Direct synthesis of zeolite coatings on cordierite supports by in situ hydrothermal method

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Abstract

A simple and green in situ hydrothermal method, free of organic templates or zeolite seeds, was examined and introduced by depositing several typical microporous aluminosilicate zeolites (Linde A, Linde Y, mordenite and ZSM-5) on cordierite supports. Such preparative factors as crystallization time, crystallization temperature and basic strength were systematically investigated to discuss their effect on the growth of zeolites on cordierite supports. The as-prepared zeolite/cordierite samples were characterized by various techniques and a supposed in situ growth mechanism of zeolites on supports was given. The aluminium atoms on cordierite supports were activated by OH⁻ and these activated atoms subsequently built a zeolite framework together with the silicon atoms and aluminium atoms of the synthesis gel. Based on this, the in situ deposition of zeolites can be easily extended to other aluminium-containing supports. With respect to pure zeolite powders, the in situ coated zeolites on supports exhibited much better stability and accessibility, which were thought essential for industrial applications.

Keywords: Zeolite coatings; In situ synthesis; Cordierite; Stability; Accessibility; TOF

1. Introduction

Crystalline molecular sieves with microporous structure have been extremely successful as catalysts for oil refining, petrochemistry and organic synthesis in producing fine and specialty chemicals, particularly when dealing with molecules having kinetic diameters below 10 Å [1]. In most cases, these materials are synthesized by hydrothermal method and the particle size obtained by this method is generally small [2]. The direct use of materials with small particle size may cause many problems, such as high pressure drops and difficulty in separation and operation. A simple way to solve these problems is to make use of zeolite crystals coated on structured support materials [3]. Ceramic, especially honeycomb cordierite (2MgO-2Al₂O₃-5SiO₂), is the support in common use because of its superior mechanical stability and hydrothermal stability as well as its plasticity. The usual coating techniques are dip-coating, slip-coating and slurry-coating [4]. However, it is well known that crystalline zeolite materials are difficult to washcoat, and that the use of binder may increase the diffusion problem and reduce the accessible porosity. Then, it has been proposed to prepare the zeolite component from crystallites grown on support surfaces, so-called in situ synthesis [5]. The main advantage of in situ synthesis over other coating techniques is that the support is used as a base for nucleation and that a chemical bonding between crystals and outer support layer is formed [6]. This results in a natural transition from support to zeolite layer and consequently a high thermal, chemical and mechanical stability of the zeolite/support monolith.

Various zeolites such as ZSM-5 [7–11], TS-1 [12] and mordenite [13] have been successfully coated on supports by the in situ hydrothermal synthesis method. Moreover, in situ
synthesized monolithic zeolite/support and modified zeolite/support have been proved to be successful catalysts for many important reactions [14–20]. Currently, the study of in situ synthesis focused on the optimized preparation of zeolite coatings (mainly ZSM-5) on various supports, such as honeycomb cordierite [10,11], ceramic foam [7], stainless steel [21], and carbon materials [8]. The synthesis process usually involves the use of organic templates or zeolite seeds, which makes the growth of zeolite crystals on a support rather complicated.

In the present study, a series of zeolites (Linde A, Linde Y, mordenite and ZSM-5) were synthesized on honeycomb cordierite supports by an in situ hydrothermal method in the absence of organic templates or zeolite seeds. Such a simple synthesis system would provide us a better understanding of the growth of zeolites on supports. Based on the synthesis and characterization results, we demonstrated how zeolite crystals could grow on a cordierite support in this work. The advantages of in situ synthesis were also discussed and modified zeolite/cordierites were tested as catalysts for the direct decomposition and selective reduction of nitric oxide.

2. Experimental

2.1. Synthesis

Cordierites manufactured by Corning Incorporated (60 cells/cm², 0.3 mm average wall thickness) were used as support materials. Before being used as supports, the commercial cordierites were cleaned in HCl (0.1 M) by ultrasonic for 20 min, washed by deionized water and then dried at 373 K.

For the synthesis of zeolites, tetraethylorthosilicate (TEOS, AR) was used as silicon source and aluminium sulfate (AR) as aluminium source. No template was needed throughout the synthesis processes. TEOS, sodium hydroxide, aluminium sulfate and water were mixed at certain proportions. After 3 h vigorous stirring, the gained transparent liquid and bulk cordierites were put into a PTFE-lined stainless steel autoclave together for static crystallization at certain fixed temperatures for a period of time. Then the samples were taken out, washed in deionized water by ultrasonic, and then dried at 373 K overnight.

Cu-ZSM-5/cordierite was prepared from synthesized ZSM-5/cordierite by the solution ion-exchange with 0.1 M Cu(CH₃COO)₂ at room temperature under slow stirring four times, 48 h each time, to ensure an ion-exchange level of 100%. The ion-exchanged sample was washed four times in an ultrasonic generator, 15 min each time, to remove the metal ions adhering on the surface to a large extent, and then calcined at 823 K for 4 h in air.

2.2. Characterization

X-ray diffraction (XRD) analysis of the as-synthesized zeolite/cordierite samples was performed on a Rigaku D/max 2500 diffractometer, equipped with a graphite monochromator and using Cu Kα radiation. The zeolite/cordierite monoliths were cut into small thin pieces (8 mm × 8 mm) for analysis.

A HITACHI S-3500N scanning electron microscope (SEM) was used for studies of external and internal surface morphology of zeolite/cordierites. SEM images were recorded on the samples covered with a thin layer of gold deposited by sputtering.

Surface areas and pore diameters were determined by nitrogen adsorption on the ASAP 2010M facility (Micromeritics).

Zeolite loading in zeolite/cordierite was obtained by calculating the weight increase of cordierite after hydrothermal synthesis. The Si/Al ratio of zeolite on cordierite support was calculated from the contents of Si and Al, which were determined by ICP (IRIS Advantage, TJ Advantage, TJA solution).

<table>
<thead>
<tr>
<th>Table 1</th>
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<tr>
<td>Hydrothermal synthesis conditions for the synthesis of zeolites [22]</td>
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<table>
<thead>
<tr>
<th>Sample zeolite/structure</th>
<th>Batch molecular composition</th>
<th>Synthesis conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>SiO₂</td>
<td>Al₂O₃</td>
</tr>
<tr>
<td>Linde A/LTA</td>
<td>2</td>
<td>1</td>
</tr>
<tr>
<td>Linde Y/FAUb</td>
<td>10</td>
<td>1</td>
</tr>
<tr>
<td>Mordenite/MOR</td>
<td>30</td>
<td>1</td>
</tr>
<tr>
<td>ZSM-5/MFI</td>
<td>80</td>
<td>1</td>
</tr>
</tbody>
</table>

* Cordierite supports excluded.
* A little seed gel (10Na₂O·Al₂O₃·10SiO₂·200H₂O) was used.
2.3. Catalytic test

Cu-ZSM-5/cordierite was studied as catalyst for direct decomposition of NO and for selective catalytic reduction of NO by propane in excess oxygen. Both reactions were carried out in a fixed-bed flow microreactor at atmosphere pressure. For the decomposition of NO, the reactant gas consisted of 2000 ppm NO, balanced with He to 100%. For the SCR of NO, the typical reactant gas mixture consisted of NO (1000 ppm), C₃H₈ (1000 ppm) and O₂ (5.0%), balanced with He to 100%. For both the reactions, the total flow of the inlet gas was set at 167 mL min⁻¹ and 0.5 g catalyst with particle size of 0.3–0.4 mm was packed into the reactor. The products were analyzed on-line using a gas chromatograph (HP 6890 series) equipped with a TCD detector. A molecular sieve 5A column served for separation of N₂, O₂ and CO, and a porapak Q column served for separation of CO₂, C₃H₈, N₂O, NO and H₂O. Before reaction, all catalysts were treated in a flow of He at 773 K for 2 h.

3. Results and discussion

3.1. Characterization of zeolite/cordierites

The XRD patterns of blank cordierite and as-synthesized zeolite/cordierites are shown in Fig. 1. As seen in the figure, cordierite support had its own typical diffraction peaks at 10.36°, 18.03°, 18.98°, 21.60°, 26.35°, 28.38°, 29.38° and 33.90°, corresponding to the structure of ceramic. In the XRD patterns of zeolite/cordierite composites, the typical diffraction peaks of cordierite could be clearly seen as identified with stars. Besides diffraction peaks of cordierite support, diffraction peaks corresponding to the pure phase of

Fig. 1. XRD patterns of blank cordierite and zeolite/cordierite composites; typical diffraction peaks of cordierite are identified as * in the XRD patterns of zeolite/cordierite composites.
zeolites could also be seen in the XRD patterns of zeolite/cordierite composites. These zeolites were recognized as Linde A, Linde Y, mordenite and ZSM-5, respectively, corresponding to the framework structures of LTA, FAU, MOR and MFI in turn [23].

Fig. 2 shows the SEM images for the surface of blank cordierite and the surfaces of zeolite/cordierites after in situ synthesis. The cordierite supports have irregular macroporous structure, as seen in the figure; such structure was utilized efficiently for the crystallization process by in situ synthesis method. The cordierite supports were used as bases for nucleation; zeolites grew not only on the external surface of cordierite supports but also inside the macroporous location (so-called internal surface). It is easily seen that zeolite crystal grains with regular shapes completely and compactly cover the irregular external surface of cordierites so that the irregular surface of cordierite support could not be seen any more. The grown of zeolite crystal grains on the internal surface could

Fig. 2. SEM images of cordierite and zeolite/cordierite composites: external surface and internal surface.
also be clearly seen in the figure. It is interesting to find some differences in crystal shape and crystal size between the zeolite crystals grown on the external surfaces and those grown on the internal surfaces of cordierite supports. For example, mordenite appears as prisms of about 20 μm on the external surface, while it appears as clubbed crystal grains of about 6 μm in length and 1 μm in diameter on the internal surface. As seen in the figure, one can easily conclude that zeolites tend to form larger crystal grains on the external surfaces than on the internal surfaces of the support. In our opinion, the growth of zeolite crystals was restricted by the macroporous structure when they grew on the internal surface of cordierite supports. Thus the crystal grains tend to be smaller and the crystal shape may differ from that on the external surface without structure restriction. With zeolite crystals growing not only on the external surface but also on the internal surface of the supports, a rather high zeolite loading might be achieved even with a thin zeolite layer.

More results of in situ synthesis can be found in Table 2. From the comparison between BET surface areas and the zeolite loadings after synthesis listed in the table as well as from the different diffraction peak intensities in XRD patterns (Fig. 1), one could conclude that mordenite grew on cordierite support most easily, followed by ZSM-5, then Linde A and Linde Y. The growth of zeolites on cordierite was mainly determined by the initial hydrothermal synthesis conditions of various zeolites, such as their crystallization temperature and their crystallization time. The effect of crystallization time on synthesis results of mordenite and ZSM-5 is displayed in Fig. 3. In general, the material tended

![Image](blank_cordierite.png)

**Fig. 2.** (Continued).

<table>
<thead>
<tr>
<th>Sample</th>
<th>Batch Si/Al</th>
<th>Powders Si/Al</th>
<th>Coating Si/Al</th>
<th>Zeolite loading (wt.%)</th>
<th>BET surface area (m² g⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Linde A/cordierite</td>
<td>1</td>
<td>0.98</td>
<td>0.96</td>
<td>6.9</td>
<td>8.0</td>
</tr>
<tr>
<td>Linde Y/cordierite</td>
<td>5</td>
<td>2.43</td>
<td>2.37</td>
<td>11.6</td>
<td>39.8</td>
</tr>
<tr>
<td>Mordenite/cordierite</td>
<td>15</td>
<td>8.60</td>
<td>6.40</td>
<td>28.0</td>
<td>70.0</td>
</tr>
<tr>
<td>ZSM-5/cordierite</td>
<td>40</td>
<td>23.67</td>
<td>12.17</td>
<td>16.0</td>
<td>56.5</td>
</tr>
</tbody>
</table>

* a Referred to precursor batch for synthesis, cordierite supports excluded. 
* b Referred to as-synthesized zeolite powders. 
* c Referred to synthesized zeolite coatings separated from zeolite/cordierite monolith by long time ultrasonic. 
* d Referred to zeolite/cordierite monolith.

![Image](mordenite_cordierite.png)

**Fig. 3.** XRD patterns of mordenite/cordierite and ZSM-5/cordierite synthesized for different crystallization time.
to form thicker zeolite coatings on cordierite with longer crystallization time. As seen in the figure, the relative intensity of typical zeolitic diffraction peaks increased, while the relative intensity of cordierite support diffraction peaks declined obviously with increasing crystallization time from 24 to 48 h, clearly indicating the formation of thicker zeolite coatings. Zeolite loadings increased greatly with increasing crystallization time and higher zeolite loadings could be obtained by increasing crystallization time. For example, ZSM-5 loadings on cordierite supports increased from 16 to 25% and mordenite loadings from 28 to 37% when the crystallization time was doubled from 24 to 48 h. However, it was not always good to make coatings by in situ hydrothermal method for too long crystallization time: the stability of coatings on cordierite supports may decrease when overloaded.

Besides crystallization temperature and crystallization time, many factors may also have great effects on the growth of zeolites on cordierite supports. For example, the crystal shape was a very important factor. Small crystals with clubbed crystal shape were more easily coated on supports (especially on the internal surfaces) and were helpful to obtain higher zeolite loadings. As seen in the SEM images in Fig. 2, clubbed crystals of mordenite were formed and packed on the internal surface of cordierite, which probably leads to the zeolite loadings (Table 2) being higher than ZSM-5 ones under similar synthesis conditions. In fact, the in situ synthesis results are affected by many factors and are rather complicated. Other factors, such as basic strength and the Si/Al ratio of synthesis gel, might also influence the synthesis results.

For a better understanding, a possible simple growth mechanism of zeolites on cordierite supports free of organic templates or zeolite seeds is described in Fig. 4. As is known, a lot of aluminium is contained in cordierite (2MgO·2Al₂O₃·5SiO₂) supports and the aluminium atoms in the surfaces (both external surface and internal surface) of cordierite could be activated under proper basic circumstances; this was thought of as the initial step of in situ synthesis. Under hydrothermal conditions, the activated aluminium atoms build the framework of zeolites together with the silicon atoms in the synthesis gel. This part of aluminium atoms, shared by the zeolite framework and cordierite supports, acted as a bridge connecting zeolite crystals and cordierite support. Strong interactions formed between the zeolite and the support, and then zeolites were coated on the supports successfully by the in situ method. From this point of view, it is easy to understand the effects of crystallization temperature and crystallization time mentioned above.

Typically, the conventional in situ synthesis process usually involved in the function of various organic templates [7–9, 24] or even zeolite seeds [11, 25–27]. The synthesis process was rather complicated and hard to understand. In this work, in situ synthesis of zeolite coatings on cordierite support was achieved free of any organic templates or zeolite seeds. This route not only illustrates a simple and green way to make zeolite coatings, but also provide a better understanding of in situ synthesis. Based on the given growth mechanism, it can be supposed that some kinds of microporous aluminosilicate zeolites can not only be coated on cordierite support but can also be coated on other aluminium-containing supports under proper synthesis conditions.

To test the supposition, we carried out the experiments to prepare ZSM-5 on aluminium plate supports; there was no aluminium source but the aluminium plate support was provided. From the XRD patterns (Fig. 5) and SEM images (top view and side view, Fig. 6) of as-synthesized ZSM-5/Al sample, it was easily seen that ZSM-5 coatings had been successfully prepared on aluminium plate by this in situ synthesis method. The Si/Al ratio of ZSM-5 coatings was 23, as determined by ICP analysis. Such a value indicated that, under proper synthesis conditions, some aluminium atoms from supports could build the framework of ZSM-5 zeolite in situ together with the silicon atoms in the synthesis gel quite well.
The alkalinity of synthesis gel was found to have great effects on in situ synthesis results. In too weak alkalinity circumstances, no ZSM-5 crystals could be obtained, because a certain amount of OH$^-$ was necessary for the crystallization process of zeolites [28,29]. However, in too strong alkalinity circumstances, aluminium from supports would leak into the synthesis gel as AlO$_2^-$ . Thus ZSM-5 zeolite crystals grew preferentially in liquid phase rather than on the surface of aluminium template. Only in proper alkalinity circumstances, outer layer aluminums were activated by OH$^-$ and built ZSM-5 framework with the silicon atoms in synthesis gel. Thus stable ZSM-5 coatings formed on the aluminium plate support as they did on cordierites.

As discussed above, various zeolite coatings with different structures could be prepared on the cordierite supports without any organic template by the in situ hydrothermal method. This special synthesis method brought us more advantages than just being a coating technique. For example, the stability and accessibility of zeolite on cordierite could be greatly improved, which would be discussed later.

A comparison of hydrothermal stability between synthesized ZSM/cordierite and pure ZSM-5 powders with the same Si/Al ratio was made. The XRD results were shown in Fig. 7. A crystallinity decline of more than 10% was observed on pure ZSM-5 zeolite powders after hydrothermal treatment at 1023 K for 3 h, while no obvious change in crystallinity was found for ZSM-5/cordierite under the same conditions. Such results indicate that the in situ synthesized ZSM-5/cordierite possess much better hydrothermal stability than the pure ZSM-5 powders, agreement with the research results over TS-1/cordierite in our previous work [30].

The good hydrothermal stability of zeolites on cordierite supports comes from the in situ synthesis method. As is well known, the decline of the crystallinity of zeolites was caused mostly by a dealumination process. During hydrothermal treatment, the framework Al may react with H$_2$O and produce extra-framework Al, accompanied with extra-framework Si-Al phases [31–33]. Thus the framework of zeolite would be partly destroyed, leading to the decline in crystallinity. Under in situ synthesis conditions, aluminium atoms of the cordierite becomes the base for zeolite nucleation and go into the framework of the zeolites, as discussed above. The aluminium atoms are then greatly stabilized. Thus the dealumination process can be suppressed to a large extent and the hydrothermal stability of the zeolites on cordierite supports was greatly improved. Meanwhile, the acid and alkali resistance of zeolites might also be improved owing to the suppression of the dealumination process. Thorough researches on this are being done.

![Fig. 6. SEM images of ZSM-5/Al: top view (left) and side view (right).](image)

![Fig. 7. XRD patterns of ZSM-5 powders and ZSM-5/cordierite before and after hydrothermal treatment.](image)
3.2. Catalytic tests

Zeolites and modified zeolites have proved to be successful catalysts for many reactions, but a serious problem lies in their insufficient stability, which inhibits further development of this type of catalysts. As for pure zeolite catalysts, the dealumination process results in changes in acidity and decline in surface area [34,35]. As for ion-exchanged zeolites, the dealumination process can disturb the exchanged cations and then result in a deactivation of active centres [36,37]. By in situ synthesis, the dealumination process of zeolite could be suppressed efficiently and the potential of zeolites might be further developed.

Copper ion-exchanged zeolites, especially Cu-ZSM-5, have been proved to be excellent catalysts for NO decomposition and selective reduction using hydrocarbons as reductants [38–41]. In this study, Cu-ZSM-5/cordierite (Cu loading 0.65%) and Cu-ZSM-5 (Cu loading 4.62%) powders with similar Si/Al ratios and copper ion-exchange levels (100%) are studied as catalysts for the above two reactions to demonstrate the advantages of the in situ synthesis method. As for direct decomposition of NO, a stable NO conversion to N\textsubscript{2} of about 24.5% after 50 min reaction was obtained on Cu-ZSM-5 catalyst, while NO conversion of about 10.0% was obtained on Cu-ZSM-5/cordierite under same reaction conditions (seen in Fig. 8). For selective reduction of NO with propane, NO conversion to N\textsubscript{2} on Cu-ZSM-5 powders was higher than that on Cu-ZSM-5/cordierite at reaction temperatures below 673 K, while it was lower at the reaction temperatures over 673 K, as seen in Fig. 9. Since Cu-ZSM-5/cordierite obviously contained much less catalytic component with respect to pure Cu-ZSM-5 powders, it was difficult to tell which catalyst was better only by comparing their catalytic activities. Thus, the turnover frequency (TOF: number of molecules converted per active surface site per second [45]) is usually considered an alternative standard to compare catalysts. For Cu-ZSM-5 type catalyst, Cu ions incorporated with ZSM-5 framework ([Cu–O–Cu\textsuperscript{n+}]) are regarded as active sites for both decomposition and selective reduction of NO [42–44]. Based on this, TOFs of Cu-ZSM-5 powders

Table 3

<table>
<thead>
<tr>
<th>Catalysts</th>
<th>NO decomposition</th>
<th>NO selective reduction</th>
</tr>
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<tbody>
<tr>
<td></td>
<td>NO conversion (%)</td>
<td>TOF (s\textsuperscript{-1})</td>
</tr>
<tr>
<td>Cu-ZSM-5 powders</td>
<td>24.5</td>
<td>1.75 \times 10\textsuperscript{-4}</td>
</tr>
<tr>
<td>Cu-ZSM-5/cordierite</td>
<td>10.0</td>
<td>4.47 \times 10\textsuperscript{-4}</td>
</tr>
</tbody>
</table>

\(^a\) Average of stable activity after 50 min reaction at 673 K.

\(^b\) All the TOFs were calculated based on the Cu incorporated with ZSM-5 framework ([Cu–O–Cu\textsuperscript{n+}]).

\(^c\) At the reaction temperature of 623 K.

\(^d\) At the reaction temperature of 673 K.
and Cu-ZSM-5/cordierite were calculated to compare the catalytic efficiency, as displayed in Table 3 (for the selective reduction of NO, only two temperature points, 623 and 673 K, were chosen as examples). It could be seen that monolithic Cu-ZSM-5/cordierite showed much higher TOFs than Cu-ZSM-5 powders under all conditions studied. It means that the efficiency of catalytic component on cordierite support is greatly enhanced by the in situ synthesis method. Thus the dosage of catalysts could be reduced, which results in lower costs for zeolite and modified zeolite catalysts.

But why did in situ synthesized monolithic zeolite/cordierite catalyst show higher efficiency? In our opinion, by in situ synthesis, the zeolite crystals nucleated directly on cordierite support and mainly grew along a certain axes. The order in crystal growth and the highly dispersion of zeolite crystals could greatly improve the accessibility of zeolites, which effectively avoided the “dead volume” caused by the random packing of zeolites. What is more, for modified zeolite/cordierite, the agglomeration of modifier (probably the active sites) caused by the destruction of zeolite framework might also be prevented. Thus, when this type of material was used for catalytic processes, the selectivity of the catalytic reactions and the anti-poisonous properties of the catalysts might be improved. As for the selective reduction of NO with propane, monolithic Cu-ZSM-5/cordierite displayed an obvious higher selectivity between the main reaction \( (\text{C}_3\text{H}_8 + 2\text{NO} + 4\text{O}_2 \rightarrow \text{N}_2 + 3\text{CO}_2 + 4\text{H}_2\text{O}) \) and the side reaction \( (\text{C}_3\text{H}_8 + 5\text{O}_2 \rightarrow 3\text{CO}_2 + 4\text{H}_2\text{O}) \) than Cu-ZSM-5 powders within the entire temperature range investigated, expressed as NO/propane consumed in Fig. 10.

4. Conclusion

Free of organic templates or zeolite seeds, a series of microporous aluminosilicate zeolites were successfully coated on cordierite supports by a simple and green in situ hydrothermal synthesis method. And such preparative parameters as crystallization time, crystallization temperature and basic strength were found to produce a profound effect on the direct growth of zeolites on cordierite supports. Based on the synthesis and characterization results, a likely growth mechanism of zeolites on cordierite supports was given. The aluminium atoms from surface of cordierite support were considered to be activated by OH\(^-\) and subsequently these activated atoms would build a zeolite framework together with the silicon atoms and aluminium atoms from the synthesis gel under hydrothermal conditions. According to this mechanism, this in situ process can be simply extended to the direct growth of microporous aluminosilicate zeolites on other aluminium-containing supports, such as aluminium template, by the proper adjustment of synthesis conditions. With respect to pure zeolites, the as-coated zeolites on supports were also observed to have better stability and accessibility; such improved properties were essential for practical applications. Compared with Cu-ZSM-5 powders, copper ion-exchanged ZSM-5/cordierite was proved to have an obviously enhanced turnover frequency for direct decomposition of NO and selective catalytic reduction of NO by propane in excess oxygen.

Acknowledgements

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