

SYNTHESIS OF MESOPOROUS SILICA AND ZEOLITE PHASE TRANSFORMATION OF COAL FLY ASH FROM KAPAR POWER PLANT

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ABSTRACT

Coal fly ash (CFA) was sintered with and without alkali additives. Supernatant of these sintered CFA were used in the synthesis of zeolites and mesoporous silica MCM41. Faujasite phase was mixed with sodium silicate phase in samples sintered with alkali additives from x-ray diffraction analyses. Mesoporous materials MCM-41 with pores of ordered 2-dimensional (2d) hexagonal structure were successfully prepared from condensation-polymerization of quaternary ammonium salt as structure directing agent and supernatant of the CFA sintered with alkali additives from Kapar power plant as silica precursor. The materials had high surface area of 732 m²/g and median pore diameter of 2.5 nm by density functional theory method (DFT). X-ray diffraction analyses revealed that alkali additives are important in extracting silica from quartz and mullite.

INTRODUCTION

Mesoporous silicas such as MCM41, MCM48 and SBA15 possessing high surface area and pore volume have attracted much attention due to their versatility in several applications. Such applications include adsorbents, reaction catalysts, catalysts supports, hazardous and gases sensors, as well as electrical and optical devices[1-10]. Their wide applications has been contributed by the surface of these mesoporous silicas that consists of silanol groups. The silanol groups (Si-OH) are highly unstable so that it could form polar interaction with water via the hydrogen-hydrogen bond that contributes to the unstability of these materials in normal environment. Fortunately, these silanols are easily modified with other functional groups such as short or long alkyl chain, amino groups and aromatic groups to suit their respective applications. Conventionally, mesoporous materials and zeolites were synthesized using several pure silica precursors such as alkoxysilanes, fumed silica, water glass or sodium silicate etc. However, major drawbacks of these methods are the high cost incurred to produce these materials. Furthermore, high toxicities of the preferred silica precursors and the difficulties of disposing post-synthesis waste also contribute to the existing environmental problems. A greener approach in synthesizing mesoporous materials and zeolites are to utilized potential industrial waste with high silica contents such as rice

husk ash (RHA) and pulverized coal fly ash (CFA) of > 90 % and 60-70 % respectively. Recently, highly siliceous zeolite, ZSM-5 were successfully prepared from silica source of rice husk ash[11]. Coal fly ash (CFA) is formed as the by-product of pulverized coal combustion that is injected in the furnace with a pre-heated air in coal-fired power station. Coal combustion method contribute approximately 37 % of the total electricity production in the world[12]. Thus, huge amount of fly ash formed at approximately 500 and 5.5 million tons per year and are expected to increase[13]. However, the reutilization rate of the fly ash is low at approximately 15 % [14]. CFA is reutilized as a substitute for fine aggregates in cements and concretes, in bricks and ceramic tiles, filler in plastics and paints etc., deposit in landfills, seaside docking areas, hazardous waste deposits lining, etc. CFA has pozzolanic properties and phase minerals consists of silica (60-70 wt %) as the major component and alumina (16-20 wt %) in the form of quartz, mullite, calcite, Fe oxides, Ca silicates and sulphites and is obtained by electrostatic and mechanical precipitation of dust-like particles from the flue gases furnaces fired with pulverized coal. Owing to the high silica and alumina contents, it is important to recover these sources for other useful applications as well as reducing the present waste. Several studies have been focusing on the zeolitization of these CFA via hydrothermal treatment in NaOH or KOH solution, and their cation exchange capacity (CEC)[15-17]. Nearly full conversion of fly ash to zeolite such as faujasite-type zeolite, zeolite P, zeolite X, hydroxysodalite, gismodine-type zeolite were observed by this method[16,18,19]. However, this method resulted in abundance of liquid waste and high ratio of solution to CFA as well as the difficulties to obtain single-phase zeolite also contribute which makes it less preferable. Shigemoto *et. al.* had concluded that by alkali fusion, silica in the form of quartz and mullite are converted into more soluble form of sodium silicate and other aluminosilicate to increase the yield of zeolites.²⁰ Park *et. al.* introduced a new method of zeolitization by molten-salt method without the addition of water where KOH, NaOH or NH₄F were used as the mineral sources and NaNO₃, KNO₃ or NH₄NO₃ salts as solvents and stabilizers of sub-building units in hydrothermal treatment and longer treatment time with molten base-salt mixture resulted in a more distinct crystalline peaks[21]. Depending on the base-salt combination, major zeolite phases obtained also varies where NaOH,KOH-NaNO₃,KNO₃ combinations gave major cancrinite than sodalite phase[22]. In this study, we report on an attempt to synthesize mesoporous materials by condensation-polymerization from supernatant of sintered CFA (Kapar Power Plant) with alkali additive as the silica source and cetyltrimethyl ammonium bromide (C₁₆TMABr) as structure directing agent and to find the optimum synthesis condition. Then, we study the properties of the synthesized mesoporous materials in comparison with those prepared from pure silica sources.

EXPERIMENTAL

Coal fly ash used in this study was obtained from Kapar Power Plant, Selangor, Malaysia and sieved at ~ 200 μ m and used as received. The chemical compositions are as listed in Table 1 respectively. tetraethoxysilane (TEOS, 99% Tokyo Kasei), n-

hexadecyltrimethylammonium bromide (CTAB, Merck), sodium hydroxide (Merck, analysis grade), n-octyltrimethylammonium bromide (Tokyo Kasei), methanol (99.8%, Kishida), ammonia solution (25% -Merck, 28%-Kishida), acetic acid (Merck, glacial 100%). All chemicals were used without further purification.

Table 1: Chemical compositions (wt %) of as-received CFA.

Oxide	wt %	Mol/ 100 g CFA	Oxide	wt %	Mol/ 100 g CFA
SiO ₂	65.7	1.094	CaO	1.16	0.021
Al ₂ O ₃	15.5	0.263	TiO ₂	0.34	0.004
Fe ₂ O ₃	15.7	0.098	MnO	0.09	0.001
K ₂ O	1.43	0.015	Na ₂ O	0.03	< 0.001

As received CFA was sintered without alkali additive and with alkali additive (alkali fusion) at different temperature. The latter was carried out as reported[25]. Alkali fused CFA powder was then dissolved into water at 1: 5 ratio and aged for 1 day with stirring at room temperature. The gel mixture was filtered to obtain sodium silicate solution as the silica precursor. Si, Al and Na ions concentrations in the supernatant measured by induce couple plasma-atomic emission spectroscopy (ICP-AES) are at 10000 ppm, 360 ppm and 41000 ppm respectively. In a typical synthesis procedure cetyltrimethyl ammonium bromide(CTAB) was dissolved in 70 mL of water at room temperature. Then, silica source from the supernatant was added to the aqueous micellar solution under vigorous stirring. The pH of solution mixture was adjusted to approximately 10 ~ 11 by adding 25 % ammonia solution and the final molar composition of the gel was CTAB : Si : H₂O = 0.15 : 1 : 167. After that, the solution mixture was stirred at room temperature for 1 h and placed in a Teflon lined autoclave and heated at 373 K for 5 days in which the pH was adjusted several times to approximately 8 to 10 respectively. The resulting solid was filtered, washed several times and air-dried at 373 K overnight to obtain the as-synthesized samples of silica–surfactant complex. Then, the as-synthesized samples were calcined at 823 K for several hours to burn out the template to obtain surfactant-free sample, hereafter called MCM41-CFA.

MCM41 was prepared by the hydrolysis and co-condensation of tetraethoxysilane (TEOS) at room temperature as reported.[23,24] As-synthesized materials were calcined at 823 K for more than 6 hours to burn out the template to obtain surfactant-free sample, hereafter named as MCM41.

X-ray diffraction patterns were recorded on an automatic diffractometer Rigaku Geiger-Flex using CuK_α radiation (30 kV, 20 mA) for 2θ angles from 1.6 to 10 degrees (mesoporous materials) and 10-80 degrees (sintered CFA with/without alkali additive). CFA chemical compositions were analyzed with Li₁₂B₄O₇ by the X-ray fluorescence method (XRF) using Shimadzu XRF1700. The particle morphologies were observed by a scanning electron microscope (SEM) of Philips X2500, JEOL JSM6300 and LEO 1450VP with acceleration voltage of 20 kV. The samples were deposited on a carbon tape mounted on a sample holder and sputtered with gold at 60 nm. Nitrogen

adsorption isotherms were measured by a Quantachrome AUTOSORB-AS6B at 77 K. Samples were outgassed under 1mPa for 24 h at 573 K prior to nitrogen adsorption measurements. Particle size distribution of the CFA was measured by Micromeritics Sedigraph 5100.

RESULTS AND DISCUSSIONS

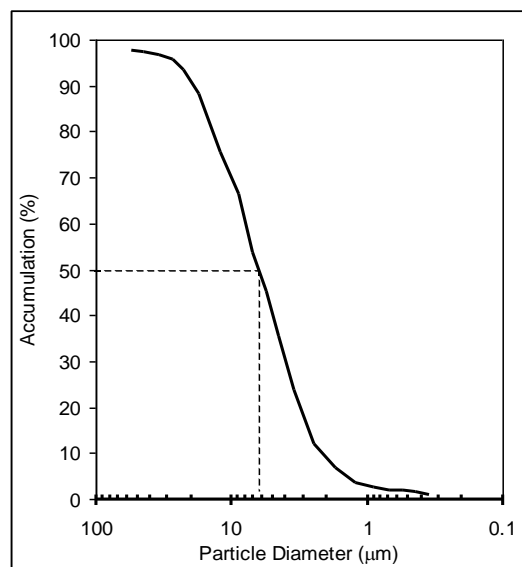


Figure 1: Particle size distribution of CFA.

The particles sizes of CFA plays an important roles in determining their reactivity with smaller particles exhibiting higher reactivity. The mean particle size of CFA in this study was 6 μm as shown in Figure 1.

X-ray diffraction patterns of as received CFA and fused CFA at 823 K shown in Figure 2 exhibited that major crystalline phases found in as received CFA are mullite, quartz and several form of aluminosilicate glass in amorphous phase. Sintering without the alkali additive was not successful in extracting quartz and mullite to soluble silicate species. However, X-ray diffraction patterns of fused CFA exhibited major sodium silicate phase and minor faujasite phase. The disappearance of quartz and mullite phases in the as-received CFA suggests that silica in its natural crystalline form had reacted with NaOH to form soluble sodium silicate species. Thus, fusion process had successfully extracted silicon from quartz and mullite to sodium silicate.

X-ray diffraction patterns of as-synthesized mesoporous materials as well as surfactant extracted mesoporous materials synthesized from fused CFA supernatant silica source in Figure 3 exhibited one pronounced peak at 2θ 2.30° and 2.36° for as-synthesized and surfactant free samples respectively attributable to the reflection from 100 plane while the reflection from 100 plane in pure silica MCM41 was at 2.4°. The (100) peak shifted to a higher 2θ angle for MCM41-CFA and MCM41 indicating a decrease of interplanar d spacing from 3.84 nm to 3.54 nm respectively. Another two peaks were observed at 2θ 2.21° and 19.4° attributable to the reflections from 110 and 200 planes. These results suggested the successful formation of 2 dimensional hexagonal structure of a

typical MCM 41 mesoporous material and the pore structure was retained after surfactant removal. The appearance of higher angle reflections peaks indicated the existence of long ranged order of 2-dimensional hexagonal structures.

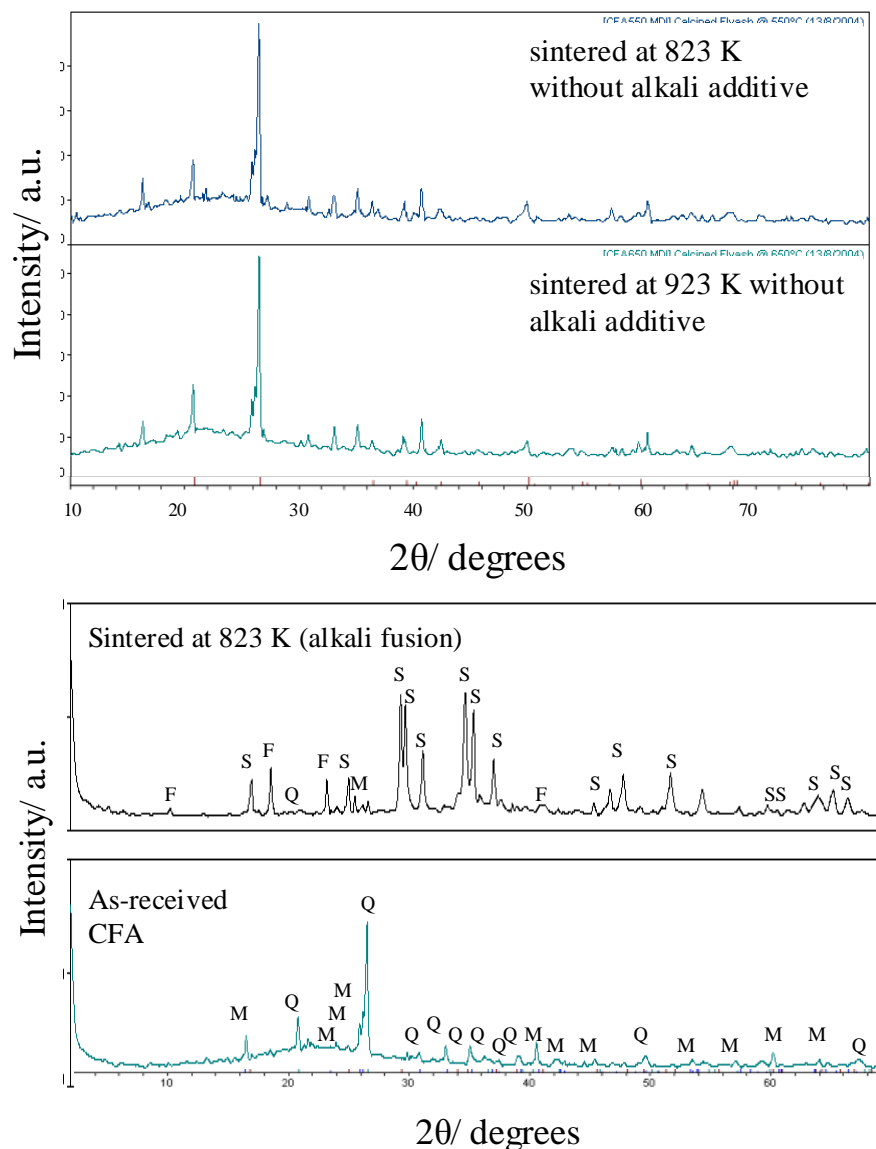


Figure 2: X-ray diffraction patterns of as-received CFA, sintered at 823 K with alkali addition, and sintered at 823 K and 923 K without alkali additive and with alkali additive (alkali fusion) CFA at 823 K (above). [M-mullite, Q-quartz, F-faujasite and S-sodium silicate].

BET equation was applied to the region of precondensation on each isotherm and mean pore diameter was estimated by the Dollimore-Heal method and density functional theory method (DFT). The BET surface area of MCM41-CFA was smaller than that of MCM-41. Specific surface area of mesoporous materials is highly dependent on the reactivity of the chosen silica source with more reactive silica source producing higher surface area. However, the value obtained in this study was in good agreement from that of other mesoporous materials in literature.²³

SEM images of CFA and fused CFA are shown in Figures 4a and 4b. As-received CFA exhibited a number of smooth spherical particles of cenospheres morphology interspersed with aggregates of crystalline compounds. The spherical particles with diameter less than 20 μm which are smooth and glassy are amorphous aluminum silicate. The crystalline compound observed suggested mullite and quartz. On the other hand, fused CFA exhibited amorphous

Figure 4. SEM images of a) as-received CFA and b) CFA sintered at 873 K with alkali addition

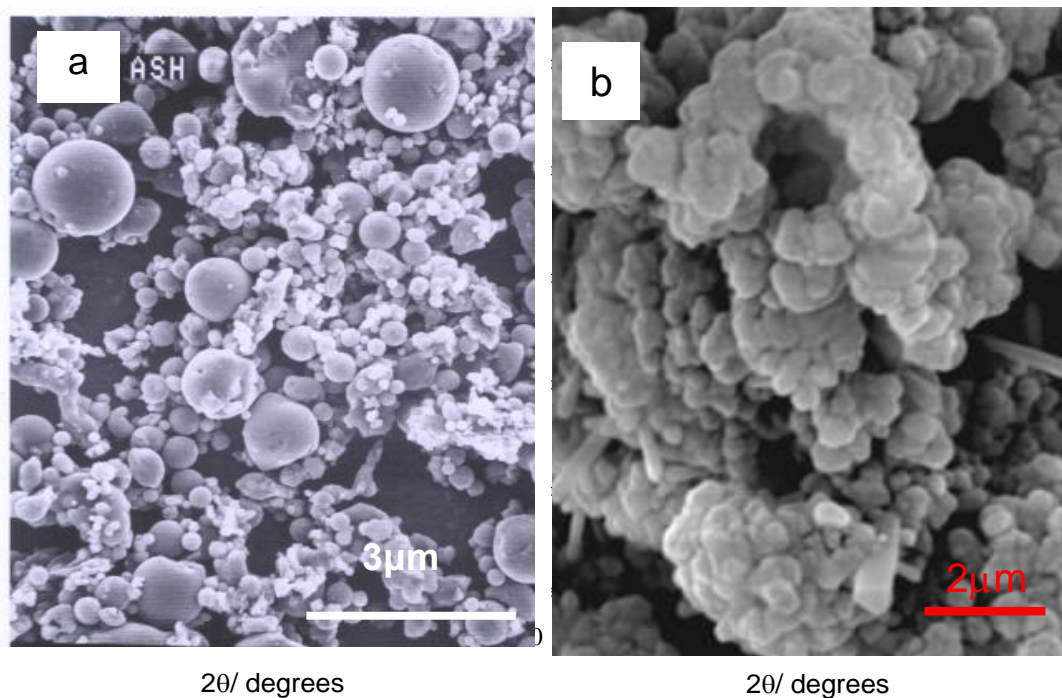


Figure 3: X-ray diffraction patterns of a) MCM41 b) MCM41-CFA as-synthesized (above), surfactant-free (below).

Table 2: Pore characteristics of MCM41 and MCM41-CFA

Sample	specific surface area ^a m ² .g ⁻¹	pore volume mL/g	pore diameter (nm)	d ₁₀₀ (nm)
MCM41	1100	0.83	2.7 ^b	3.54
MCM41-CFA	732	-	2.5 ^c	3.84

^a by BET plot ^b by Dollimore-Heal method ^c by DFT method

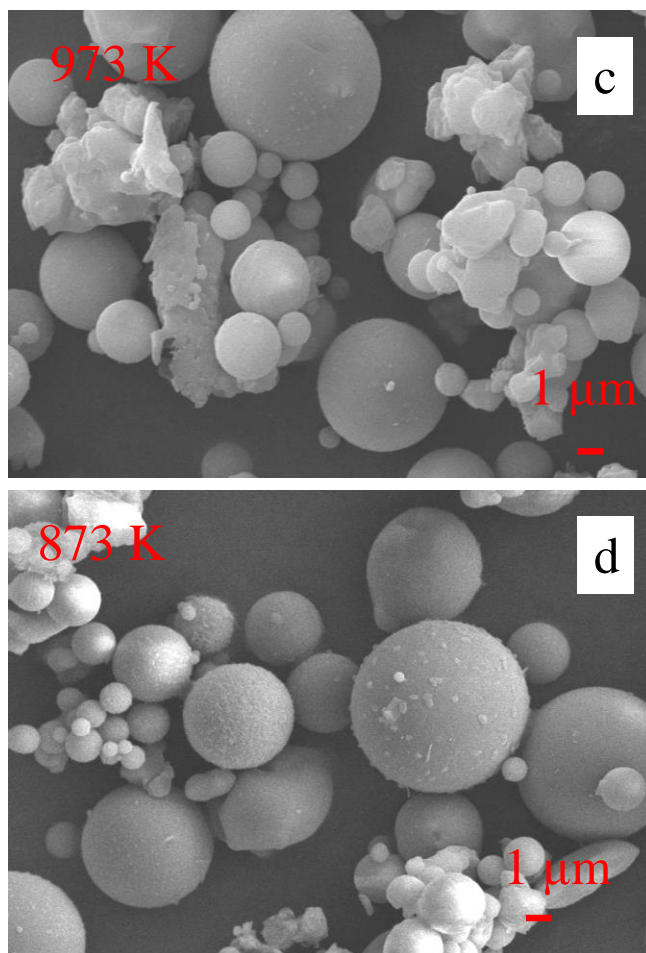


Figure 4 : SEM images of c) CFA sintered at 973 K and d) CFA sintered at 873 K without alkali additive

spherical agglomerates interspersed with crystalline compound with distorted octahedron morphology. The amorphous agglomerates were sodium silicate and sodium aluminosilicate while the crystalline compound was found to be faujasite from the x-ray diffraction analysis of CFA sintered with alkali additive[26]. These results suggested that by fusion process at certain temperature the possibility to obtain single phase of faujasite is high. SEM images of as-synthesized MCM41-CFA and surfactant-free MCM41-CFA are shown in Figures 5a and 5b. As-synthesized mesoporous materials exhibited mixtures of spherical top, ribbon-like, 2 dimensional hexagonal as well as torous shaped particles less than 1 micron. Surfactant-free MCM41-CFA particles were mainly agglomerations of hexagonally shaped particles. SEM image of surfactant-free MCM-41 prepared from pure silica is shown in Figure 5c. The particle morphology consists of hexagonally shaped particles and rod-like particles of 2-dimensional hexagonal structure of approximately 1 micron in size.

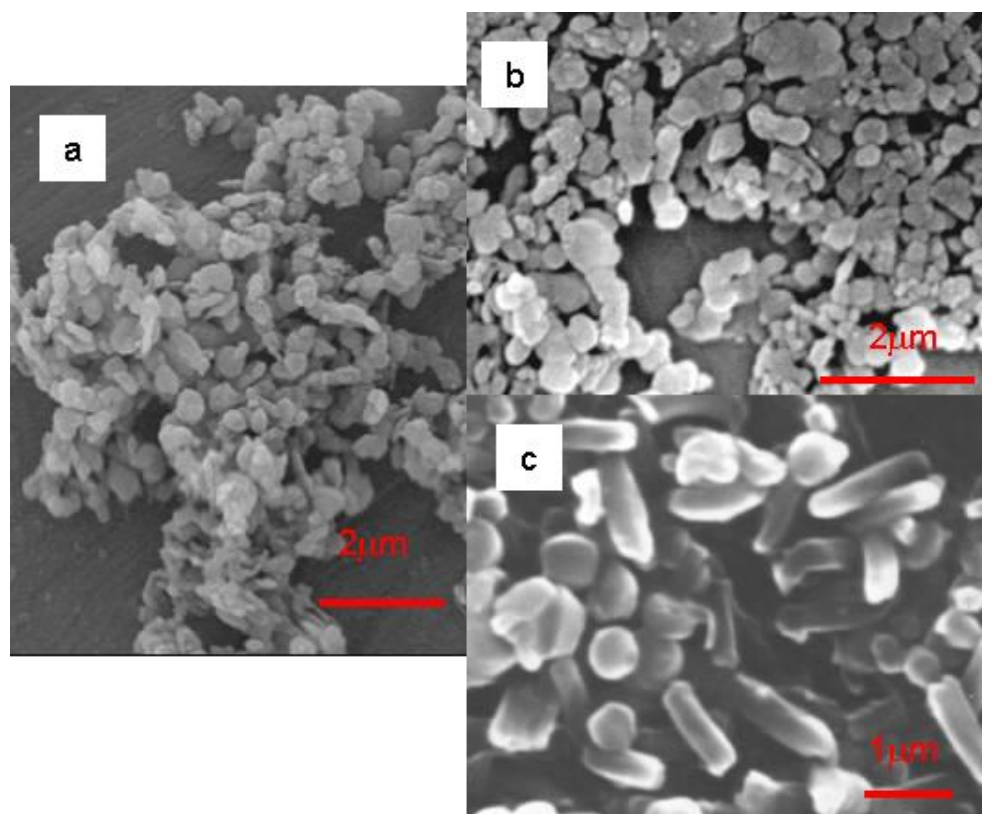


Figure 5: SEM images of a) as-synthesized MCM41-CFA b) surfactant-free MCM41-CFA and c) MCM41 from pure silica source.

CONCLUSIONS

In this study, mesoporous silica materials MCM-41 were successfully prepared from supernatant fused CFA. CFA is a cheaper and environmental friendly alternative silica source in mass production of versatile mesoporous materials. Thus, further studies on the synthesis of other types of porous mesoporous materials from CFA and their application will be investigated.

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