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**MOLYBDENUM CATALYSTS SUPPORTED ON HYDROUS "TITANATES"
FOR LOW SEVERITY COPROCESSING OF HEAVY OIL AND COAL**

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MOLYBDENUM CATALYSTS SUPPORTED ON HYDROUS "TITANATES"
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ABSTRACT

Molybdenum catalysts promoted with nickel, cobalt and aluminum were prepared by ion exchange of a sodium hydrous "titanate" support. These catalysts were tested in an autoclave system with a constant flow of hydrogen for the low severity coprocessing of one part subbituminous coal and two parts residual oil from vacuum distillation of an Alberta heavy oil. X-ray photoelectron spectroscopy provided information on the difference between cobalt-molybdenum active sites on hydrous titanates and alumina. Experimental results indicated that the coal conversion and the product distribution were affected by the relative acid site density of the catalysts which was evaluated by dynamic adsorption of ammonia.

INTRODUCTION

The concept of simultaneously processing large quantities of coal and bitumen or heavy oil (coprocessing) may be an option for the production of synthetic fuels in Canada, where large deposits of coal and heavy oil are located in proximity. Recently, catalysts supported on hydrous titanates demonstrated higher coal conversion and oil yield as well as improved product quality (1). The molybdenum-exchanged catalyst compared favourably with commercial hydrotreating catalysts. In the present work, additional ions (cobalt, nickel, aluminum) were added to molybdenum-exchanged hydrous titanates as promoters. A discussion is presented on the performance of promoted molybdenum catalysts supported on hydrous titanates for low severity coprocessing in relation to their characterization - acid site density, nature of the molybdenum and cobalt active sites and pore distribution. Comparisons are also made with respect to the surface analysis by X-ray photoelectron spectroscopy between alumina and "titanates" supports.

EXPERIMENTAL

Catalysts supported on hydrous titanates were developed by Dosch et al. (2) and Stephens et al. (3). The procedures we followed for the preparation of the support ($\text{NaTi}_2\text{O}_5\text{H}$) and the exchange of metal ions were described previously (1). Promoter ions such as nickel (<13%: MB-603,613,621,622,623), cobalt (<5%: MB-592,626B,630) and aluminum (<1%: MB-626B,630) were incorporated to the molybdenum catalysts (<11% Mo) by successive exchanges. Catalysts were calcined in air at 400°C for 2 h (heating rate: 5°C/min). Their surface area, measured by nitrogen adsorption, varied from 50 to 190 m²/g. They formed lumps from about 30 to 60 μm diameter of agglomerated particles of 1 μm and were microcrystalline and very porous (1). A commercial Co-Mo on Al₂O₃ catalyst (Harshaw HT-400E, BET surface area 190 m²/g) was used as reference catalyst (MB-531) in a powder form (grain size <149 μm).

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The relative acid site density of the catalysts was estimated by dynamic adsorption of NH_3 (4). Pulses of ammonia were injected in a catalyst bed (0.1 g) which is maintained at 120°C under a constant flow of helium. The number of acidic sites expressed in $\mu\text{mole NH}_3/\text{gram}$ was calculated from the cumulative amount of ammonia adsorbed at each pulse. The catalyst was pre-sulphided with a mixture of 10% H_2S in H_2 at 350°C for 2 h. Similarly, dispersion of the metal ions (Mo, Co, Ni) was evaluated using oxygen instead of ammonia.

Information on catalyst activity for hydrodesulphurization was obtained from thiophene HDS performed at 360°C and 400°C. For these tests, 0.1 g of catalyst was placed in a small tubular reactor (3.5 mm ID) and pre-sulphided with the reactant mixture of 8% thiophene in hydrogen (flow rate of 40 mL/min). Separation of the products was achieved with a 20% BMEA column (7.2 m long) with the gas chromatograph oven maintained at 70°C.

The calcined and spent Co-Mo catalysts MB-592 (titanate support) and MB-531 (alumina support) were examined by X-ray photoelectron spectroscopy (XPS) using a Physical Electronics Industries spectrometer (PHI-548E, Mg anode). The instrumentation and operating conditions were described previously (5). All peak energies were referenced to Ti $2p_{3/2}$ at 458.6 eV (or to Al $2p$ at 74.4 eV) and cross-checked against the hydrocarbon (C $1s$) line. The C $1s$ peak position was found at 284.6 eV for all calcined catalysts. However it decreased to 284.2 eV for the two spent catalysts indicating graphite-like deposits. An electron flood gun (charge neutralizer) was used to minimize specimen charging. As a second precaution, the full width at half maximum (FWHM) and the position of the support's cation peak were closely monitored with and without the neutralizer for each sample. Neither the FWHM nor the position of Ti $2p$ (2.0, 458.6 eV) and Al $2p$ (2.7, 74.4 eV) varied during this study. The energy scale of the spectrometer is calibrated using sputter cleaned gold foil (Au $4f_{7/2}$ = 83.8 eV).

The hydrocarbon feedstock was a mixture of 33 wt % Forestburg subbituminous C coal (as received) and 67 wt % Cold Lake vacuum bottoms (CLVB) from an Alberta heavy oil reservoir. The coal was used in a powder form (<149 μm diam. particles). The CLVB had an initial boiling point of 420°C and contained about 72 wt % oil (pentane soluble). The feed slurry initially contained about 2.3 wt % sulphur, corresponding to a minimum of 12 S atoms per atom of exchanged cation and sulphiding was assumed to occur in situ under reaction conditions. Properties of these materials are described elsewhere (1).

The catalytic tests were performed at 410°C in a 300 mL stirred autoclave equipped to provide continuous hydrogen flow. A back-pressure regulator maintained the pressure inside the autoclave at 3.4 MPa. A cold trap placed before this regulator removed the distillates from the outlet gases. The hydrogen flowrate of about 275 mL (STP)/min was sufficient to replace the internal gas volume in about 15 min. These conditions were chosen so that reaction occurred at the threshold of coking as shown previously (6). A reaction time of 225 min was maintained in an attempt to observe the hydroprocessing selectivity while reasonably enhancing the distillate yield.

For each run, a product distribution was calculated and expressed as wt % maf feed mixture. Residues were analyzed by extraction with pentane, toluene and THF, for the oil content, asphaltenes, preasphaltenes and THF insolubles respectively. Total oil content was calculated by adding the weight of the distillates, excluding water, and the oil drained from the autoclave to the weight of the pentane solubles.

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RESULTS AND DISCUSSION

As shown in Table 1, the molybdenum $3d_{5/2}$ photoline is located at a binding energy of 232.2 eV for Co-Mo catalysts on titanates after calcination at 500°C. This value, indicative of a Mo^{6+} oxidation state, differs from the Co-Mo/ Al_2O_3 catalyst MB-531 found at 232.6 eV. This difference in peak positions indicates that on titanates the state of molybdenum is more electronegative and may suggest the existence of $CoMoO_4$ or $MoTiO_5$ (both tetrahedral Mo^{6+}). On MB-531 catalyst, molybdenum is likely present as Mo^{6+} in either a MoO_3 -like or $Al_2(MoO_4)_3$ -like phase (7-9).

Table 1: XPS binding energy^a, E_b in eV (± 0.2 eV)

	$T_{calc.}$	Mo $3d_{5/2}$	Co $2p_{3/2}$	O 1s
Co-Mo on titanates (MB-592)	150	232.4	781.8	530.4
	350	232.4	781.4	530.2
	400	232.2	781.4	530.0
	500	232.2	781.4	530.0
Co-Mo/ Al_2O_3 (MB-531)	(500) ^b	232.6	781.9	531.6
THF-592 ^c (spent MB-592)		232.2	781.4	530.0
		228.6	779.0	532.0
				533.4
THF-531 ^c (spent MB-531)		232.6	ND ^d	530.6
		228.6		532.2
				533.4

- a) Peak positions are referenced to Ti $2p_{3/2}$ at 458.6 eV for MB-592 and Al 2p at 74.4 eV for MB-531
 b) Possible calcination temperature used by the manufacturer
 c) Contains more than one species of molybdenum and cobalt; also contains Fe 2p (711.0 eV), Ca 2p (347.0), Al 2p (74.4), Si 2p (102.4), Mg 1s (1305.0)
 d) ND: not detectable

Cobalt on titanates appears as Co^{2+} with a binding energy for Co $2p_{3/2}$ of 781.4 eV and most likely indicates $CoMoO_4$, $Co(OH)_2$ or $CoTiO_3$ but not CoO or Co_3O_4 . On MB-531, cobalt is probably present as Co^{2+} in a $CoAl_2O_4$ -like environment (8-10). No sodium is detected by XPS on the surface of the catalysts (detection limit: 0.1 at %) indicating a very high ionic exchange rate with the aqueous Mo and Co complexes. Our XPS results therefore indicate a more electronegative state for Mo and Co on titanates compared to alumina support, and are in accord with the results for titania by Nishijima et al. (11).

The surface content of Mo and Co after calcination at 400°C agrees well with the bulk analysis for MB-592 and MB-531 catalysts as shown by Table 2. When the temperature of calcination is raised from 350°C to 500°C, the XPS Co/Ti and Mo/Ti peak intensity ratios increase approximately by 50% indicating diffusion of Co and Mo atoms to the titanate particles' exterior. It is noted that the titanium peak intensity and the Co/Mo intensity ratio remain almost unaffected by temperature of calcination. It also indicates nearly equal diffusion rates for Co and Mo on titania. Rearrangement of highly

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dispersed Co and Mo atoms to form dispersed particles of CoMoO_4 after calcination at 500°C is further supported by the Co 2p and Mo 3d XPS peak shapes

Table 2: Elemental surface composition^a of Co-Mo catalyst, at % ($\pm 10\%$)

$T_{\text{cal.}}^\circ\text{C}$	On hydrous titanates (MB-592)				On alumina (MB-531)
	150	350	400	500	
Co	3.3 (7.6)	3.5 (7.8)	3.5 (7.7)	4.9(10.5)	0.8 (2.3)
Mo	2.4 (9.0)	3.1(11.3)	3.8(13.6)	3.6(12.6)	1.9 (8.8)
Ti[Al]	20.9(39.2)	21.4(38.7)	20.8(37.1)	21.2(36.7)	[30.8(39.9)]
O	61.5(38.6)	63.5(38.4)	63.6(38.8)	65.2(37.9)	56.2(43.3)
C	11.8 (5.6)	8.5 (3.9)	8.4 (3.8)	5.1 (2.2)	10.3 (5.9)

a) Values in brackets are in weight per cent

b) Bulk analysis - MB-592: 2.8 (10.1)% Mo, 2.2 (5.0)% Co, 22.2 (40.5)% Ti
 - MB-531: 2.0 (8.9)% Mo, 1.0 (2.6)% Co, 35.8 (43.9)% Al

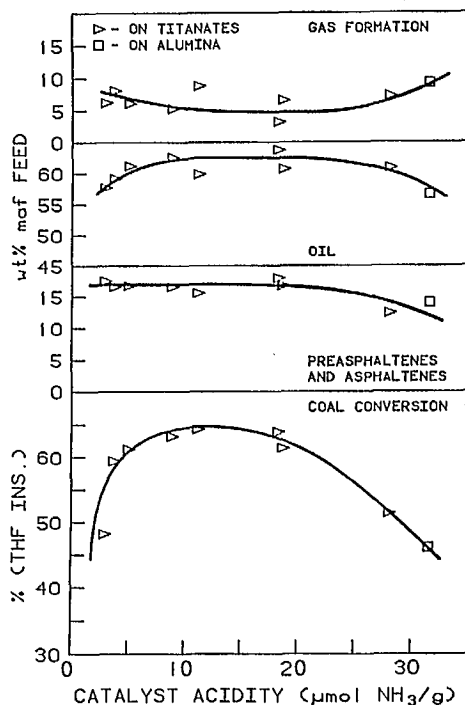


Fig. 1: Coal conversion and product distribution as functions of catalyst acidity.

for CLVB in the feed, indicating an appreciable decrease of the average molecular weight of the oil.

and positions. The dispersion of the molybdenum sites for MB-531 and MB-592 was evaluated by dynamic adsorption of oxygen. These data indicated a higher concentration of molybdenum on titanates (10.9 atoms Mo/nm^2) than on alumina (3.6 atoms Mo/nm^2), further supporting the XPS results which suggest the presence of CoMoO_4 agglomerates.

The titanate catalysts were tested for coprocessing and their acid site density was evaluated. In Figure 1, the conversion of THF-insoluble materials and the distribution of products are plotted as functions of the acidity of the catalysts, measured by dynamic adsorption of ammonia. First, the THF insolubles (indicative of coal conversion) increase sharply, then reach a "plateau", and finally decrease with the most acidic catalysts tested (the Co-Mo catalysts supported on alumina or on titanates promoted with 1 wt % Al). The oil production shows a somewhat different pattern, steadily increasing to a level of about 65-68 wt % maf feed (from only 35 wt % in a test without catalyst). In general, it was observed that 30-40% of the oil products boil below the initial boiling point

These patterns may seem contradictory since one would expect both coal

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conversion and oil production to follow the same trend. The pattern peculiar to the coal conversion may be related to the hydrogen-donor ability of the vehicle oil. This consideration is addressed in the following three paragraphs.

Numerous papers have described the importance of the presence of compounds such as hydroaromatics and heteroatom-containing aromatics in terms of hydrogen transfer to the intermediate radicals participating in the reaction network. The contribution of aromatics in coal-derived solvents is an important factor for the solvolysis of coal according to Curtis et al. (12) who observed a general increase in coal dissolution with increased hydroaromaticity. This is also confirmed by Aiura et al. (13) who showed that in brown coal liquefaction the transferable hydrogen from hydroaromatics present in the feed solvent is the most important factor for solvent quality. Similar conclusions were reached from work on recycle solvent upgrading by catalytic hydrotreatment. According to Awadella et al. (14), the highest coal conversion is achieved when using an intermediate extent of solvent hydrogenation to achieve a maximum concentration of hydroaromatics. Similarly, Sakabe et al. (15) observed an increase in the capacity of a solvent to donate hydrogen with the hydrogen addition up to 170 L H₂ (STP)/L feed, the level above which highly saturated compounds such as naphthenes begin to form. Curtis et al. (16) recently suggested the existence of a similar effect of hydroaromatics on the capacity of the solvent to be a hydrogen-donor during coprocessing.

The presence of a coprocessing catalyst is expected to affect the vehicle oil. Experiments of Kabe et al. (17) with ³H-labelled tetralin and hydrogen, and ¹⁴C-labelled naphthalene indicated that the catalyst activity essentially promotes the hydrocracking of the coal products and the hydrogenation of the solvent. Liquefaction in naphthalene proceeds much faster with a catalyst, because of the successive hydrogenation-dehydrogenation (18). Consequently, one may expect the vehicle oil to be chemically transformed in a slightly different way depending on the catalyst used in the reactor.

Wilson et al. (19) have published the composition in various aromatics and naphthenes of middle distillates hydrotreated at 17.4 MPa between 340°C and 440°C. A minimum was observed for aromatics at about 380°C-390°C, above which thermodynamic equilibrium plays a considerable role by preventing complete hydrogenation of aromatics to naphthenes, thus working towards the solvent enrichment in terms of hydrogen transfer capability. The benzocycloparaffins in these middle distillates were partly cracked by ring opening upon hydrotreatment above 410°C (19). Ring opening occurs even more readily as the number of rings increases (3>2 rings; 4>3; etc.). In addition, 3-ring hydroaromatics seem to be better hydrogen donors than 2-ring hydroaromatics (20). In parallel to this, higher cracking rates are observed with more acidic catalysts. Thus the catalyst acidity would probably increase cracking and affect the concentration of hydroaromatics and other hydrogen donors. At acid site densities corresponding to less than 10 μmol NH₃/g, an increase in acidity is beneficial to coprocessing since the oil yield is raised thus increasing the volume of hydrogen donors, which enhances coal conversion. On the contrary, with acidic catalysts corresponding to more than 20 μmol NH₃/g, the coal conversion is retrograded due to the disappearance of hydrogen donors.

With regard to hydrodesulphurization reactions, the acid site density of a catalyst has a positive effect as shown in Fig. 2. A straight line correlates the performance of all the titanate catalysts with acidity.

An additional factor contributing to the difference in product

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distribution between molybdenum catalysts supported on titanates and alumina

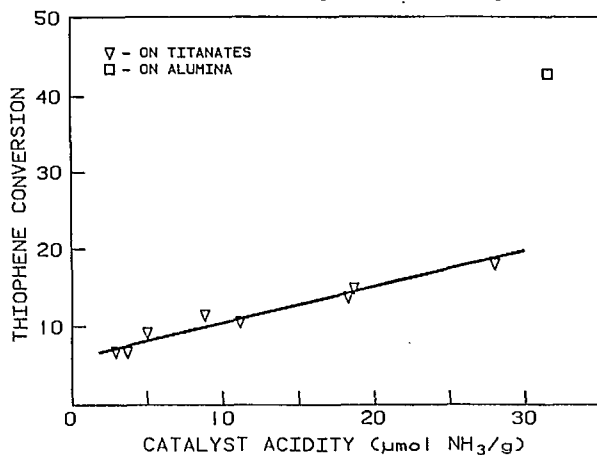


Fig. 2: Conversion of thiophene as a function of the acid site density of the catalyst.

during coprocessing with the amount of carbon deposited on the spent catalysts, after thiophene HDS, since it was not possible to recover the spent catalyst from the THF insolubles in coprocessing tests. The trend indicates

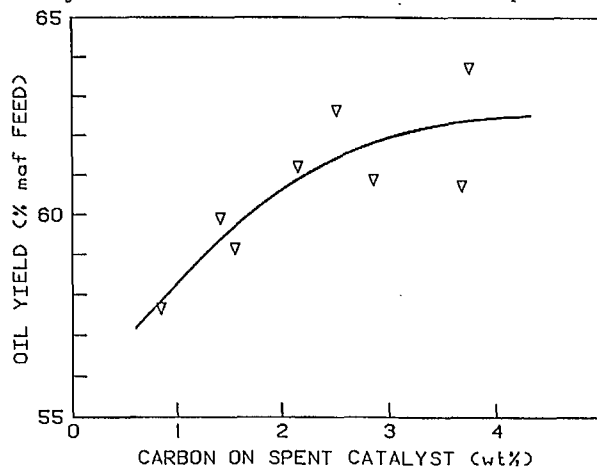


Fig. 3: Oil production from coprocessing versus carbon content in spent catalyst after thiophene HDS.

is the distribution of pore diameters. In an earlier publication (1), we presented mercury porosimetry data indicating the presence of a very wide range of pore diameters for MB-592, from 15 to 100 nm. Such a pore distribution is certainly advantageous for the diffusion of large "molecules" of asphaltenes and preasphaltenes to the active sites. This contrasts remarkably with the limited pore size distribution of MB-531, centering at about 9 nm, given in an earlier publication (1).

Figure 3 correlates the fraction of oil produced during coprocessing with the amount of carbon deposited on the spent catalysts, after thiophene HDS, since it was not possible to recover the spent catalyst from the THF insolubles in coprocessing tests. The trend indicates an increase in oil with increase in deposited carbon possibly a result of higher affinity of hydrocarbons to the catalyst during reaction. The surface concentration of carbonaceous species is expected to be higher for more active catalysts. The fouling tendency caused by these deposits seems to be a complex phenomenon and evidence for different "reactivities" of these deposits was presented by Ternan et al. (21). These types of correlations were also observed in the catalytic upgrading of SRC-II light ends (22) and in the hydrocracking of bitumen (23).

Detailed XPS analysis of the spent alumina (THF-531 in Table 1) and titanate-supported catalysts (THF-592) indicates most or all of the Mo and Co is sulphided during the coprocessing reaction (Fig. 4). Some re-oxidation was unavoidable during transfer from the reactor to the Soxhlet extractor then to the spectrometer. Several sulphur oxidation states (6+, 4+, 0, 2-) are present in the spent catalysts (Fig. 4). Sulphur sited as sulphide (161.8 eV), organic sulphur and elemental sulphur (164 eV), sulphite (167 eV) and sulphate (169 eV) was measured from the XPS S 2p spectrum of the spent catalyst (Fig. 4). The 167 eV and part of the 162 eV peak may be indicative of thiosulphate ($\text{S}_2\text{O}_3^{2-}$) or dithionite ($\text{S}_2\text{O}_4^{2-}$) type species formed during coprocessing or during THF extraction. The sulphate species is most likely associated with mineral matter, iron from oxidized pyrite and calcium as gypsum. Mo sulphide was previously found to be very resistant to oxida-

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tion when careful handling procedures were employed as in this study. XPS analysis of these spent catalysts also indicates the presence of several additional species: Ca, Fe, Na, Mg, Si, and Al, probably the coal's mineral matter (ash) that could not be separated from the catalyst after reaction with the coal-oil feedstock. THF insoluble carbon (coke) is the major component of the spent catalyst surface (≈ 75 at %) and exhibits an XPS fingerprint similar to that of graphite.

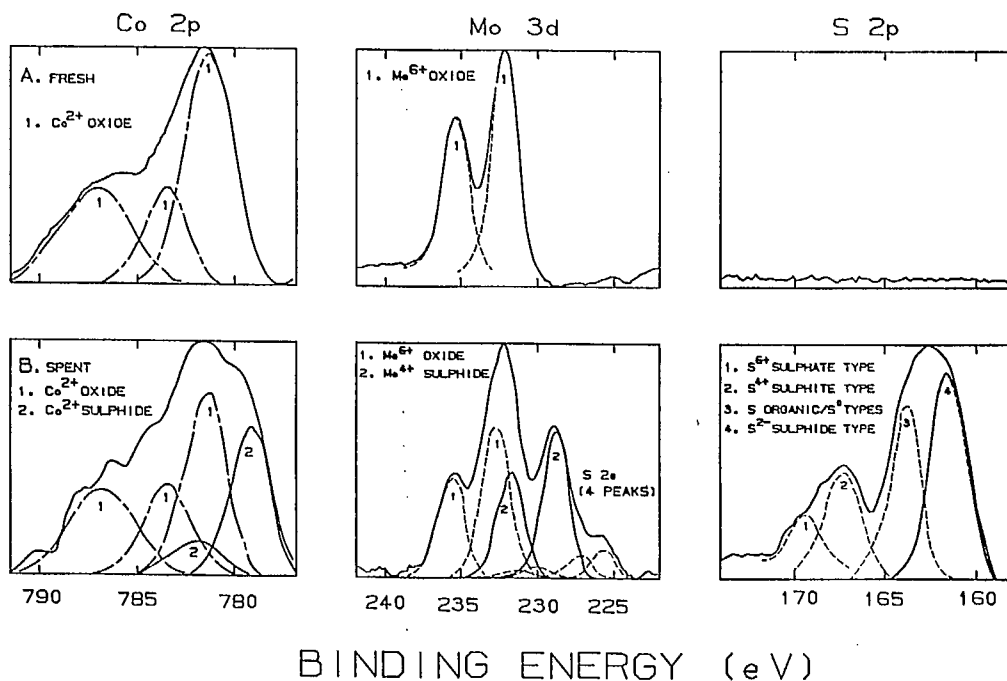


Fig. 4: XPS spectra (Co 2p, Mo 3d, S 2p) of cobalt-molybdenum supported on hydrous "titanates".

CONCLUSIONS

Molybdenum catalysts on "titanates" were found effective for coprocessing mixtures of coal and heavy oil. Their oil yields and coal conversions compared favourably with the alumina-supported Co-Mo catalyst. They have shown advantages which can be attributed to the following characteristics: increased electronegativity of Mo and Co, making the reactants more strongly adsorbed; wider range of pore diameters enhancing diffusion within the pores of hydrocarbon molecules; suitable acid site density for proper solvent enrichment in terms of hydrogen transfer capability; larger number of active sites per unit surface area as shown by O_2 chemisorption; and fewer acid sites where coke could form. The coal conversion may be significantly modified by the catalytic effect on the type and concentration of the hydrogen donors in the vehicle oil.

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