Catalytic Cracking of *n*-Octane over Zeolites with Different Pore Structures and Acidities

Je Sik Jung, Tae Jin Kim and Gon Seo[†]

Department of Applied Chemistry, Chonnam National University, Gwangju 500-757, Korea
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Abstract−Catalytic cracking of *n*-octane has been studied over FAU, FER, MWW, MFI, BEA and MOR zeolites in order to investigate the effects of pore structure and acidity on their catalytic properties. The conversion of *n*-octane was largely dependent on the number of strong acid sites, while their pore structure determined the rate of catalyst deactivation due to carbon deposit. Continuous and high catalytic activity, therefore, was obtained on the MFI zeolite with sinusoidal pores and small Si/Al molar ratio, because its pores suppress the formation of large intermediate and its large number of strong acid sites accelerates the cracking of *n*-octane.

Key words: Catalytic Cracking, *n*-Octane, MFI Zeolite, Pore Structure, Acidity

INTRODUCTION

Lower olefins such as ethylene and propylene are important raw materials of the petrochemical industries, because they are used as starting materials for the production of various chemicals and polyolefins. Although a part of them are separated from natural gas and off gases of refineries, most of them are produced by thermal cracking of naphtha in the presence of steam at 750-850 °C [Park et al., 2003]. The thermal cracking is very large and energy intensive so as to consume a large amount of energy; about 40% of it used in the petrochemical industries.

Catalytic cracking of naphtha has been intensively studied to reduce fuel consumption by lowering cracking temperature with maintaining high olefin selectivity [Kissin, 1996]. Since the evolution of carbon dioxide has also been regulated due to its green house effect, low temperature cracking is very attractive in terms of the carbon dioxide reduction. Furthermore, catalytic cracking enhances the selectivity for propylene, providing a way to meet propylene shortage.

Saturated paraffins of C_6-C_{12} hydrocarbons produce olefins in their catalytic cracking even at lower temperatures. Although various catalysts - acidic zeolite catalysts [Anderson et al., 2002] and basic catalysts of CaO and SrO [Lemonidou and Vasalos, 1989] - have been tested, no commercial plant is operated yet, because the yields of olefin on these catalysts are still low or they are deactivated too rapidly.

SINOPEC company reported the development of a catalytic cracking process producing lower olefins over zeolite catalysts from heavy feedstocks, but any running results confirming the success in commercial operation were not reported. Japan also carried out a national project named "catalytic cracking of naphtha" and developed MFI zeolite catalysts modified by lanthanum oxide and phosphorus [Yoshimura et al., 2000]; however, its commercial application was not reported.

Brönsted acid sites work as active centers in the cracking reactions of saturated hydrocarbons, because they produce carbenium and carbonium ions. Since Lewis acids produce radicals from saturated hydrocarbons, they are also active for the catalytic cracking. Strong acidity, therefore, is required for the catalytic cracking, but strong acid sites simultaneously initiate a rapid deactivation of catalysts due to carbon deposit. As a result, catalysts suitable for the catalytic cracking of paraffin should have a large number of strong acid sites to initiate the cracking reaction by producing reactive intermediates and specific pore structures to suppress the formation of large hydrocarbons which are converted to high boiling carboneous materials. The high hydrothermal stability of the catalysts is also indispensable because the catalytic cracking is operated at high temperatures in the presence of steam.

Acidity of zeolites is largely dependent on their Si/Al molar ratios and cations as well as their types [Lee et al., 1997]. Their pore structures are different according to zeolite type. MFI zeolite has been studied as a promising catalyst for the fluidized catalytic cracking, because of its high acidity and small carbon deposit [Degnan et al., 2000]. Its sinusoidal pores suppress the formation of long hydrocarbons, resulting in a small carbon deposit and long catalyst life.

In this study, we employed various zeolites as catalysts for the catalytic cracking of *n*-octane to investigate the effects of acidity and pore structure of zeolites on their catalytic activity and selectivity for olefin. In addition, MFI zeolites with different contents of aluminium were used as catalysts to verify the role of acid sites in the cracking reaction.

EXPERIMENTAL

Si/Al molar ratios and sources of zeolite catalysts employed in this study are listed in Table 1 accompanied with their BET surface areas determined from adsorption isotherms of nitrogen. Most of them were obtained from the Catalyst Society of Japan and zeolite producing companies, but the MFI(100) and the MWW(10) zeolites were synthesized. The MFI(100) zeolite was synthesized from a mixture of colloidal silica (DuPont, Ludox HS-40, silica content= 40%), aluminium hydroxide (Junsei, C.P. grade), sodium hydroxide (Tedia, >95%) and tetrapropylammonium bromide (Fluka, >98%) by a hydrothermal reaction at 175 °C and 7 days. The synthesis method of the MWW(10) zeolite used in this study was described elsewhere [Corma et al., 1995]. Hexamethyleneimine (Aldrich, >99%)

[†]To whom correspondence should be addressed.
E-mail: gseo@chonnam.ac.kr

Table 1. Si/Al molar ratios and BET surface areas of zeolite catalysts

Zeolite	Si/Al molar ratio	BET surface area (m²/g)	Source
FAU(2.65)	2.65	570	JRC-Z-HY(5.3)
BEA(13)	13	690	Tosho Co.
MOR(10)	10	410	JRC-Z-HM(20)
MWW(10)	10	420	Synthesized
MFI(25)	25	390	Zeolyst Co.
MFI(75)	75	401	PQ Corp.
MFI(100)	100	279	Synthesized
FER(8.5)	8.5	334	Tosho Co.

was used as a structure directing agent. H-form zeolites were obtained from Na-form ones by the ion-exchange with ammonium nitrate (Duksan, >98%) followed by calcination at 550 °C. The numbers in the parenthesis following after code names of zeolites mean their Si/Al molar ratios.

Si/Al molar ratios of synthesized zeolites were determined by using an ICP spectrometer (Jobin Yvon, JY 38 PLUS, Korea Basic Science Institute, Gwangju Branch) from their samples dissolved in hydrofluoric acid (Aldrich, >40%). X-ray diffraction patterns of zeolites were recorded on an X-ray diffractometer (Rigaku, DMAX/1200) by using Ni-filtered Cu $K\alpha$ X-ray at 30 kV and 40 mA. Adsorption isotherms of nitrogen on zeolites were obtained by using a home-built volumetric adsorption apparatus. Zeolites were evacuated under a vacuum of 2.0×10^{-3} Torr at 200 °C for 2 h prior to being exposed to nitrogen gas at liquid nitrogen temperature.

Acidity of zeolites was investigated from their TPD profiles of ammonia. Zeolites were dehydrated in a helium flow at 550 °C for 2 h and then cooled at 80 °C. Ammonia was introduced to the dehydrated zeolite samples as pulses at the same temperature until they were saturated with ammonia. Physically adsorbed ammonia
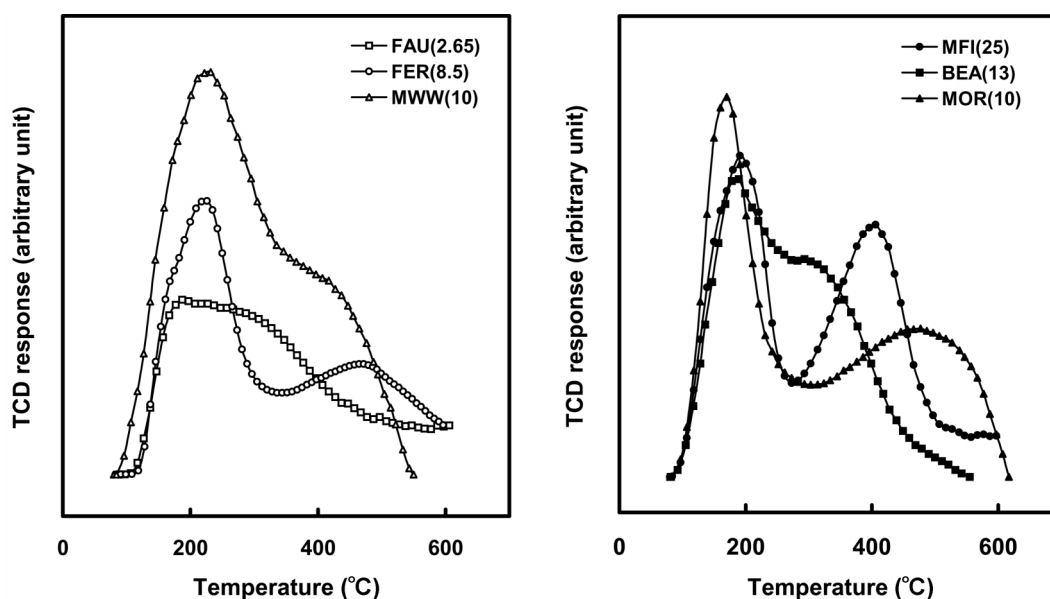
was removed by purging with helium. The temperature of zeolite bed increased with a ramping rate of 10 °C·min⁻¹ and desorbed ammonia from zeolites within a helium flow of 200 ml·min⁻¹ was monitored by a TCD detector and a mass spectrometer (Balzers, QMS422).

Catalytic cracking of n-octane was carried out by using a conventional atmospheric flow reactor. Zeolite catalysts of 0.15 g were charged at the center of the stainless steel tubular reactor with O.D. of 1/2" and activated in a nitrogen flow of 50 ml·min⁻¹ at 500 °C for 2 h. After the reactor temperature was adjusted to the desired one, n-octane vapor diluted in the nitrogen flow of 50 ml·min⁻¹ was supplied to zeolite catalysts. Feeding rate of n-octane was 0.029 mmol·min⁻¹ when the temperature of n-octane bubbler was maintained at 59.9 °C using a circulating bath (KOMA, KR-08). In order to examine the effect of space velocity on their catalytic properties, the flow rate of nitrogen was changed from 30 to 100 ml·min⁻¹. Products were sampled by a six port sampling valve and sent to an online gas chromatograph (Donam, DS6200) equipped with a Porapak Q column (1/8" mm×2 m) and an FID detector. The conversion of n-octane denotes the percentage of n-octane cracked as mole and the selectivity for olefin shows the percentage of n-octane consumed for the production of total olefin per reacted n-octane as mole.

RESULTS AND DISCUSSION

XRD patterns of zeolites were in good accord with those reported in literature [Treacy et al., 1996], indicating their high crystallinity. The high BET surface areas listed in Table 1 also suggest the presence of well-developed micropores.

Acidic properties of zeolites were strongly dependent on their types as well as Si/Al molar ratios. Fig. 1 shows TPD profiles of ammonia from zeolites. Most of these profiles were composed of two desorption peaks so-called l-peak and h-peak. Since h-peaks observed at high temperatures are attributed to strong acid sites, the area and the temperature at the maximum of the h-peaks represent the amount and strength of strong acid sites, respectively. The tem-

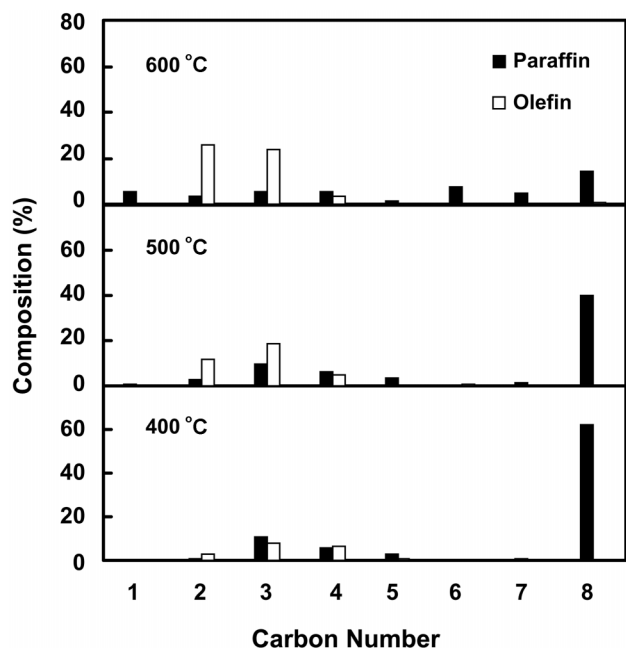**Fig. 1. TPD profiles of ammonia from various zeolites.**

Fig. 2. Product compositions over the MFI(25) catalyst in the cracking of *n*-octane at different reaction temperatures.

perature at the maximum of the *h*-peaks increased with the order listed below:

BEA(13)≈FAU(2.65)<MWW(10)≈MFI(25)<FER(8.5)<MOR(10)

However, the order of *h*-peak areas varied slightly with the setting temperature. The order listed below is determined from the *h*-peak areas above 400 °C to compare the number of strong acid sites relatively.

BEA(13)<FAU(2.65)<FER(8.5)<MWW(10)<MFI(25)<MOR(10)

Based on these results, we could summarize that the MOR(10) and MFI(25) zeolites were most acidic in terms of acid strength and the number of strong acid sites. On the other hand, the BEA(13) and FAU(2.65) zeolites had small amounts of strong acid sites.

Catalytic activities of zeolites are strongly dependent on their pore structures and acidities. Fig. 2 shows product compositions obtained over the MFI(25) zeolite at different reaction temperatures. At 400 °C, small amounts of C_3 and C_4 hydrocarbons were produced. The contents of ethylene and propylene in product stream increased with increasing reaction temperature. Various hydrocarbons ranging from C_1 to C_7 were produced at 600 °C accompanied with decreasing the fraction of non-reacted *n*-octane. This variation of the product composition with reaction temperature was common over all zeolite catalysts in the catalytic cracking of *n*-octane, although the conversion levels of *n*-octane were considerably different according to zeolite species.

The conversion of *n*-octane and the selectivity for olefin denote the activity and selectivity of zeolite catalysts in the cracking of *n*-octane. The changes in the conversion and selectivity with the lapse of reaction time represent the deactivation of zeolite catalysts. Fig. 3 compares the conversions obtained at 500 °C over various zeolites at 1 h and 5 h. The initial conversions at 1 h were high over the MOR (10) and MFI(25) catalysts, while those over the FAU(2.65) and
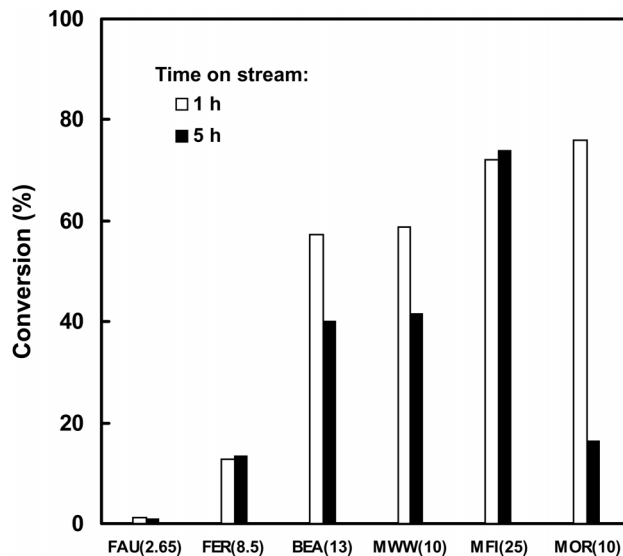

Fig. 3. The conversion of *n*-octane over various zeolite catalysts at 500 °C.

FER(8.5) catalysts were very low. The BEA(13) and MWW(10) catalysts showed intermediate values.

Since ferrierite has a crossed pore system composed of an 8-membered ring and 10-membered ring, the mass transfer of reactant and products in the FER(8.5) zeolite must be slow. The limitation on mass transfer brings about the high selectivity for the skeletal isomerization of *n*-butene proceeding through a monomolecular reaction path [Kim et al., 1998]. However, the steric hindrance of ferrierite pores causes low conversions in the catalytic cracking of *n*-octane, even though it has a medium amount of strong acid sites.

On the contrary, faujasite has three-dimensionally connected large pores composed of 12-membered ring. But the conversion of *n*-octane over the FAU(2.65) catalyst was extremely low. The color of the FAU(2.65) catalyst became deep black even after a short time running of the cracking reaction. This suggests that the rapid deactivation of faujasite catalyst is due to a severe carbon deposit. Its supercages provide enough space for the formation of large reaction intermediates, easily convertible to carbon deposit.

The MOR(10) catalyst also shows rapid deactivation: the conversion decreases from 80% to 20% during 4 h reaction. One-dimensional pores of mordenite are easily blocked even with a small amount of carbon deposit. Considering the deactivation rate, the conversion at the starting period over the MOR(10) zeolite may be much higher than that over the MFI(25) zeolite.

If we eliminate the FAU(2.65) and FER(8.5) catalysts because of their rapid deactivation and mass transfer restriction, the order of the conversion over zeolite catalysts at 1 h nicely coincides with that of the acid strength and the amount of strong acid sites deduced from the TPD profiles of ammonia. This means that the catalytic cracking of *n*-octane is initiated on strong acid sites. Since the cleavage of C-C bonds in saturated hydrocarbons requires strong acid sites [Corma and Orchillés, 2000], the highest activity of the MOR (10) catalyst in the catalytic cracking of *n*-octane can be expected from its highest acidity.

On the other hand, the catalyst life of zeolites is largely dependent on their pore structures. Almost the same conversions at 1 and

5 h over the MFI(25) catalyst indicate a negligible deactivation. A slightly high conversion at 5 h of the MFI(25) catalyst compared to that at 1 h might be due to the fluctuation of the reaction condition. Its sinusoidal pore structure suppresses the formation of large intermediates, the precursor of carbon deposit, resulting in constant conversion during the catalytic cracking of *n*-octane.

Although the conversion of *n*-octane and deactivation rate of zeolite catalysts are considerably different according to zeolite species, the selectivity for olefin was not varied with zeolite species as shown in Fig. 4. The selectivity of the FAU(2.65) catalyst was not presented because of its extremely low conversion. The FER(8.5) catalyst showed poor conversion compared to the MFI(25) catalyst (Fig. 3), but the selectivity over it was not low. No significant change in the selectivity with the time on stream was also observed. These results suggest the cracking path of *n*-octane is similar over zeolite
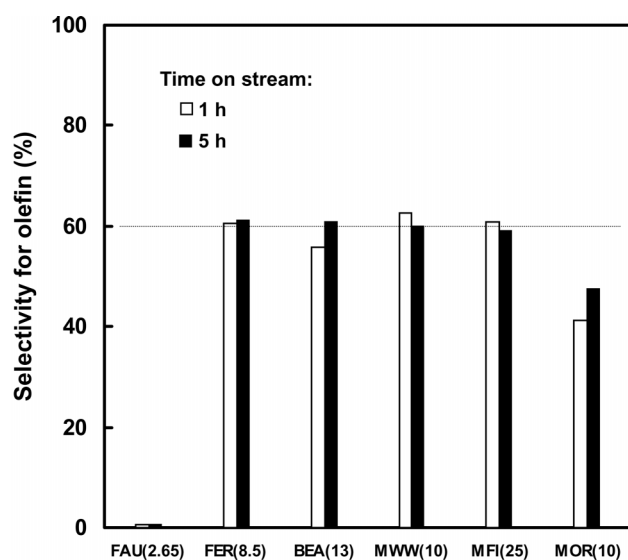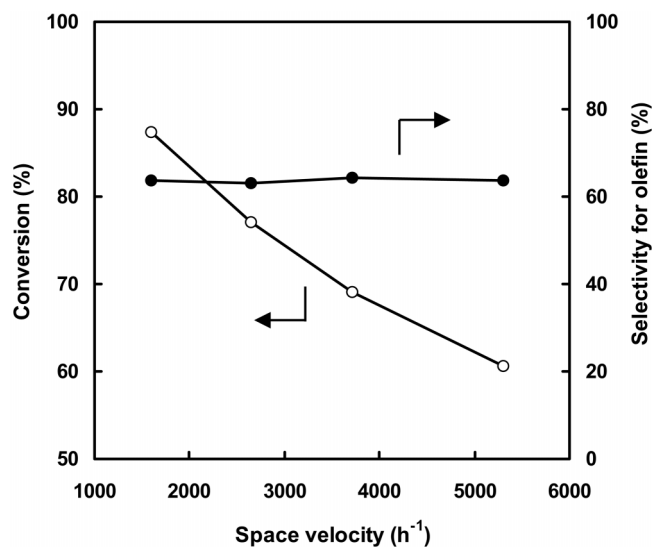

Fig. 5. Variations of the conversion and the selectivity for olefin with space velocity over the MFI(25) zeolite in the catalytic cracking of *n*-octane at 500 °C.

catalysts regardless of their pore structures and acidities. The re-equilibration of lower olefin and paraffin established in zeolite pores resulted in similar selectivities for olefin over various zeolites [Chang, 1983].

The variations of the conversion and the selectivity for olefin with space velocity also provided a similar suggestion. The conversion decreased considerably with increasing the flow rate of nitrogen due to the shortening of residence time of the reactant at catalyst bed as shown in Fig. 5. However, the selectivity for olefin did not change with space velocity, indicating that the re-equilibration among olefin and paraffin was already established in zeolite pores even at short residence time. Since zeolite pores are small, a slow diffusion of reactants and products in the pores brings about sufficient extent

Fig. 4. The selectivity for olefin over zeolite catalysts at 500 °C.
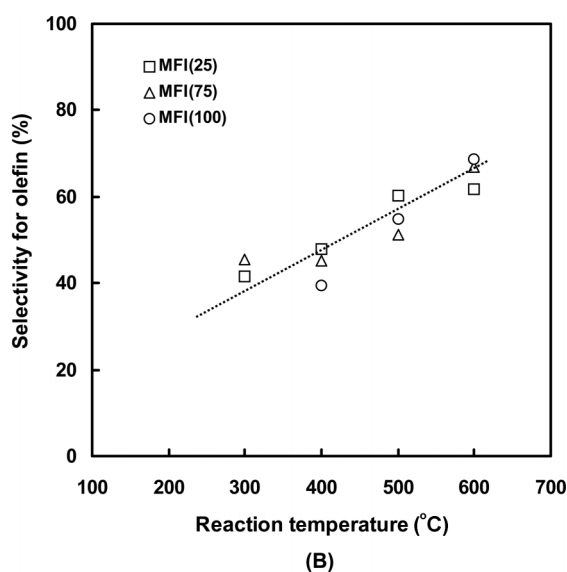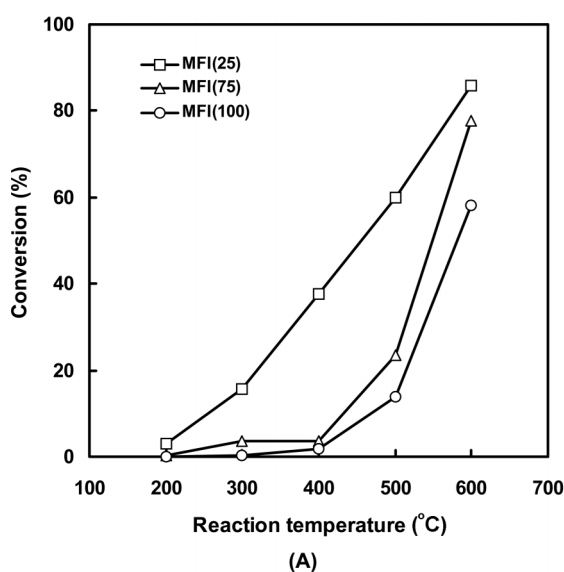

(A)

(B)

Fig. 6. The conversion (A) and the selectivity for olefin (B) in the catalytic cracking of *n*-octane over MFI zeolites with different Si/Al molar ratios.

of cracking and re-equilibration reactions inducing similar product distributions.

In order to elucidate the effect of the number of acid sites on the catalytic cracking of *n*-octane, MFI zeolites with different Si/Al molar ratios were employed as catalysts. The increases in the Si/Al molar ratio of MFI zeolites induced a significant decrease in the conversion at this temperature range as shown in Fig. 6. However, the selectivity for olefin slowly increased with reaction temperature regardless of their Si/Al molar ratio. Since the cracking reaction brings about an increase in entropy, it is reasonable to increase the selectivity for olefin with increasing reaction temperature. This means that the number of strong acid sites does influence considerably the conversion, but it does not influence the selectivity.

CONCLUSIONS

The conversion of *n*-octane in its catalytic cracking over zeolite catalysts was largely dependent on the number of strong acid sites, while their pore structures determined the rate of catalyst deactivation due to carbon deposit. The high performance of the MFI(25) zeolite in the catalytic cracking can be explained by its high content of aluminium producing a large number of strong acid sites and by its sinusoidal pores suppressing the formation of large hydrocarbons. Therefore, a catalyst with a large number of strong acid sites accelerating the cleavage of C-C bonds and with a specific pore structure sustaining its catalytic activity can achieve high conversion with a negligible deactivation.

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