterns of the different catalysts.

Table 1

Surface area, total pore volume and average pore size of the catalysts.

Catalysts	Surface area (m ² /g)	Total pore volume (cm ³ /g)	Average pore size (nm)
In/Ta	250	0.70	11.2
Ag/TA	260	0.72	11.0
InAg/Al	252	0.72	11.4
InAg/TA	213	0.58	10.8

Fig. 3. TEM images (a–d) and particle size distribution (e–h) of the catalysts. (a, e) Ag/TA; (b, f) In/TA; (c, g) InAg/Al; (d, h) InAg/TA.

species. Hence, it was deduced that good dispersibility might be responsible for the high catalytic activity of InAg/TA.

3.3. Surface properties

Table 2 illustrates the XPS data of the different catalysts. The characteristic peak of Ag $3d_{5/2}$ had a binding energy of 368.0 or 368.1 eV for the Ag/TA, InAg/Al and InAg/TA catalysts. Generally, it is difficult to identify the valence state of Ag from its XPS peak position because the chemical bond energies of Ag⁰ and Ag⁺ have very similar values (368.3 and 367.5 eV, respectively) [15]. UV-vis spectra was used to distinguish the silver species on the surface. According to the literature [16], the broad band around 450 nm was attributed to metallic Ag. However, no obvious band at 450 nm was observed in Fig. 4, indicating that

Table 2
XPS data of the different catalysts.

Catalyst	Binding energy (eV)		Surface atomic concentration (%)	
	In $3d_{5/2}$	Ag $3d_{5/2}$	In	Ag
In/TA	444.0	—	2.18	—
Ag/TA	—	368.1	—	3.37
InAg/Al	444.6	368.0	1.36	2.73
InAg/TA	444.2	368.1	4.43	4.16

* Ratios of the elements in the catalyst.

Fig. 4. UV-vis spectra of InAg/TA, InAg/Al, Ag/TA.

only Ag⁺ species existed on the surface of Ag/TA, InAg/Al and InAg/TA. The In $3d_{5/2}$ binding energy of In/TA, InAg/Al and InAg/TA were around 444 eV, corresponding to the In₂O₃ state [11]. Although the In $3d_{5/2}$ binding energy of InAg/Al and InAg/TA was a little higher than In/TA, there may still exist an interaction between the indium and silver species [23]. InAg/TA displayed the highest surface concentration of indium and silver species among the different catalysts (Table 2). This may be because the indium and silver species can easily migrate to the catalyst surface when TA was the support [14]. Large amounts of indium and silver species on the surface may be responsible for its high activity due to the increase in adsorption sites.

3.4. Redox properties

H₂-TPR data are depicted in Fig. 5. The composite support TA showed no obvious reduction peak. Catalyst Ag/TA showed a reduction peak of Ag₂O or Ag⁺ [15] at 396 °C. For In/TA, the peaks at 342 and 366 °C were assigned to the reduction of dispersed and bulk (or aggregated) In₂O₃ phases [24]. Compared to InAg/Al, the corresponding bulk (or aggregated) In₂O₃ peak of InAg/TA was shifted from 488 to 407 °C, which may be due

Fig. 5. H₂-TPR curves of the different catalysts.

to the fact that TiO_2 (being an n-type semiconductors) tends to produce a large number of oxygen vacancies and Ti^{3+} in the reduction atmosphere. Ti^{3+} can donate electrical charge to In^{3+} and become stable Ti^{4+} [25]. Thus, the indium species surface reduction would be facilitated, which is important for NO dissociation. Accordingly, the interaction between the indium species and TiO_2 may also contribute to the high catalytic activity.

The TPR profile of the InAg/TA sample showed one obvious reduction peak at 407 °C, suggesting the existence of an interaction between the indium and silver species. The intensity of the reduction peak at 407 °C was increased as compared to the other catalysts, reflecting that the dispersed In_2O_3 species was increased, which was consistent with the absence of a bulk In_2O_3 peak in the XRD patterns. Moreover, one reduction peak appeared in the H_2 -TPR spectrum which also indicated similar hydrogen adsorption and diffusion rates of the catalyst particles, and the reduction simultaneously proceeded for both the silver and indium species, indicating the excellent uniformity of the particle size [26].

3.5. FTIR results

The NO adsorption capacity is crucial for the reduction of NO with CO. To test the NO adsorption capacity of the different catalysts, in situ FTIR NO adsorption experiments were performed for In/TA, Ag/TA, InAg/Al and InAg/TA at 30, 250 and 500 °C (Fig. 6). In the case of NO adsorption at 30 °C, an IR band at 1630 cm^{-1} was observed for all catalysts, which was assigned to the bridge nitrate [27]. However, this band disappeared above 250 °C, suggesting that bridge nitrates are not the key species in the catalytic reaction. All catalysts showed monodentate nitrate (around 1459 cm^{-1}) and bidentate (around 1574 cm^{-1}) adsorption [27] at 30, 250 and 500 °C. The NO adsorption capacity is reflected by the intensity of the monodentate and bidentate nitrate peaks. It can be observed from Fig. 6

Fig. 6. FTIR spectra of NO adsorbed on In/TA (1), Ag/TA (2), InAg/Al (3) and InAg/TA (4) at 30 °C (a), 250 °C (b) and 500 °C (c).

Fig. 7. Stability test of the InAg/TA catalysts at 450 °C for 72 h. Reaction conditions: 0.72% NO, 2.1% CO, 1.0% O_2 and He as a balance, GHSV = 7000 h^{-1} .

that InAg/TA showed a higher NO adsorption capacity than of In/TA and Ag/TA. This was attributed to the fact that the existence of silver species improved the dispersion of indium species and increased the surface content of indium species, thus NO adsorption on the catalyst surface was enhanced accordingly. On the other hand, InAg/TA showed a higher NO adsorption capacity than InAg/Al, which means that the existence of TiO_2 promoted NO adsorption capacity. These results are consistent with the study by Macleod et al. [20], who described that TiO_2 affected Pd particles so as to strongly favor NO adsorption.

3.6. Stability of the InAg/TA catalyst

A catalyst stability test was performed for the reduction of NO with CO under lean burn conditions at a fixed temperature (450 °C) for 72 h. As shown in Fig. 7, no obvious change of catalyst activity was observed within the reaction period, indicating the good stability of InAg/TA.

After the stability test, the aged InAg/TA catalyst was used for another catalytic reaction run. The aged catalyst indicated a comparable activity to the fresh catalyst (inset of Fig. 7). The XRD patterns and TEM image were also used to characterize the aged catalyst. Compared to the fresh catalyst, four weak peaks at 2θ values of 30.60°, 35.46°, 38.12° and 44.31° were observed in the XRD pattern of aged InAg/TA (Fig. 8). The peaks at 30.60° and 35.46° corresponded to In_2O_3 [14], which means that In_2O_3 was still present on the aged InAg/TA after a continuous reaction for 72 h at 450 °C. The weak peaks at 2θ of 38.12° and 44.31° corresponded to Ag [15], which would be formed by the reduction of Ag oxide to Ag in the presence of CO. Nevertheless, the reaction activity seemed not affected by the existence of the small amount of Ag (as demonstrated in Fig. 7). Tanaka et al. [16] found that the redox reaction between Ag^+ and Ag^0 existed in the presence of CO, CO_2 , CH, SO_x and H_2O when using Ag/Ti/Al $_2$ O $_3$ as catalyst. We assume such a redox reaction of silver species (between Ag^+ and Ag^0) also occurred in our catalytic system. This redox reaction would be beneficial

Fig. 8. XRD patterns of fresh InAg/TA (1) and aged InAg/TA (2).

since In_2O_3 species would be stabilized in the presence of CO and O_2 through the competitive redox of the silver species. Despite the XRD pattern indicating a small amount of particle aggregation, the catalyst still showed good dispersion of the active species. This result was also in good agreement with the TEM result (Fig. 9).

4. Conclusions

A $\text{TiO}_2/\gamma\text{-Al}_2\text{O}_3$ supported In/Ag catalyst (InAg/TA) was prepared and applied as the catalyst for the reduction of NO with CO under lean burn conditions. InAg/TA is a good catalyst for the reduction of NO to N_2 , with > 60% N_2 yield obtained under our reaction conditions. The high catalytic activity was attributed to the high dispersion of the active species, good stability and high NO adsorption capacity of InAg/TA. The proximity of silver species to indium in the catalyst improved the dispersion of the indium species, thus resulting in a large amount of the surface active components of the catalyst. The silver species may have stabilized the indium species by the competitive redox of the silver species between Ag^+ and Ag^0 . In addition, the introduction of TiO_2 into the $\gamma\text{-Al}_2\text{O}_3$ support promoted NO adsorption capacity and improved the dispersion of the indium species and silver species.

Fig. 9. TEM image of aged InAg/TA.

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Graphical Abstract

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NO reduction by CO over $\text{TiO}_2\text{-}\gamma\text{-Al}_2\text{O}_3$ supported In/Ag catalyst under lean burn conditions

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The highly dispersed $\text{TiO}_2/\gamma\text{-Al}_2\text{O}_3$ supported In/Ag catalyst shows good catalytic performance and stability for the reduction of NO with CO under lean burn conditions.

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贫燃条件 In-Ag/TiO₂-γ-Al₂O₃ 催化 CO 选择性还原 NO

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摘要: 汽车尾气中主要污染成分 CO 和 NO_x 可导致酸雨、光化学烟雾和臭氧空洞效应, 对生物、环境及生态系统造成重大危害。污染源中 CO 是性能优良的还原剂, 如能不添加还原剂实现 CO 催化还原 NO_x, 将成为最具经济技术优势的 NO_x 脱除技术。在富氧、低温条件下, 利用 CO 选择性催化还原 NO_x 为 N₂, 是目前选择性催化还原研究中的热点和难点。催化 CO 还原 NO_x 常用的贵金属 Ir, Rh, Pt 和 Pd 矿藏稀少, 价格昂贵, 有氧条件下活性急降, 而分子筛催化剂和一些金属氧化物催化剂普遍存在反应温度高, 尤其对 N₂ 选择性差等问题。

为解决上述问题, 需寻找新的适合我国矿产资源的催化体系。研究发现, 稀散金属基催化剂对氮氧化物的净化具有一定效果, 因而可将我国的稀散金属资源优势转化为技术优势和经济优势。因此, 本文以 TiO₂-γ-Al₂O₃ (TA) 为载体, In/Ag 为活性组分, 采用等体积浸渍法制备了 InAg/TA 以及 In/TA, Ag/TA 和 InAg/Al (γ-Al₂O₃ 为载体) 催化剂, 考察了贫燃条件下 CO 选择性还原 NO 的催化活性。研究表明, 双金属催化剂 InAg/Al 和 InAg/TA 的活性比单金属催化剂 In/TA 和 Ag/TA 高, In/TA 催化剂中引入 Ag 物种能降低起燃温度; 另外, 相比于 InAg/Al 催化剂, InAg/TA 催化剂具有较高的催化活性, 550–600 °C 时 N₂ 产率超过 60%, 说明载体中引入 TiO₂ 可以提高催化剂活性。

为了深入研究 InAg/TA 催化剂中 Ag 物种和 TiO₂ 对 In 物种的作用, 通过比表面测定、X 射线衍射 (XRD)、透射电子显微镜 (TEM)、X 射线光电子能谱、紫外-可见光吸收光谱、氢气程序升温还原、傅立叶变换红外光谱等方法分析了催化剂结构和表面形态。结果表明, Ag 物种可以提高 In 物种的分散性, In 和 Ag 物种在 TA 载体表面可以很好地分散, 从而有利于提高催化活性。In 和 Ag 物种在 TA 载体表面以氧化态形式存在, 并且 Ag 物种可以提高 In 物种表面含量, 表面 In 和 Ag 物种含量越高, 吸附活性位越多, 催化活性越高; 同时, TiO₂ 也可以促进 NO 吸附, 从而提高 InAg/TA 催化剂活性。

InAg/TA 催化剂在 450 °C 连续反应 72 h 进行稳定性测试, 测试前后分别在 50–600 °C 进行活性测试, 并用 XRD 和 TEM 对反应后的催化剂进行表征测试。结果表明, InAg/TA 催化剂具有较好的稳定性, 连续反应前后催化剂活性基本保持不变, 推测可能由于在有 CO 和 O₂ 存在的体系中, Ag 物种利用自身 Ag⁺ 与 Ag⁰ 之间的氧化还原反应抑制了活性组分 In₂O₃ 的还原和聚集, 稳定了 In 物种乃至催化剂活性。

InAg/TA 催化剂用于贫燃条件下 CO 还原 NO 具有较好的催化效果, 主要归因于催化剂活性组分分散性好, 稳定性高, 对 NO 吸附能力强。Ag 物种可以稳定 In 物种并提高其分散性, TiO₂ 可以改善 In 物种和 Ag 物种的分散性并促进 NO 吸附。

关键词: 一氧化碳还原一氧化氮; 贫燃; 铜/银双金属催化剂; 脱硝

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