

# Examination of vanadium contaminated pillared rectorite catalysts with the atomic force microscope

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## Abstract

When vanadyl naphthanate solutions in toluene are used to V-contaminate rectorite pillared with alumina clusters, V migration from the pillared clay microporous structure to the outer surface occurs during the thermal treatments used in catalyst preparation. The presence of V on the clay catalyst surface can be inferred from atomic force microscopy (AFM) images showing a marked decrease in surface roughness resulting from the presence of vanadia. AFM images show what are believed to be islands as well as stacks of vanadia layers on the clay surface. Irrespective of the thermal and hydrothermal treatments used to prepare these catalysts, atomic scale details of V-contaminated clay samples retain the surface parameters characteristic of the silicate layers in smectites. These results suggest that V on the clay surface is present as V=O groups attached to the three basal oxygens of the SiO<sub>4</sub> units that form the clay silicate layers. These VO units form an hexagonal arrangement of white spots having next neighbor ( $d_c$ ) and lateral distance ( $d_l$ ) of 5.2 Å and 9.1 Å, respectively.

## 1. Introduction

Rectorite is a mixed-layers clay [1] that, when reacted with polyoxocations of Al or Zr, yields expanded structures with thermal and hydrothermal stability to 800°C [2–4]. Thus, these clay catalysts can withstand the severe process conditions found in fluidized cracking catalyst units (FCCU), the main process for gasoline production. At microactivity test conditions, a steamed sample of natural rectorite (from Garland Co., Arkansas) pillared with alumina clusters was found (during gas oil cracking) to be as active as commercial fluid cracking catalysts (FCC) containing zeolites with the faujasite structure [4].

The resistance to V-deactivation was also high, and only at V levels above 0.5 wt% did pillared rectorites begin losing activity; at 1 wt% V, the catalyst lost all of its useful catalytic properties [5].

High-resolution electron microscopy (HREM), together with X-ray diffraction (XRD) and energy-dispersive spectroscopy (EDS) data, has shown that steaming in the presence of 1% V causes decomposition of the pillars followed by twisting and bucking of the clay silicate layers [5]. Migration of V species on the surface of clay crystals was observed by EDS [5]. Solid state <sup>51</sup>V NMR results have indicated that before steaming V is mainly in an octahedral environment, probably trapped between the pillars, and that after steaming surface species are present in which V

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is in a tetrahedral environment [5]. It is the purpose of this paper to examine surface features of V-contaminated pillared rectorite catalysts with the atomic force microscope (AFM) [7,8,12].

## 2. Experimental

The natural rectorite sample from Garland Co., Arkansas, and the preparation of a pillared catalyst with aluminum chlorhydroxide (ACH) solutions have been described in another paper [10]. A solution of vanadyl naphthenate in toluene was used to metal-load pillared rectorite samples according to an established procedure [6]; the naphthenate was obtained from Pfalz and Bauer, Inc., and contained 2.9 wt% V. The decomposition of the naphthenate was accomplished by heating in air at 540°C/10 h. Steam aging was then performed by passing steam at 760°C over the catalysts for 5 h.

Rectorites, as well as pillared rectorite flakes, were glued onto steel disks with epoxy resin. After the glue dried, the AFM tip was carefully placed in the middle of a flake. The AFM used for these experiments was a contact mode microscope based on the optical lever cantilever detection design of Amer and Mayer [7] and Alexander, et al. [8]. The AFM works like a record player [12]. An *xyz* piezoelectric translator raster scans a sample below a stylus attached to a cantilever. The motion of the cantilever as the stylus moves over the topography of the surface is measured by reflecting a laser beam off the end of the cantilever and measuring the deflection of the reflected laser light with a two-segment photodiode. A digital electronic feedback loop is used to keep the deflection of the cantilever, and hence the force of the stylus on the surface, constant. This is accomplished by raising and lowering the sample in the *z* direction of the *xyz* translator as a sample is scanned in the *x* and *y* directions. The images contain either 256 × 256 or 512 × 152 data points, and nearly all images were acquired within a few seconds. The Si<sub>3</sub>N<sub>4</sub> cantilevers with integral tips used for imaging were 120 μm in length and pos-

sessed a spring constant of approximately 0.6 N/m. The force applied for these images ranged from 10–100 nN. Approximately 700 clay images have been examined in the present and related studies [11].

## 3. Results and discussion

The V-loaded pillared rectorite was prepared by the incipient wetness impregnation technique using a solution of vanadyl naphthenate in benzene. Therefore, after drying (100°C/10 h in flowing air), all of the vanadium is located mainly in the clay microporous structure. However, following the oxidative decomposition of the ligand at 540°C/10h in air, EDS indicates that some vanadium migrated onto the clay surface [10]. Consistent with EDS results [15], V NMR signals from calcined samples were found to arise from vanadium species on the clay external surfaces as well as from V inside the pillared clay microporous structure.

The presence of vanadia on the calcined pillared rectorite (containing 1% V) can be inferred also from the large-scale top view and contour images shown in Fig. 1. In fact, surface irregularities (valleys, cracks, and trenches) such as those shown in Fig. 1A become less evident when vanadia is present on the clay surface. The contour images in Fig. 1A–1D contrast what are believed to be sections of the metal-loaded rectorite catalyst with and without V. The apparent agglomeration of V shown in Fig. 1D has also been observed on the surface of fluid cracking catalysts (FCC) containing 2–4% V [16]. In calcined samples, V is often observed to form on the clay surface, terraces separated by steps about 100–200 nm high, Fig. 1E.

The atomic scale top-view image in Fig. 1F closely resembles the one of the parent (V-free) pillared rectorite [11], since it contains a collection of bright spots in a well-ordered hexagonal pattern. In 2:1 clay minerals [9–11], the bright spots represent the three basal oxygens of a SiO<sub>4</sub> unit, and the dark spots represent the hexagonal holes formed by these units [9–11]. After V-load-

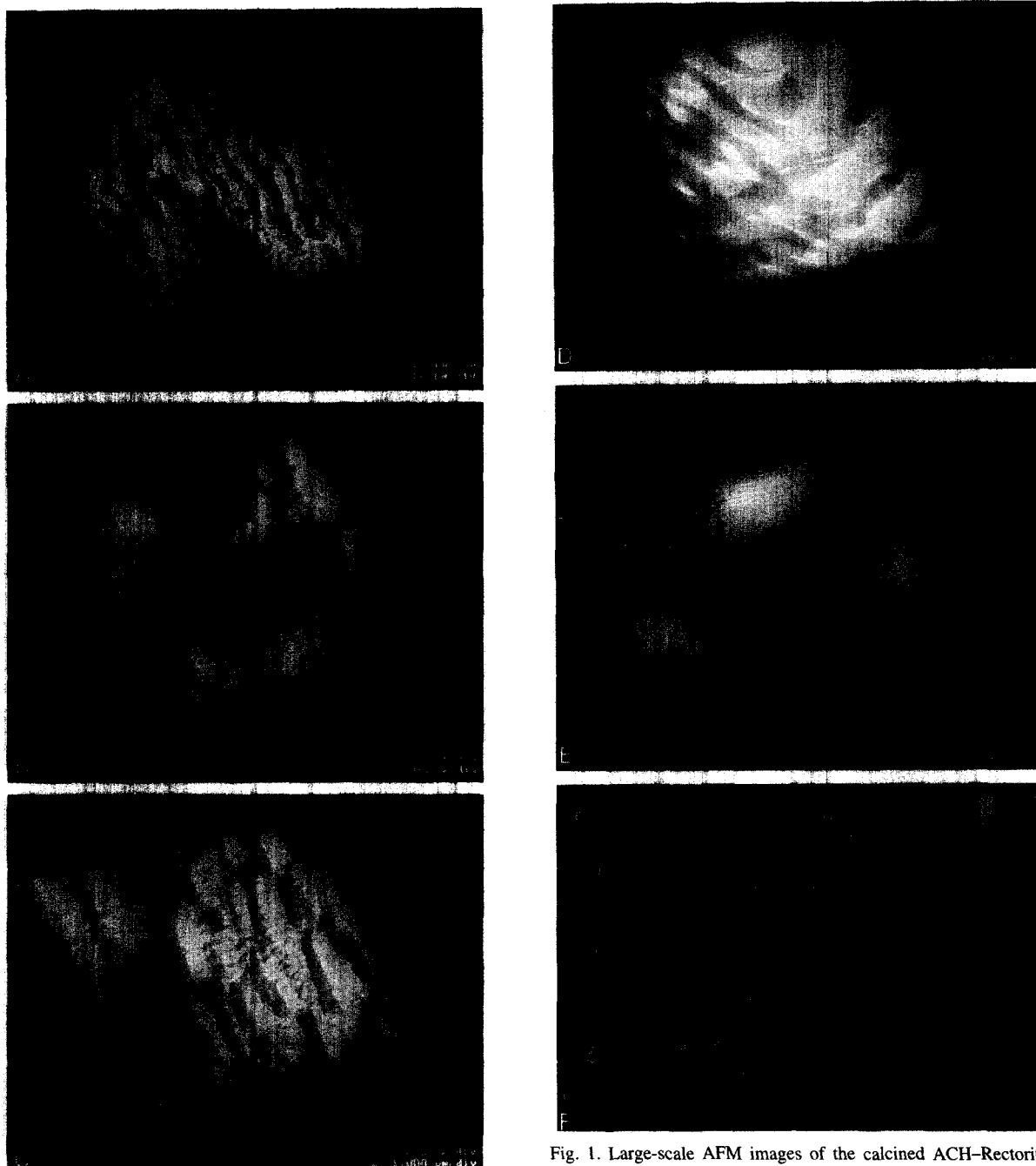


Fig. 1. Large-scale AFM images of the calcined ACH-Rectorite surface (A) without V; (B) and (C) with 1 wt.% V. Vanadium agglomeration on the clay surface is shown in (D) and (E). Atomic scale images of the calcined, V-contaminated pillared clay is given in (F).

ing and calcination, the pattern remains hexagonal although a distortion has occurred. The bright spots in Fig. 1F have lateral neighbors at about 9.0 Å and nearest neighbor distance ( $d_c$ ) at 5.2 Å. These molecular parameters are similar to those of pillared rectorites reported in Table 1 [10]. Thus, it appears that the presence of vanadium did

not greatly affect the rectorite surface features.

Elemental analysis by energy-dispersive spectroscopy (EDS) [5] has indicated that after steam-aging more V migrated from the catalyst interior onto its surface. Furthermore,  $^{51}\text{V}$ -NMR

spectra consist now of a single sharp resonance near -680 ppm, indicating a more uniform environment in which V is in four-coordination [5].

The effects of steaming on the surface topography are shown in Fig. 2. The presence of greater amounts of  $V_2O_5$  seem to eliminate, even more than calcination, the sharp features of the clay surface (see Fig. 2A). Valleys and ridges appear

Table 1

Molecular parameters for the pillared rectorite surface before and after V-loading

Sample	% V	$d_c$ (Å)	s.d.	$d_l$ (Å)	s.d.	Images
ACH(Rectorite), C	0.0	$5.3 \pm 0.2$	0.14	$9.4 \pm 1.0$	0.30	12
ACH(Rectorite), ST	0.0	$5.2 \pm 0.3$	0.14	$9.0 \pm 0.4$	0.30	6
ACH(Rectorite), C	1.0	$5.2 \pm 0.4$	0.18	$9.1 \pm 0.5$	0.35	11
ACH(Rectorite), ST	1.0	$5.2 \pm 0.4$	0.14	$9.1 \pm 0.5$	0.33	6

C = calcined at 540°C in air; ST = steamed at 760°C, 1 atm.

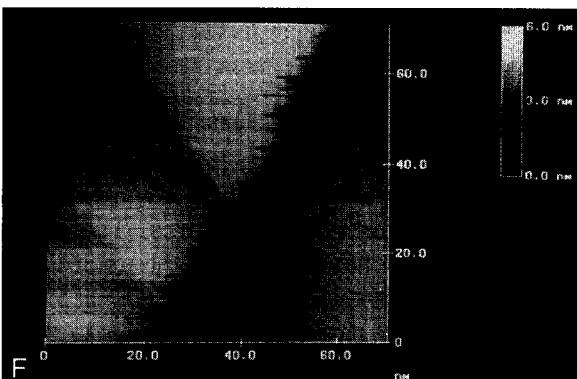
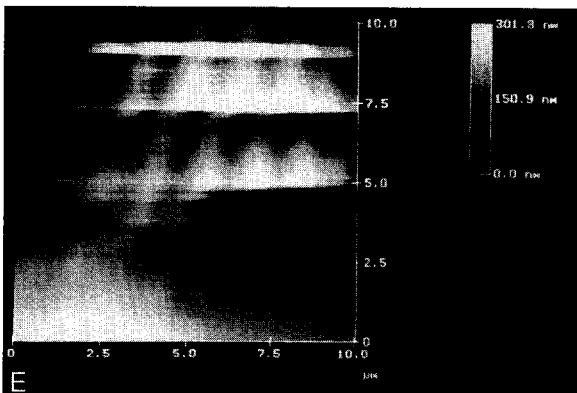
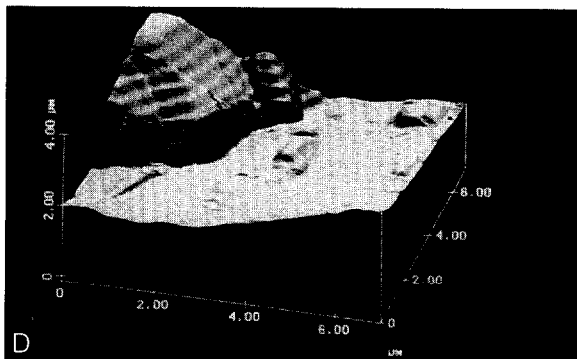
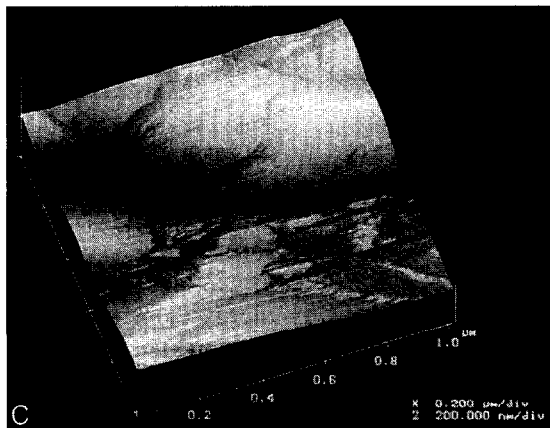
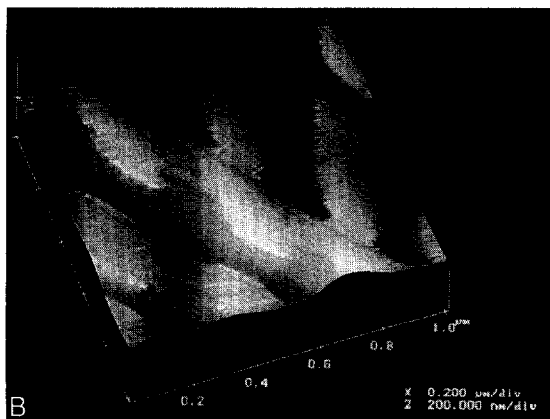
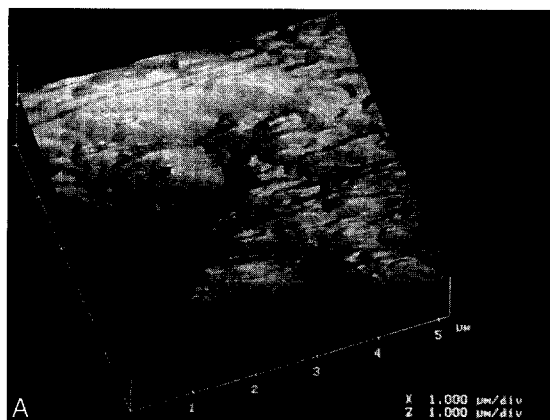


Fig. 2 (continued).

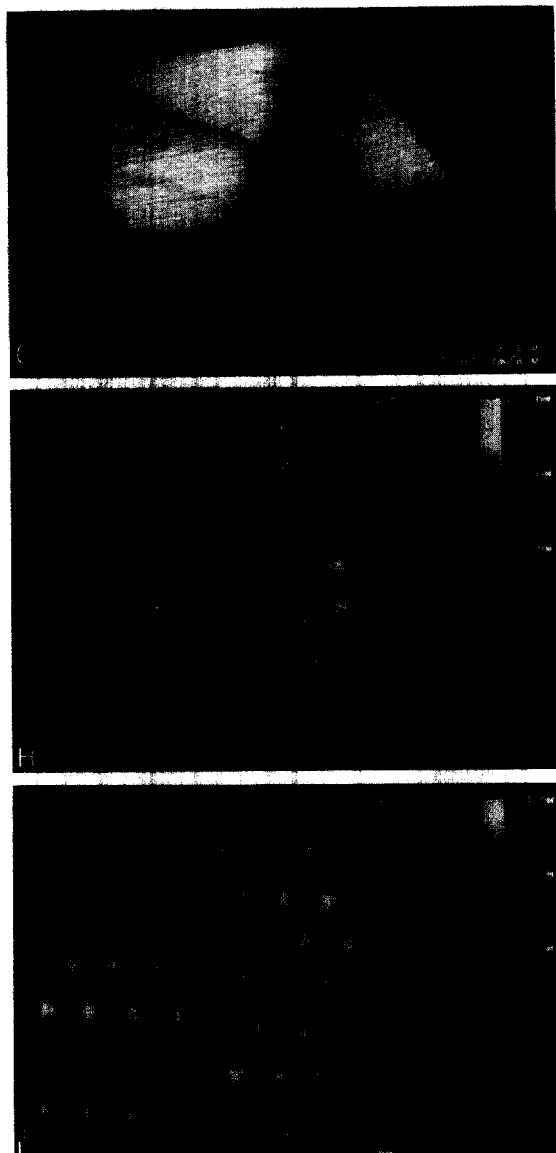


Fig. 2. Large-scale AFM images of the steamed ACH-Rectonite surface: (A) without V; (B) and (C) with 1 wt.% V. The different mode of V-agglomeration on the steam-aged surfaces is shown in (D), (E), (F) and (G). Atomic scale images of steam-aged surfaces before and after V-loading are shown in (H) and (I), respectively.

coated with what has been attributed to be layers of  $V_2O_5$  (see Fig. 2B, 2C). In general, the clay surface appears flattened and surface roughness decreased as in Fig. 2C. Fig. 2D and 2E show again what is believed to be aggregates of Vanadia. V-distribution on the steam-aged surface is now seen more frequently and stacking of  $V_2O_5$  layers becomes more easily observable. In the

small scale images in Fig. 2F-2G, at least 4 layers of  $V_2O_5$  are evident.

Atomic scale images of steam-aged pillared rectorite without V and with 1 wt.% V are compared in Fig. 2H and 2I. The molecular parameters in these images are similar to those shown in Fig. 1F for the calcined sample and to those of the parent rectorite described elsewhere [11]. The white spots in this image have lateral distance  $d_l$  of 9.1 Å and nearest neighbor distance  $d_c$  of 5.2 Å which are well in agreement with the atomic scale parameters in Fig. 1F for calcined ACH-rectonite and for the parent clay [11]. Thus, although steaming causes additional V to migrate to the surface [5], it does not appear to perturb the atomic scale features of this V-contaminated clay catalyst.

In Figs. 1F, 2H, and 2I, the retention of surface features at the atomic scale level after V-impregnation followed by thermal and hydrothermal treatments can be explained by proposing that V on the rectorite surface is present as  $VO_4$  units, with each V attached to the three basal oxygens of the clay  $SiO_4$  layer (Fig. 3). This explanation is consistent with  $^{51}V$  NMR spectra, indicating that after steaming, V is present mainly in a tetrahedral environment [5]. At the hydrothermal conditions used, some of these  $VO_4$  units could react with steam and leave the clay surface as  $H_4V_2O_7$  [13,14]. Intraparticle transport of vanadium in FCC has been observed in microreactor testing [13] as well as when analyzing equilibrium FCC from a refinery [15].

#### 4. Summary and conclusion

AFM images have shown that the presence of vanadia-like phases [14,16] reduce the surface roughness of the clay catalyst and that V-islands as well as stacks of vanadia 3-5 layers thick are probably present. The V-contaminated surface retains the atomic scale parameters of the silicate layers in smectites, suggesting that V can also be present as  $V=O$  units joined to the basal oxygens

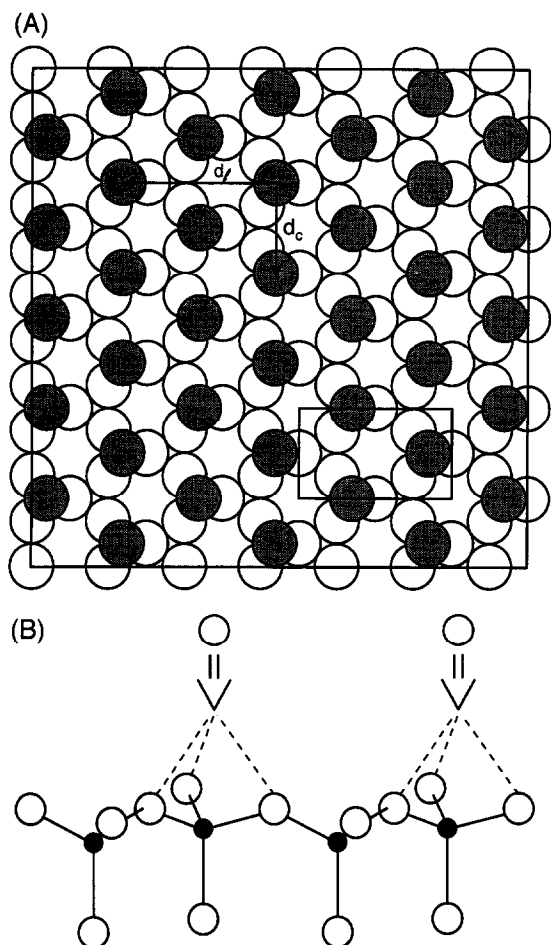


Fig. 3. A schematic representation of the V-contaminated pillared rectorite surface. (A) The three basal oxygens of the  $\text{SiO}_4$  units in the clay silicate layer, form hexagonal oxygen rings onto which  $\text{V}=\text{O}$  units (shown as gray circles) are attached. A unit cell and the lateral distances  $d_l$  and  $d_c$  at which  $\text{V}=\text{O}$  units can be found, are shown by solid lines. (B) Side view of a possible distribution of  $\text{V}=\text{O}$  units on the clay silicate layer.

of the  $\text{SiO}_4$  tetrahedra that form the clay silicate layer.

Scanning probe microscopy is becoming an increasingly important tool to study catalyst surfaces at the macroscopic and atomic level. However, observations and conclusions remain tentative since the AFM cannot provide chemical composition information of the surface it can describe with such an unprecedented resolution. Furthermore, it must be noted that the AFM can

generate artifacts resulting from probe irregularities as well as from morphological deformation induced by the excessive rigidity of the cantilever used.

Variability in image quality was observed from sample to sample and when changing cantilevers. On rough surfaces, the surface contour is traced with an accuracy controlled by the tip size and by the cantilever spring constant. The interpretation of the images shown in Figs. 1 and 2 was assisted by taking side views and by rotating the images in different directions.

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