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Lean NO_x reduction CuZSM5 catalysts: evaluation of performance at the spark ignition engine exhaust

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Abstract

CuZSM5 catalysts, prepared by ion exchange of HZSM5 (Si/Al = 80), enable selective lean NO_x reduction at the spark ignition engine exhaust. All catalysts, even if exchanged to very high copper loading (556% apparent exchange level) give no evidence for segregated copper oxide phases. In the presence of water they are easily reduced in vacuum at 550°C and are stable to redox cycles (O_2, vacuum) treatments. Increasing Cu content to about 200% apparent exchange level results in increasing NO_x, CO and HC conversions. From 200 to 550% exchange CuZSM5 catalysts give similar performances. Preliminary investigation shows that after catalytic tests there is evidence for CuO formation only in the copper-richest catalysts.

1. Introduction

Three-way catalysts for automobiles are very effective in simultaneously removing nitrogen oxides (NO_x), hydrocarbons (HC) and carbon monoxide (CO), but require the air/fuel ratio to be maintained very close to the stoichiometric point (air/fuel mass ratio, A/F = 14.6). Best fuel economy, together with lower CO_2 emissions, could be achieved by engines operating in lean-burn conditions. Thus, the development of a new type of catalyst, able to control NO_x emissions in the presence of oxygen, has become an important research topic in recent years. Direct catalytic NO decomposition, being independent of any reducing agent, would be the ideal process, but catalysts with good activity are not available at the moment [1]. Recently, copper ion-exchanged ZSM5 zeolite has been proposed as a potential catalyst for NO_x abatement being the hydrocarbons in lean exhaust gas claimed to be the reducing agents of NO_x to N_2 [1,2]. The most interesting results have been obtained using $NO–C_3H_6–O_2$ [1,3], or $NO–C_2H_4–O_2$ [3], or $NO–i–C_4H_{10}O_2$ [4] mixtures as feed, i.e. in reaction conditions different from those of engine exhaust gas. Few literature data regarding lean NO_x catalytic control in actual engine exhaust are available [2,5]. In a previous paper we have shown that CuZSM5 and CuY catalysts give similar NO_x conversion at the spark ignition engine exhaust [6]. In contrast, CuZSM5 was much more active than CuY in NO decomposition [7].

The aim of this paper is to evaluate the effect of copper content on the activity and selectivity of CuZSM5 for NO_x reduction in actual lean exhaust gases of a spark ignition engine.

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2. Experimental

2.1. Catalysts preparation

The zeolite HZSM5 (Si/Al = 80) used as starting material was prepared according to the following procedure [8]. A solution of 1 g of $Al(NO_3)_3 \cdot 9H_2O$ in 20 g of ethyl alcohol was added to 45 g of tetraethylsilicate (TES). This solution was poured in a 400-ml pyrex glass vessel containing 100 g of a 20% aqueous solution of tetrapropylammonium hydroxide (TPA-OH). The resulting mixture was kept at 60°C for 3 h and then heated under autogeneous pressure in a 350-ml stainless steel autoclave in an oven at 175°C, without stirring, for 24 h. The crystalline product was separated from the liquid by centrifugation (4500 rpm —30 min), washed several times with distilled water, dried 2 h at 110°C and finally calcined at 550°C for 5 h. We used the following reagents: TES and TPA-OH from Fluka (purum and free from alkaline impurities), $Al(NO_3)_3 \cdot 9H_2O$ from C. Erba (RPE-ACS). X-ray diffraction was used to control both purity and crystallinity of the ZSM5 phase (see Fig. 1a).

Copper was introduced into the zeolites by the ion-exchange method. The prepared CuZSM5 catalysts and their main features are reported in Table 1. They are identified by the Si/Al atomic ratio and the Cu apparent exchange level in percentage (100% exchange corresponds to 1 Cu^{2+} per 2 Al atoms). The exchange was performed employing dilute aqueous solution of cupric acetate. In the preparations 2 g of zeolite were treated

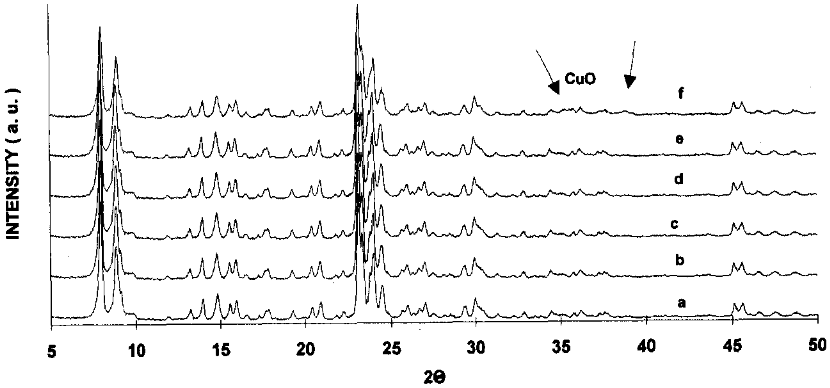

Fig. 1. XRD patterns: HZSM5(80) before treatment (a); CuZ(80)556 before treatment (b); CuZ(80)556 after the treatment at 515°C for 1 h in vacuum (c); in 350 Torr of O_2 (d); again in vacuum (e); after the catalytic test (f).

Table 1
Catalysts preparation and their main features

Sample [a]	$[Cu^{2+}]$ [b] (mmol/l)	Initial pH	Final pH	$(Cu/Z)_S$ [c]	$(Cu/Z)_Z$ [d]	Cu (wt.-%)	Exchange (%)
CuZ(80)43	0.4	–	–	0.30	0.26	0.27	43
CuZ(80)58	0.8	–	–	0.61	0.34	0.36	58
CuZ(80)113	3.2	5.49	4.86	2.42	0.67	0.70	113
CuZ(80)190	8.0	–	–	6.06	1.13	1.17	190
CuZ(80)521	60	–	–	45.5	3.10	3.15	521
CuZ(80)556	100	5.45	5.25	75.8	3.31	3.36	556

[a] The samples are identified by the Si/Al atomic ratio and by the Cu percentage of exchange.

[b] Cu^{2+} concentration in mmol/l in the solution used for the ionic exchange.

[c] $(Cu/Z)_S = V_g \times [Cu^{2+}] \times 6056.5 \times 10^{-6}$ represents the ratio between the mole of copper and the mole of unit cell of HZSM5(80) in solution. Note that 6056.5 represents the grams of HZSM5 per mole of fully hydrated unit cell (containing 16 water molecules).

[d] $(Cu/Z)_Z = \text{Cu wt.-\%} \times 6056.5 / [(6354 - \text{Cu wt.-\%} \times 61.54)]$ represents the mole of copper exchanged in the zeolite per mole of unit cell of HZSM5(80). Note that the percentage of exchange is calculated as $200 \times (Cu/Z)_Z / 1.19$, where 1.19 is the number of Al atoms per unit cell of HZSM5(80).

with 250 ml of solution of given copper concentration for 2 h whilst stirring at 50°C. The samples after filtration were washed several times with distilled water, dried at 110°C for 2 h, and stored over a saturated solution of NH_4Cl at room temperature (79% of relative humidity). Copper content in the zeolite was determined by atomic absorption (Varian SpectrAA-30) and expressed either as Cu wt.-% (on a wet basis), or as the percentage of apparent exchange.

2.2. *Catalyst characterization*

X-ray powder diffraction (XRD) patterns of samples before treatment, after redox cycles treatments, and after lean NO_x reduction at the spark ignition engine exhaust, were obtained with a Philips automated PW 1729 diffractometer. Scans were taken with a 2Θ size of 0.01° using Cu $K\alpha$ radiation (Ni filtered).

Diffuse reflectance (DRS) spectra of samples before treatment, after redox cycles treatments, and after lean NO_x reduction at the spark ignition engine exhaust were recorded using a Cary 5 spectrometer with a diffuse reflectance accessory in the wavelength range 200–2500 nm, covering UV, visible and near-infrared regions. Note that the reflectance spectra after the redox cycles treatments were recorded in situ using a quartz reactor specifically developed for this purpose. The redox cycles consisted in treatments in vacuum and in O_2 (350 Torr) at 515°C for 1 h.

2.3. *Apparatus for catalytic activity tests*

In Fig. 2 the experimental apparatus used for catalytic activity tests is shown. The engine, a spark ignition four cylinder, 1350 cm^3 displacement, was installed on test bench and coupled to an electric dynamometer. A portion of the exhaust gas (0.4 Nl/min) was collected by a probe heated at 180°C and sent to the reactor by a pump heated at 120°C. The reactor, a stainless steel tube of 10 mm i.d., was inserted in a tubular electric oven, connected to a temperature programmer. The catalyst was loaded as powder (200–400 μm). The pollutant (NO_x, HC, CO) and the oxygen concentrations were measured by on line analyzers: chemiluminescence for NO_x, flame ionization for HC, IR for CO and electrochemical for O_2. For all catalytic activity tests the engine operating conditions were the following: 3000 rpm, 20 kW, air/fuel mass ratio $A/F = 17\ kg_{air}/kg_{fuel}$. Commercial unleaded gasoline was used as fuel. The selected condition corresponded to the following exhaust gas volumetric composition, as calculated from air and fuel flow-rate fed to the engine: $CO_2 = 11\%, H_2O = 12\%, O_2 = 3\%, N_2 = 74\%$. The NO_x, HC, CO and O_2 concentrations as measured at the engine exhaust were: $NO_x = 1240$ ppm, $HC = 420$ ppm (expressed as propane), $CO = 1310$ ppm, $O_2 = 4\%$. These concentrations are the average values measured with the analyzers during each catalytic test. The maximum variation of these values given by the analyzers was in the range of $\pm 8\%$ for NO_x and $\pm 4\%$ for HC and CO during each catalytic test. The NO/NO_x average ratio was 0.9, the balance being NO_2. Programmed temperature reaction tests were performed in the range 25–600°C. Temperature cycles consisted of 25°C/min heating steps from 25° to 600°C, by keeping constant the reaction temperature for 15 min respectively at 150°C, 300°C, each 50°C from 300°C to 500°C, and at 600°C. The conversions of NO_x, HC, and CO were determined measuring their concentrations at inlet and outlet of the catalytic reactor.

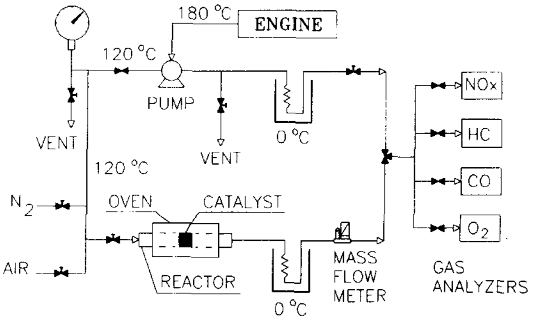

Fig. 2. Experimental apparatus used for catalytic activity tests.

3. Results and discussion

3.1. *Catalyst characterization*

The data of Table 1 show that over-exchanging ZSM5 zeolite with high Si/Al ratio (apparent exchange levels >100%) is very easy. Similar results were reported by Parrillo et al. [9].

To explain the over-exchange of ZSM5 zeolite, the possibility that Cu may be exchanged not only at protonic sites associated with framework Al sites, but also at defect sites, such as the 'nested silanols' at Si vacancy defects [10] can be taken into account. (If this is the case the extent of over-exchange will depend on the particular sample being studied, since defect concentrations can be altered by synthesis and pretreatment conditions for ZSM5.) Another possibility is the exchange of copper-containing polymeric species, as suggested in Ref. [11]. The formation of a multinuclear complex, such as $[Cu_x(OH)_y^{(2x-y)+}]$ in the cage of copper-exchanged mordenite has been reported [12]. Further work is in progress in our laboratories to clarify this important point. Note that all the prepared CuZSM5(80) samples, as well as the samples treated in evacuated or treated in 350 Torr of O_2 at 515°C for 1 h, present the typical XRD pattern of the parent HZSM5 zeolite. In Fig. 1 we report the XRD pattern for the samples with the greatest Cu percentage of exchange (556%).

DRS of the exchanged HZSM5 show that the d–d transitions lie in the range expected for Cu^{2+} in octahedral environment of O-containing ligands (range 10000–15000 cm^{-1}) [13]. O^{2-} to Cu^{2+} charge transfer transitions occur in the range 39000–44000 cm^{-1} as one broad and intense band. The redox cycles studies have clearly shown that Cu^{2+} species in the exchanged zeolite can be easily reduced to Cu^{+} under vacuum at 515°C for 1 h. In Fig. 3 we show the DRS results for CuZSM5(80)556. After evacuation (Fig. 3b) the intensity of the d–d transitions is confused in the background indicating an almost complete reduction of Cu^{2+} to Cu^{+}. The treatment in O_2 at 515°C for 1 h of these reduced samples (Fig. 3c) leads to the formation of Cu^{2+} species that are now, in the absence of water, stable to a second treatment under vacuum at high temperature (Fig. 3d). We conclude that in the CuZSM5 samples (Fig. 3a) the water molecules in the coordination shell of the Cu^{2+} ions play a key role in the auto-reduction process under vacuum. Note that the CuZSM5 samples treated under O_2 at 515°C show a clear blue shift in the d–d band maximum with respect to the untreated samples (Fig. 3). This points to a more planar-type of coordination of the Cu^{2+} species, like a square pyramidal and a planar configuration [13]. It is remarkable that even samples with Cu exchange levels as high as 556% remain stable under the treatment in O_2 at 515°C for 1 h and to several

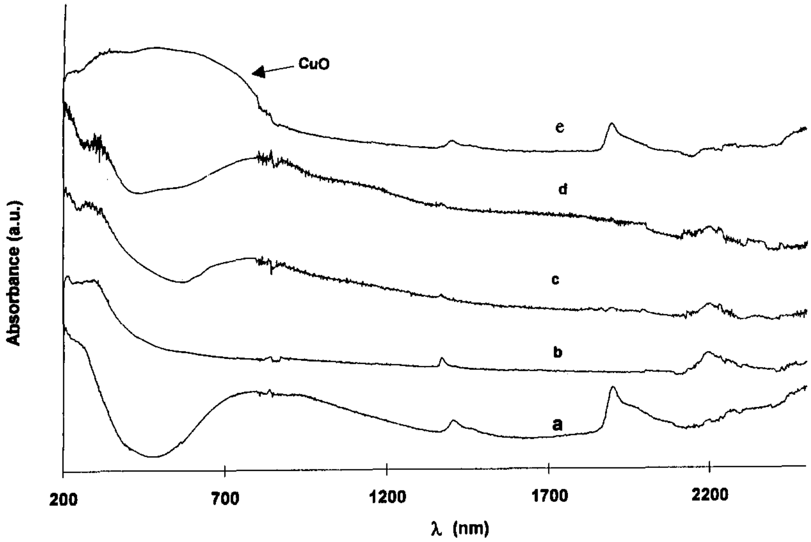

Fig. 3. DRS (in situ): CuZ(80)556 before treatment (a); after treatment at 515°C for 1 h in vacuum (b); in 350 Torr of O_2 (c); again in vacuum (d); after the catalytic test (e).

redox cycles (O_2, vacuum) at the same temperature. The segregation of CuO particles larger than 30–40 Å can be excluded on the basis of XRD and DRS evidence (Fig. 1 and Fig. 3).

3.2. Catalyst performance

In Fig. 4, Fig. 5, and Fig. 6 the results of the programmed temperature tests carried out at the engine exhaust on CuZSM5 catalysts (Si/Al = 80) are reported in terms of pollutant conversion percentage for different copper contents. In these experiments a W/F value of 0.15 g·s/cm^3 was adopted.

Fig. 4 shows that in the range of experimental conditions investigated HZSM5 was not active in converting NO_x, whereas the loading of copper, also at partial exchange level, resulted in active catalysts for NO_x selective reduction. Hamada et al. [14] has reported that proton-exchanged zeolites show catalytic activity for the selective reduction of NO_x, but also those results have been obtained with simulated exhaust gas. Fig. 4 shows that the greatest NO_x conversion was provided by the over-exchanged samples. In particular, a conversion of 39% at 400°C was obtained for the catalyst containing 190% of Cu apparent exchange level, and similar conversion values were shown by the samples at higher ion-exchange level. For all copper contents the NO_x conversion curve is characterized by a maximum value at 400°C, the same temperature for a nearly complete conversion of CO and HC (Fig. 5 and Fig. 6). The decrease of NO_x conversions for temperatures higher than 400°C, observed for all catalysts tested, can be attributed to the competition between NO_x reduction by hydrocarbons and HC oxidation by oxygen, the latter becoming the predominant reaction when the temperature increases. However, the maximum NO_x is expected to be enhanced by a higher hydrocarbon concentration. The more or less favoured formation of reaction intermediates depending on reaction temperature, could also be taken into account. Adsorption effects disguised the real HC conversion values at lower temperatures (Fig. 5), while, depending on the temperature and the copper content, apparent conversion of CO lower than zero was obtained (Fig. 6), deriving by the partial oxidation of hydrocarbons with oxygen.

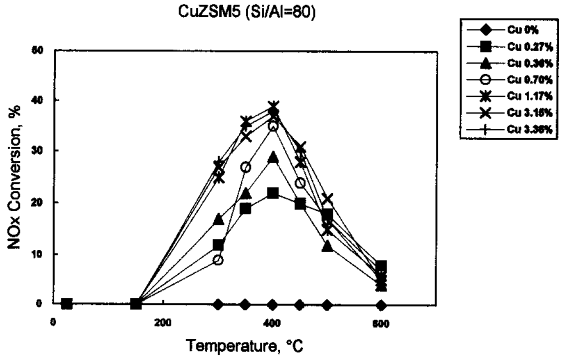

Fig. 4. Effect of reaction temperature on NO_x conversion in programmed temperature catalytic tests. (For reaction conditions see the Experimental section.)

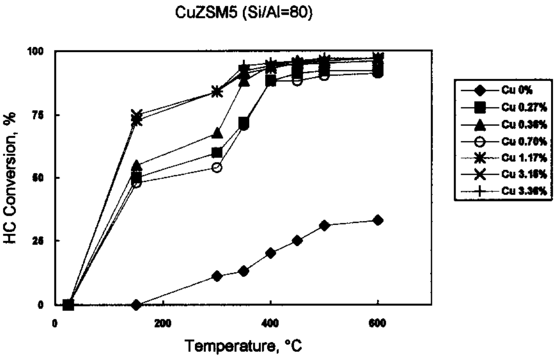

Fig. 5. Effect of reaction temperature on HC conversion in programmed temperature catalytic tests. (For reaction conditions see the Experimental section.)

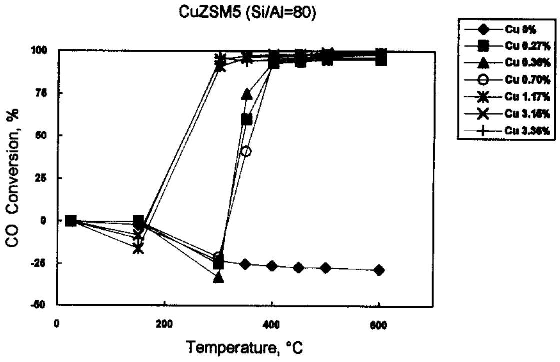

Fig. 6. Effect of reaction temperature on CO conversion in programmed temperature catalytic tests. (For reaction conditions see the Experimental section.)

The effect of HC/NO_x ratio in the exhaust on the catalytic performance is shown by the com-

Table 2
Percentage conversions of NO_x, CO and HC in programmed temperature catalytic tests on CuZ(80)113. (Engine exhaust average concentrations were $NO_x = 620$ ppm, HC = 410 ppm, CO = 1480 ppm, $O_2 = 4\%$, other conditions as in Fig. 4)

Temp. (°C)	Conv. (%)							
	250	150	300	350	400	450	500	600
NO_x conversion	0	0	28	40	44	33	27	10
HC conversion	0	50	67	84	95	97	97	98
CO conversion	0	0	−21	77	97	98	98	98

parison of results reported in Fig. 4 and in Table 2.

Decreasing NO_x concentration from 1240 to 620 ppm resulted in enhanced conversions of all the pollutants; at 400°C maximum NO_x conversion of 44% was reached, in respect to 35% conversion obtained by feeding 1240 ppm NO_x. Moreover, the higher HC/NO_x ratio resulted in increasing the HC conversion from 88 to 95% at the same reaction temperature (Table 2 and Fig. 4 and Fig. 5).

Comparing the present results with those previously obtained with Cu-exchanged HZSM5 with Si/Al ratio = 17 [7], it may be concluded that the effect of Si/Al ratio is not significant on both the NO_x and the HC conversions, but is very marked on CO conversion. The catalyst containing 0.27 wt.-% Cu (43% of exchange) provides high CO conversion at temperatures higher than 300°C, and total CO conversion at 400°C (Fig. 6), whereas a catalyst prepared from HZSM5 (Si/Al = 17) containing 0.92 wt.-% Cu (31% of exchange) provided an increase of CO concentration after passing through the reactor [7]. However, the formation of CO, due to the partial oxidation reaction of hydrocarbons by oxygen, seems to be favoured by the presence of acidic sites. It must be taken into account that at a comparable level of ion exchange the concentration of acidic sites in the catalyst obtained from HZSM5 at Si/Al ratio of 17 is about 5 times higher in respect to that of the catalyst prepared from HZSM5 at Si/Al ratio of 80.

The effect of copper content on catalyst performance at 400°C is evidenced in Fig. 7 for CuZSM5 (Si/Al = 80) samples. The NO_x, HC and CO conversions depend on copper concentration up to the apparent exchange level of about 200% (corresponding to about 1.2 wt.-% Cu), after which the conversion curves of the three pollutants are unaffected by further Cu exchange.

A preliminary investigation of catalyst durability was also carried out by characterizing some catalyst samples after the catalytic test. In Fig. 1f we report XRD patterns for the samples with Cu percentage apparent exchange levels equal to 556%, after the test at the engine exhaust. We see that the XRD pattern exhibits the strongest signals of copper oxide, CuO. The DRS of the same catalyst, reported in Fig. 3e, indicates the segregation of CuO particles larger than 30–40 Å, easily detected through the CuO adsorption edge, in agreement with the XRD pattern (Fig. 1f). In contrast, both the XRD and the DSR spectra of catalyst Cu(80)113 are unchanged after the catalytic test.

All the CuZSM5 samples after the catalytic lean NO_x reduction test present only a slight loss of ZSM5 crystallinity. Our results therefore agree, in part, with those reported by Kharas et al. [15]. For the highly over-exchanged CuZSM5 it is the sintering of the catalytically active components, rather than the support degradation, that dominates the deactivation process. The results obtained on samples with exchange levels of

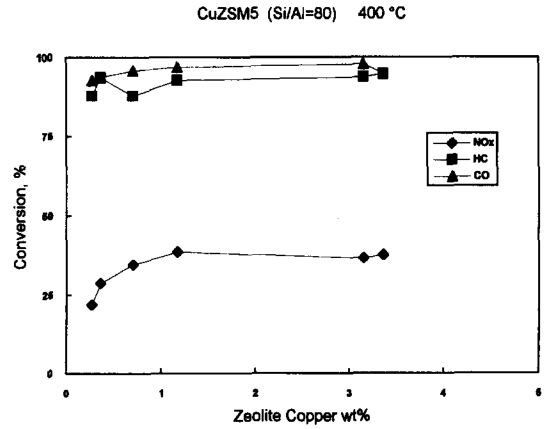

Fig. 7. Effect of Cu content on NO_x, HC and CO conversions at 400°C (Other reaction conditions are given in the Experimental section.)

113%, which do not show the segregation of CuO particles, as demonstrated by XRD and DRS spectra, suggest that the deactivation process could also depend on other factors, such as the copper content and the nature of copper species inside the zeolite and presence of water in the exhaust gas. An investigation of catalyst durability is in progress in our laboratories.

4. Conclusions

It has been found that Cu-exchanged HZSM5 zeolite is a selective catalyst for the reduction of NO_x in lean-burn gasoline engine exhaust, but the performances are not so effective as reported for the reduction of NO_x in simulated exhaust gas. The conversions of NO_x depend on the copper content of exchanged zeolite, the greatest conversion values having been obtained at 400°C with catalysts with apparent Cu exchange level equal or higher than 200%. The fresh catalysts, even if over-exchanged, contain divalent copper, but do not give any evidence for the presence of segregated copper oxide phases. The first results of CuZSM5 characterization after NO_x lean reduction catalytic tests have evidenced the formation of CuO only in the catalysts with the greatest copper content.

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