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Design of stable and reactive vanadium oxide catalysts supported on binary oxides

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Abstract

A series of titania based mixed oxides viz., TiO_2–SiO_2, TiO_2–Al_2O_3, TiO_2–ZrO_2, and TiO_2–Ga_2O_3 were prepared by a co-precipitation method. These mixed oxides were impregnated with V_2O_5 ranging from 2 to 30 wt% by using ammonium metavanadate as source of vanadium oxide. The mixed oxide supports and the vanadia impregnated catalysts were then subjected to thermal treatments from 773 to 1073 K and were investigated by XRD, FTIR, O_2 uptake and BET surface area methods to establish the effects of vanadia loading and thermal treatments on the surface structure of dispersed vanadia species and thermal stability of the catalysts. Calcination of coprecipitated support hydroxides at 773 K resulted in the formation of an amorphous phase, and further heating to 1073 K resulted in the formation of titania anatase phase, except with TiO_2–ZrO_2 support where a $ZrTiO_4$ compound was observed. All these mixed oxides exhibited a high thermal stability. Oxygen uptake results suggested a high dispersion of vanadia on these mixed oxide supports when calcined at 773 K. The mixed oxide based V_2O_5 catalysts studied are found to be very active and selective for the synthesis of isobutyraldehyde from methanol and ethanol, and for the selective oxidation of 4-methylanisole to anisaldehyde. © 1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

Vanadium oxide containing mixed oxides are the basic components of industrial catalysts for the selective oxidation of hydrocarbons and for the selective catalytic reduction (SCR) of nitrogen oxides [1–3]. Selective oxidation plays an important role both in the production of materials required and in the destruction of undesired products by total catalytic oxidation. The SCR of NO_x with ammonia or hydrocarbons is largely employed to reduce atmospheric pollution from stationary power sources and this process has also gained tremendous importance recently due to more stringent emission regulations in many countries. Therefore, several efforts are being made on the one hand to develop various kinds of new catalysts to satisfy the needs of practical application, and on the other hand, to explore the nature and structure of the active phase of the catalysts by using several modern physico-chemical techniques.

The V_2O_5/TiO_2 is used in practice as one of the best catalysts for the medium temperature range SCR of NO_x with NH_3 and for selective oxidation of various

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hydrocarbons [4]. In both cases, TiO_2 in the form of anatase is used as the support. This is primarily because of the remarkable fit of the crystal planes in contact at the vanadia–titania interface, which is assumed to give rise to the epitaxial growth of the vanadia (0 1 0) plane at the monolayer level [5]. In spite of this advantage, titania as a support suffers from limited surface area, lack of abrasion resistance, poor mechanical strength, and high price. In addition, the anatase phase of titania has a poor thermal stability at high temperatures. Temperature stability in catalysis is of vital importance, since in high temperature oxidations or SCR, long-term thermal stability dictates the catalyst life. Because of these reasons, attempts to obtain a titania based support, combined with a highly stable support in order to improve the thermal stability, mechanical strength and high surface area have been the object of some very recent investigations [6–12]. Therefore, a mixed oxide support having titania as a major or a minor component has been preferred over a single titanium oxide support. In view of this, a comprehensive investigation was undertaken to synthesize various mixed oxides useful as supports as well as catalysts for different applications. In the present study an attempt has been made to explore the effect of thermal treatments on the dispersion and stability of vanadia on TiO_2–SiO_2, TiO_2–Al_2O_3, TiO_2–ZrO_2, and TiO_2–Ga_2O_3 mixed oxide supports.

2. Experimental

2.1. Catalyst preparation

The various mixed oxide supports used in this study were prepared by a co-precipitation method using urea as hydrolyzing agent [13]. All the reagents used were procured either from Fluka or from Loba Chemie and were AnalaR grade. In a typical experiment, in order to obtain the desired composition of the mixed oxide support, the requisite quantities of titanium tetrachloride and sodium silicate (or sodium aluminate or zirconium oxychloride or gallium chloride) were dissolved separately in deionized water and mixed together. Cold $TiCl_4$ was first digested in cold concentrated HCl and subsequently diluted with deionized water. To the mixture solution an excess amount of urea solid was added and mixed thoroughly. The homogeneous and clear mixture solutions of mixed oxide precursors and urea were heated slowly to 368 K on a hot plate with vigorous stirring. In about 6 h of heating, as decomposition of urea progressed to a certain extent, the formation of precipitate gradually occurred and the pH value of the solution increased. The precipitate was heated for six more hours to facilitate aging. The precipitates thus obtained were filtered, washed several times with deionized water until free from chloride ions, and dried at 383 K for 16 h. In order to remove sodium ions, the oven dried precipitates were again washed with ammonium nitrate solution several times and dried once again at 383 K for 16 h and were finally calcined at 773 K for 6 h in open-air atmosphere. Some portions of these supports were once again heated at 873, 973, and 1073 K for 6 h in a closed electrical furnace in open-air atmosphere. To impregnate V_2O_5 (2–30 wt%), the required amount of ammonium metavanadate was dissolved in 1 M oxalic acid solution, and the finely powdered calcined (773 K) support material was added to this solution. Excess water was evaporated on a water bath with continuous stirring. The resultant solid was then dried at 383 K for 12 h and calcined at 773 K for 5 h in flowing oxygen. Some portions of the finished catalysts were once again heated at 873, 973 and 1073 K for 6 h in open-air atmosphere. The rate of heating (as well as cooling) was always maintained at 10 K min^{-1}.

2.2. Catalyst characterization

X-ray diffraction analysis was performed on Siemens D5000 diffractometer with nickel filtered Cu K_α radiation. The XRD phases present in the samples were identified with the help of ASTM powder data files. The FTIR spectra were recorded on a Nicolet 740 FTIR spectrometer at ambient conditions, using KBr disks, with a nominal resolution of 4 cm^{-1} and averaging 100 spectra. A conventional standard volumetric high vacuum (1×10^{-6} Torr) system was used for high temperature (643 K) oxygen chemisorptions (HTOC). Before uptake measurements, the catalyst sample (ca. 0.5 g) was reduced for 4 h at 643 K followed by evacuation at the same temperature for 2 h. The amount of O_2 chemisorbed was determined as the difference between the two successive adsorption isotherms generated at 643 K. More details of this method are described elsewhere [14]. The BET surface area of the catalyst was determined by N_2 physisorption at 77 K by taking 0.162 nm^2 as the area of cross section of N_2 molecule.

3. Results and discussion

The BET surface areas of various mixed oxides prepared in this study are presented in Table 1. Monolayer surface coverage of the surface vanadia overlayer on an oxide support can be estimated from structural calculations [15]. The monolayer surface coverage is defined as the maximum amount of amorphous or two-dimensional vanadia in contact with the oxide support. From the V–O bond lengths of crystalline V_2O_5, monolayer surface coverage is estimated to be 0.145 wt% V_2O_5 per m^2 of the support. In reality the maximum amount of vanadium oxide that can be formed in the two-dimensional vanadium oxide overlayer, i.e., monolayer coverage, depends not only on the support surface area but also on the concentration of reactive surface hydroxyl groups apart from other preparative variables [1]. In view of these reasons a range of V_2O_5 contents from 2 to 30 wt% were selected in this investigation.

The XRD patterns of the titania–zirconia mixed oxide support calcined at various temperatures from 773 to 1073 K is shown in Fig. 1. As can be noted from this figure, the TiO_2–ZrO_2, mixed oxide is in amorphous or poorly crystalline state up to 873 K calcination temperature. Formation of crystalline $ZrTiO_4$ compound is seen from temperatures of 973 K and above, and the intensity of the lines due to this compound increase with increase in calcination temperature upto 1073 K. Recently, Fung and Wang [16] also reported the formation of $ZrTiO_4$ compound at temperatures of 923 K and above. Our XRD results coincide exactly with their results. In the case of TiO_2–SiO_2, TiO_2–Al_2O_3 and TiO_2–Ga_2O_3 supports no such compound formation was observed. At 773 K calcination only broad diffraction peaks of TiO_2 anatase, with no evidence of either rutile phase of TiO_2 or other component oxides were observed. Here again, with increase in calcination temperature the intensity of lines due to anatase phase increased from 773 to 1073 K.

XRD patterns of V_2O_5/TiO_2–SiO_2 catalysts together with that of TiO_2–SiO_2 support, calcined at 773 K is presented in Fig. 2. In the case of titania–silica support the diffractogram consists of broad diffraction peaks of TiO_2 anatase, with no evidence of the presence of either rutile or SiO_2 phases. However, for samples containing 25% and 30% V_2O_5, in addition to anatase reflections new broad peaks appear at d=4.37, 3.39 and 2.87 Å which are attributed to the presence of crystalline V_2O_5. The absence of V_2O_5 pattern in samples containing less than 25% of vanadia suggests unequivocally that it is in amorphous or highly dispersed state on the surface of the support. As described above, the monolayer capacity of the TiO_2–SiO_2 support (238 $m^2\,g^{-1}$) comes out to be 16 wt% V_2O_5 using one of the recommended values of 0.145 wt% V_2O_5 per m^2 of the support. XRD results thus show that crystalline V_2O_5 is formed only when the amount of vanadium oxide exceeds the quantity necessary for the monolayer capacity of the support. Another interesting point from this figure is the intensity of the peak corresponding to the diffraction by (1 0 1) plane of anatase which sharpens with increase in V_2O_5 content. The XRD patterns of V_2O_5/TiO_2–Al_2O_3 catalysts also revealed no crystalline vanadia upto 16 wt% [17]. Similarly, the monolayer capacities

Table 1
Composition, BET surface area, oxygen uptake and dispersion of various mixed oxide supported vanadium oxide catalysts

Support	Composition (mole ratio)	BET SA[a] ($m^2\,g^{-1}$)	V_2O_5 (wt%)	BET SA[b] ($m^2\,g^{-1}$)	O_2 uptake (μ mol g^{-1})	D^c (%)
TiO_2–SiO_2	1:1	238	20	125	913.1	83
TiO_2–Al_2O_3	1:1	159	16	119	681.6	77
TiO_2–ZrO_2	1:1	164	16	122	616.1	70
TiO_2–Ga_2O_3	5:1	122	12	55	532.1	81

[a] BET surface area obtained after calcination of the mixed oxide support at 773 K.

[b] BET surface area of the vanadia impregnated catalyst after calcination at 773 K.

[c] Dispersion=fraction of vanadium atoms at the surface, assuming $O_{ads}/V_{surf}=1$.

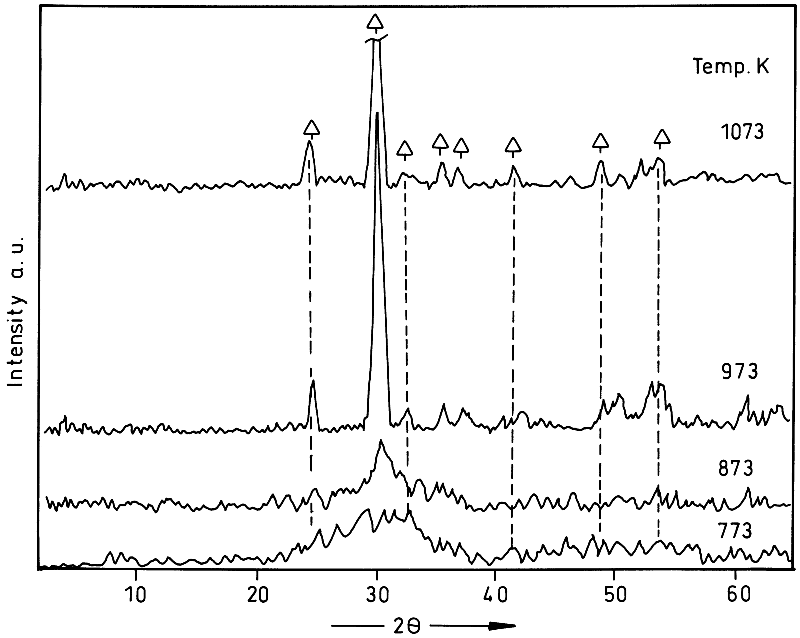

Fig. 1. X-ray powder diffraction patterns of TiO_2–ZrO_2 calcined at various temperatures: (Δ) lines due to $ZrTiO_4$.

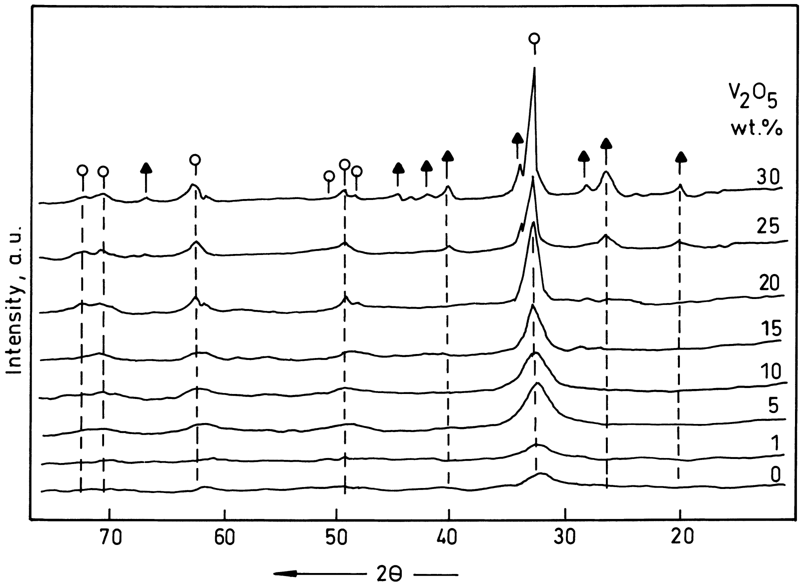

Fig. 2. X-ray powder diffraction patterns of V_2O_5/TiO_2–SiO_2 catalysts calcined at 773 K: (○) lines due to TiO_2 anatase; (▲) due to V_2O_5.

of TiO_2–ZrO_2 [18] and TiO_2–Ga_2O_3 [19] supports were observed to be 16% and 12%, respectively. These results were further supported from FTIR and O_2 uptake measurements. The XRD and O_2 chemisorption observations were further confirmed from solid state ^{51}V and ^{1}H NMR measurements on the V_2O_5/TiO_2–ZrO_2 catalysts [18] and ESCA measurements on V_2O_5/TiO_2–SiO_2 samples [20].

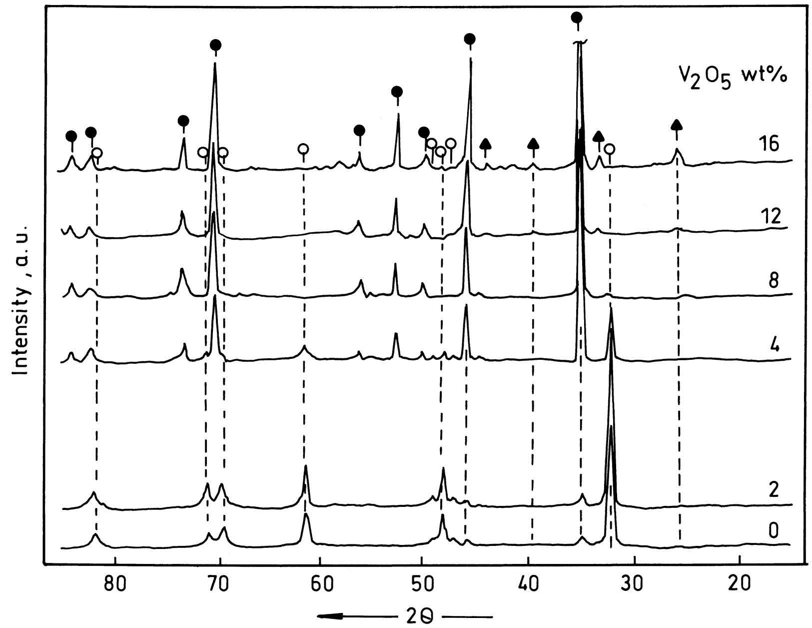

Fig. 3. X-ray powder diffraction patterns of $V_2O_5/TiO_2–Al_2O_3$ catalysts calcined at 1073 K: (○) lines due to TiO_2 anatase; (●) due to TiO_2 rutile; (▲) due to V_2O_5.

In order to see the thermal stability of supports as well as vanadia-impregnated catalysts, the 773 K calcined samples were again subjected to various high temperature treatments. XRD profiles of $V_2O_5/TiO_2–Al_2O_3$ samples calcined at 1073 K are shown in Fig. 3. Upon calcination of the samples at 873 K an improvement in the crystallinity of anatase phase was noted and its intensity also increased with increase in vanadia content. Further, a partial transformation of anatase into rutile was noted from 12% V_2O_5 and above loadings and the crystalline V_2O_5 phase was also observed. On further raising the calcination temperature to 973 K the XRD lines due to rutile become stronger with their intensity increasing with the increase in vanadia content. A total transformation of anatase into rutile was noted from 8% and above loadings. As can be noted from Fig. 3, at 1073 K the anatase phase disappears totally in the catalysts containing 8–16% vanadia. The TiO_2 remains predominantly as anatase in the pure $TiO_2–Al_2O_3$ and 2% $V_2O_5/TiO_2–Al_2O_3$ sample despite heating to 1073 K. Therefore, it may be inferred that the $TiO_2–Al_2O_3$ binary oxide support obtained by a co-precipitation method is thermally stable in the absence of vanadia on its surface. Small amounts (<2) of V_2O_5 seem to be insufficient to induce the phase transformation of anatase to rutile. Similar phenomena were noted in the case of $V_2O_5/TiO_2–SiO_2$ [12] catalysts. However, in the case of $V_2O_5/TiO_2–Ga_2O_3$ [19] samples, the anatase into rutile phase transformation was noted at temperatures of 973 K and above, and the anatase phase still present even after 1073 K calcination. All these supports obtained by homogeneous precipitation method exhibited reasonably high BET surface areas and good thermal stability upto a calcination temperature of 1073 K. It is well known in the literature that at elevated temperatures the supported vanadia phase initiates the titania anatase-into-rutile transformation [5,21]. During this transformation some of the V_2O_5 is normally reduced and gets converted into the rutile structure as $V_xTi_{(1-x)}O_2$ (rutile solid solution) [5,15,21,22].

The FTIR spectra of $V_2O_5/TiO_2–Al_2O_3$ catalysts calcined at 773 K are shown in Fig. 4 in the range 400–1600 cm^{-1}, where bands due to the $\nu_{V=O}$ mode are expected to be recorded. The spectrum of pure V_2O_5 shows sharp absorption bands at 1020 cm^{-1} and another at 824 cm^{-1}. These agree with the literature

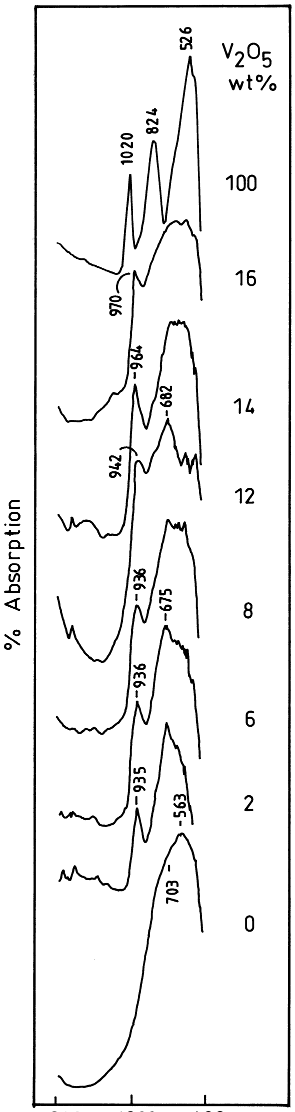

Fig. 4. FTIR spectra of $V_2O_5/TiO_2–Al_2O_3$ catalysts calcined at 773 K.

[21], which assigns the former to V=O stretching and the latter to the deformation of V–O–V bridges. Anatase and rutile phases of titania exhibit strong absorption bands in the regions of 850–650 and 800–650 cm^{-1}, respectively. The FTIR spectra of $V_2O_5/TiO_2–Al_2O_3$ catalysts indicate that the vanadium oxide is in a highly dispersed state. The spectra show essentially only one band at 935 cm^{-1} for 2% catalyst and at 970 cm^{-1} for 16% catalyst. A gradual shift from 935 to 970 cm^{-1} is noted with gradual increase in vanadia content. Peaks in the 1000–940 cm^{-1} region can be attributed to surface vanadate species as has been previously reported for amorphous two-dimensional monolayers on V_2O_5/TiO_2 catalysts [21,23]. Thus for the catalysts containing 16% or less V_2O_5, no evidence for the crystalline V=O is seen and all the vanadia is present as a two-dimensional monolayer on the support surface. Further, the FTIR results are in perfect agreement with the results of XRD analysis. However, in the case of samples calcined at 873 K and higher temperatures the formation of crystalline V_2O_5 phase was observed from both XRD and IR measurements. Similar FTIR spectra were obtained for other series of catalysts in line with XRD observations.

The oxygen uptakes at 643 K on the prereduced catalysts are shown in Table 1. The pure supports were also found to chemisorb some small amount of oxygen under the experimental conditions used in this study. Therefore, the contribution due to the support alone was subtracted from the results. The oxygen uptakes were found to increase with increase in V_2O_5 loading upto the monolayer coverage and leveling off with further loading. Irrespective of the support used, the O_2 uptakes were maximum in the case of catalysts calcined at 773 K and minimum at 1073 K. A substantial loss in the BET surface areas of the catalysts were also noted after calcination at 1073 K due to sintering. When the uptake of O_2 is plotted against V_2O_5 loading, it was observed that at very low loadings the slope approaches unity. This is an indication of a limiting stoichiometry of $O_2/V_2O_5=1$ [14,24]. Using this stoichiometry the dispersion was defined as the ratio of molecular oxygen uptake to V_2O_5 content. The dispersions derived from O_2 uptake measurements are presented in Table 1. In general, very good dispersion of vanadium oxide on various supports was observed. Among the notable is the $V_2O_5/TiO_2–SiO_2$ catalyst system. This high dispersion was also clearly reflected in their high catalytic activity, when this catalyst was employed for the single step synthesis of isobutyraldehyde from methanol and ethanol mixtures [25]. Further this mixed oxide was found to be superior to the individual single oxide supported catalysts. The acid–base characteristics of the unique $TiO_2–Ga_2O_3$ mixed oxide support and the redox properties of the vanadium oxide were utilized for the selective oxidation of 4-methylanisole to anisaldehyde more recently [26].

As in the case of single oxide supported vanadium oxide catalysts the present study on mixed oxide based catalysts reveals that vanadium oxide in the lower loading regions, i.e., below monolayer capacity, exists in a highly dispersed state, probably monomeric species at very low loadings and polymeric species at slightly higher loadings. However, at very high loadings, i.e., above monolayer capacity, it exists in the form of a microcrystalline V_2O_5 phase [1,3].

4. Conclusions

The TiO_2–SiO_2, TiO_2–Al_2O_3, TiO_2–ZrO_2, and TiO_2–Ga_2O_3 mixed oxides obtained by a co-precipitation method exhibit reasonably high specific surface and good thermal stability. Highly dispersed vanadium oxide monolayer catalysts with vanadia loadings nearly equivalent to the theoretical monolayer capacity of the supports can be obtained. The vanadia impregnated catalysts when calcined at 773 K were found to be in highly dispersed state on the carrier. When these catalysts were subject to thermal treatments from 773 to 1073 K a gradual transformation of anatase into rutile was noted. This phase transformation was highly dependent on the concentration of vanadia and is accompanied by a loss in the specific surface area of the catalysts. All the mixed oxide supports are very promising materials for the dispersion of vanadium oxide. These mixed oxide based V_2O_5 catalysts were also found to be very active and selective for the synthesis of isobutyraldehyde from methanol and ethanol [25] and for the selective oxidation of 4-methylanisole to anisaldehyde [26].

The TiO_2–ZrO_2 mixed oxide support, when calcined at 773 K, is in X-ray amorphous state and exhibits a high specific surface area. The amorphous TiO_2–ZrO_2 gets converted into $ZrTiO_4$ compound beyond 873 K calcination temperature and this compound is thermally quite stable even upto 1073 K.

Finally, further studies are required in order to understand fully the microscopic mechanism of selective interaction of vanadia with individual components in the mixed oxide support. With this understanding better mixed oxide-based vanadia catalysts can be designed for a given reaction.

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