

SCR of NO by C₃H₆ over Cu-Fe-PILC in the presence of oxygen and steam

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Abstract

Copper ion-exchanged iron-pillared interlayer clays (Fe-PILC) were tested in the Selective Catalytic Reduction (SCR) of NO by propene in the presence of water in the feed. These catalysts showed deactivation under wet reaction conditions, with a catalytic activity decrease of 15 – 30 points in the range of temperature studied. NO and C₃H₆ adsorption over Cu²⁺ active sites showed inhibition. However, C₃H₆ adsorption over CuO clusters was much more affected by the presence of water. The catalytic activity of the samples with CuO aggregates was similar to that obtained for the sample with only Cu²⁺ sites, as the promoting effect of CuO for the propene oxidation was totally inhibited by the presence of water. It was observed that inhibition by water was fully reversible. Thus, after removal of water from the feed, NO conversion was completely recovered. This kind of catalysts showed hydrothermal stability after 48 h on stream, and their textural properties were not modified under wet conditions.

Keywords: Fe-PILC, Copper, SCR, water

1. Introduction

Since the HC-SCR process was first investigated by Iwamoto et al. [1] and Held et al. [2] the reaction has been intensively studied and debated. The use of hydrocarbons as an alternative reductant to NH₃ has received great attention as the most promising deNO_x technology for stationary and oxygen-rich mobile sources [3]. Most of NO_x emissions sources contain water in the concentration ranges of 2 to 18 % [4]; therefore, the strong water tolerance of deNO_x catalyst is essential for its practical use.

A few of the representative investigations in this topic have focused on how to improve the water tolerance of zeolite catalysts and on why most SCR catalysts lose catalytic activity under wet conditions [4,5]. The deactivation has been attributed to the competitive adsorption of water on the active metal sites and to the modification of the sites caused by it [6]. The long-term hydrothermal instability of the catalyst has been attributed to active metal agglomeration and to the dealumination of the zeolite [7,8].

Some studies have been focused on the development of bifunctional catalysts, co-exchanging rare-earth metal and copper with aim of improving the water stability [9,10]. The affinity of ceria coating towards water protected the internal zeolite in CeO₂/Cu-ZSM-5 against hydrothermal degradation by restricting the diffusion of water molecules into the zeolite pores. However, this bifunctional catalyst tended to have lower activity and selectivity than the corresponding monometallic zeolite under wet conditions. Valverde *et al.* [10] reported that the presence of ceria as co-cation in Cu-Ti-PILC enhanced the SCR activity under wet conditions due to a synergistic effect between Ce-Cu on pillared clays. Ceria species suppressed the agglomeration of Cu²⁺ species and stabilized the catalyst when water was present in the feed stream.

High catalytic activity is essential for a commercial application but it also required from the view of catalyst life water tolerance. For this purpose, the present study will focus on testing the catalytic activity of Cu ion-exchanged iron pillared clays in the HC-SCR in the presence of water.

2. Experimental

2.1 Catalyst preparation

The starting clay was a purified-grade bentonite (Fisher Company), with a particle size of <2 μm and a cation-exchange capacity of 97 mequiv g⁻¹ dry clay. A FeCl₃·6 H₂O solution was added to NaOH solutions to obtain the required OH/Fe molar ratio. In order to avoid precipitation of iron species, the pH was kept constant at 1.7. The mixture was aged for 4 h under stirring at room temperature. The pillaring solution was then added dropwise to an aqueous clay suspension. The mixture was kept under vigorous stirring for 12 h at room temperature. Finally, the solid was washed, dried, and calcined for 2 h at 400 °C.

Metal was introduced by conventional ion exchange using 100 mL of metal aqueous solution per gram of iron pillared clay. A range of copper-exchanged Fe-PILC samples were prepared with solutions of Cu(CH₃COO)₂·H₂O, and the pH then adjusted by the addition of aqueous ammonia to give the desired final pH. All catalysts were calcined for 2 h at 400 °C. These catalysts are referred to as a function of the metal content and the pH of the ion-exchanged solution. For instance, Cu3.3-5.4 corresponds to a catalyst ion-exchanged with copper, leading to a loading of this metal of 3.3 wt. % using a solution with a pH equal to 5.4. More details about catalysts preparation can be found elsewhere [11 – 13].

2.2 Catalyst characterization

To quantify the total amount of metals incorporated into the catalyst, atomic absorption spectroscopy measurements were made, using a SPECTRAA model

220FS analyzer, with an error of $\pm 1\%$. The samples were previously dissolved in hydrofluoric acid and diluted to the interval of measurement.

Surface area and pore-size distribution were determined by nitrogen adsorption at 77 K in a static volumetric apparatus (Micromeritics ASAP 2010 sorptometer). Pillared clays were outgassed prior to use at 180 °C for 16 h under a vacuum of 6.6×10^{-9} bar. Specific total surface areas were calculated using the Brunauer- Emmett-Teller (BET) equation, whereas specific total pore volumes were evaluated from the nitrogen uptake at a N₂ relative pressure of $P/P_0 = 0.99$. The t-plot method was used to determine the mesopore surface area and micropore volume. The Barret-Johner-Halenda (BJH) method was used to determine the mesopore size distribution.

Temperature-programmed reduction (TPR) measurements were carried out using a Micromeritics model TPD/TPR 2900 analyzer with a thermal conductivity detector (TCD). After being loaded in the instrument, the sample was outgassed by being heated at 15 °C/min in an argon flow up to the calcination temperature of the sample and kept constant at this temperature for 30 min. Next, the sample was cooled to room temperature and stabilized under an argon/hydrogen flow ($\geq 99.9990\%$ purity, 83/17 volumetric ratio). The temperature and thermal conductivity detector signals were then continuously recorded during heating at 15 °C/min up to 450 °C. The liquids formed during the reduction process were retained by a cooling trap placed between the sample and the detector. TPR profiles were reproducible, with standard deviations for the temperature of the peak maxima being $\pm 1\%$.

Thermogravimetric analysis were performed using a Perkin-Elmer TGA 7 thermogravimetric analyzer under a flow of 20 NmL/min of He and with a heating rate of 15 °C/min up to 800 °C, with a sample weight of 10 mg.

2.3. Catalyst activity measurements

Activity experiments were carried out at atmospheric pressure in a flow-type apparatus designed for continuous operation at atmospheric pressure. This apparatus consisted of a gas feed system for each component, with individual control by mass flowmeters, a fixed-bed downflow reactor, and an exit gas flowmeter. The reactor, a stainless steel tube with an internal diameter of 4 mm, was filled with the catalyst sample (0.25 g). A temperature programmer was used with a K-type thermocouple that was installed in contact with the catalyst bed. The products were analyzed simultaneously, using a chemiluminescence analyzer (NO-NO₂-NO_x ECO PHYSICS) and a Fourier transform infrared (FTIR) analyzer (Perkin Elmer Spectrum GX) that was capable of measuring the following species continuously and simultaneously: NO, NO₂, N₂O, CO₂ and C₃H₆.

The feed composition was as follow: 1,000 ppm C₃H₆, 1,000 ppm NO, 5 % O₂, 10 % H₂O and the balance He. The feed gases were mixed and preheated before entering the reactor. The space velocity (GHSV) was 15 000 h⁻¹, and the flow rate was 125 mL/min. Before the reaction was started, the catalysts were preconditioned by being held at 400 °C under a flow of helium (125 mL/min) for 60 min. Then, the temperature was reduced to 200 °C. The reaction measurements for each temperature were carried out after 2 h to ensure that the steady state was reached. All experiments

were tested for reproducibility with analytical repeatability, with an error in NO conversion of <5%.

3. Results and discussion

3.1. Catalytic activity

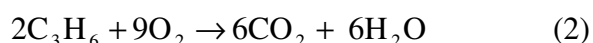
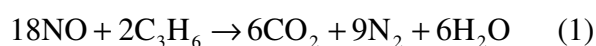
Table 1 summarizes temperatures and yields corresponding to the maximum NO conversion reached for all catalysts tested. Under wet conditions, the catalytic activity decreases, depending on the sample, between 15 and 30 points, and the maximum NO conversion shifts to higher temperatures. As copper loading increased, catalysts showed higher inhibition by water, and the C₃H₆ yield to CO₂ decreased. This fact indicates that copper species in the samples are affected by the steam. On the other hand, Figure 1 shows NO and C₃H₆ conversion in absence and presence of water for the sample Cu3.3-5.4. The same trend was observed for the other samples.

Table 1. Temperatures and yield corresponding to maximum NO conversion.

Catalysts	T _{max} (°C)	NO yield to N ₂ (%)	C ₃ H ₆ yield to CO ₂ (%)
Cu3.3-5.4	280	36.2	81.5
Cu3.3-5.4*	320	31.6	91.2
Cu4.8-7.0	260	43.0	81.2
Cu4.8-7.0*	320	34.8	89.0
Cu6.2-9.0	260	53.9	86.7
Cu6.2-9.0*	320	38.0	87.6
Cu6.5-10.5	280	45.2	95.6
Cu6.5-10.5*	320	38.7	82.0

* Wet reaction conditions (10 % H₂O).

Propene, under reaction conditions, can be involved in the following reactions:



In reaction (1) NO is directly reduced by propene with a stoichiometric proportion 9:1 to give N₂, CO₂ and water. Reaction (2) corresponds to the side reaction of propene oxidation which is favoured at high temperatures. For this reaction, propene oxidation is independent of NO consumption. Therefore, depending on the affinity of the metal sites to NO or C₃H₆, reaction (1) or side reactions can be favoured. It is interesting to plot NO conversion to N₂ versus C₃H₆ conversion to CO₂, in order to compare the experimental and theoretical values. This procedure has been described by Tzitzios et al. [14] for the N₂O reduction by methane and propene over Ag-Rh/Al₂O₃. Figure 2 shows the relationship between the conversion of NO and C₃H₆ in absence and presence of water. The dashed line (theoretical value) in the figure represents the relationship for 100 % selective reduction by propene according to reaction (1). All catalysts exhibited conversions of propene that were higher than

the theoretical value. This means that propene is oxidized in side reaction (2), where NO is not involved.

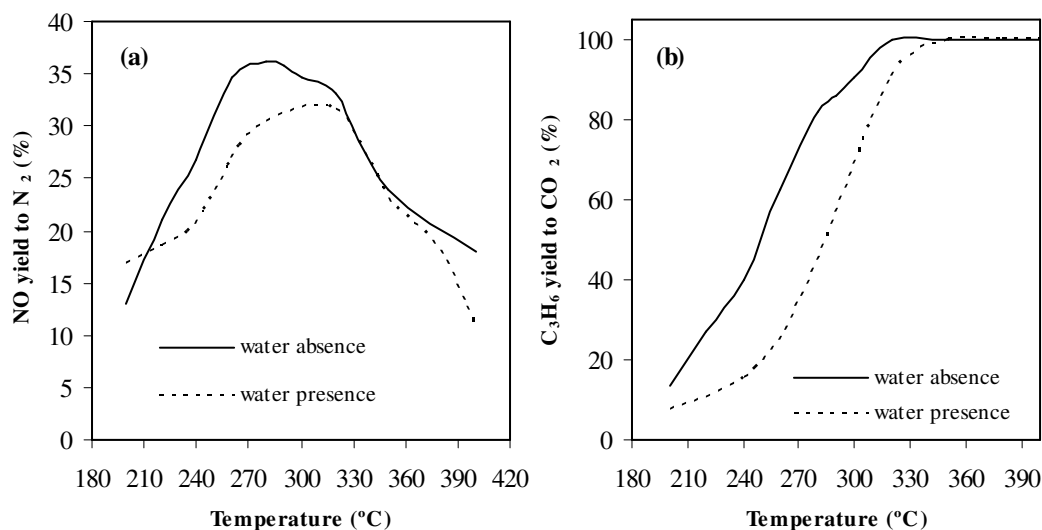


Figure 1. (a) NO yield to N₂ and (b) C₃H₆ yield to CO₂ versus temperature on Cu3.3-5.4. Reaction conditions: NO = C₃H₆ = 1 000 ppm, O₂ = 5 wt%, H₂O = 10 wt% (when used) and He = balance, catalyst = 0.25 g, and total flow rate = 125 mL/min.

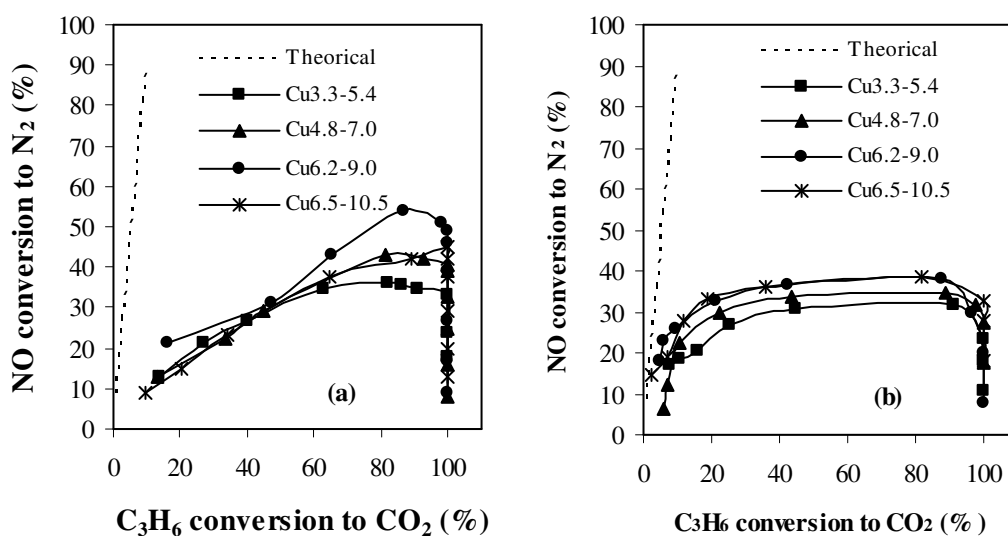


Figure 2. Relationship between the conversion of NO and C₃H₆ in absence (a) and presence (b) of water.

In a previous work [13] the distribution of the copper species present in this kind of catalysts was widely studied. Table 2 summarized the percentages of every copper species according to the quantitative analysis of the TPR profiles. Sample prepared without pH control (Cu3.3-5.4) showed in its structure only isolated Cu²⁺, while samples prepared under alkali conditions showed in their structure copper as Cu²⁺ and CuO clusters. The proportion of CuO clusters increased with the pH valued.

Table 2. Quantitative analyses of the TPR profiles.

Catalysts	$\text{Cu}^{2+} \rightarrow \text{Cu}^+$	$\text{CuO} \rightarrow \text{Cu}^0$	$\text{Cu}^+ \rightarrow \text{Cu}^0$	$\text{Cu}^{\text{II}}/\text{CuO}$
Cu3.3-5.4	0.74	--	0.26	--
Cu4.8-7.0	0.31	0.42	0.27	1.38
Cu6.2-9.0	0.24	0.54	0.22	0.85
Cu6.5-10.5	0.20	0.60	0.20	0.67

In absence of water (Figure 2 (a)) it can be observed that, catalysts with CuO in their structure, propene more involved in the NO reduction. Sample Cu6.2-9.0 showed the value of the relation NO / C₃H₆ conversion nearer to the stoichiometric line. This fact is according to the results reported in a previous work [13] where it was claimed that the presence of CuO in accessible positions together with the presence of isolated Cu²⁺, favoured the C₃H₆ adsorption which later on were involved in the reaction mechanism of NO reduction. However, under wet conditions, the samples with CuO in their structure presented higher deactivation due to the inhibitor effect of water (Table 1). Figure 2 (b) shows similar profiles for all the samples despite the different copper loading and different distribution of copper species, as the promoting effect of CuO for the propene oxidation was totally inhibited by the presence of water. At this point, it could be concluded that both Cu²⁺ and CuO show similar affinity to H₂O molecules than NO and C₃H₆ molecules, but notably, the C₃H₆ adsorption over CuO is strongly inhibited by the presence of water. To justify these results, the following thermogravimetric analyses (TGA) were carried out:

- Experiment 1: TGA run performed on catalysts after calcination.
- Experiment 2: TGA run carried out on catalysts after calcination from room temperature to 200 °C. This experiment tries to simulate the activation of the catalyst before the reaction test.
- Experiment 3: TGA run performed on catalysts after experiment 2.
- Experiment 4: TGA run carried out on catalysts which have been submitted to pre-treatment at 200 °C under a flow of 20 NmL/min of He with 10 % of H₂O.

Figure 3 shows the TGA profiles for the catalyst Cu3.3-5.4. Depending on the experiment, different weight lost values were measured in the temperature range 30 – 120 °C which corresponds to the water desorption (Table 3). On the other hand, for all the catalysts tested, it was observed weight lost around 600 °C which is attributed to the collapse and dehydroxylation of the iron pillared clays structure [11]. As it was expected, all catalysts showed similar values for experiments 1 and 2. However, experiment 4 reveals different behaviours of the samples after wet pre-treatment. First, it is worthy to underline that the support Fe-PILC shows similar weight lost after wet pre-treatment than after dry pre-treatment. This fact leads to think that the support has poor affinity to water, being copper which adsorbed the major quantity of

water. Catalyst Cu3.3-5.4 (with only Cu²⁺) showed, for experiment 4, lower weight lost than the others catalysts (with Cu²⁺ and CuO), confirming that Cu²⁺ sites adsorb water, but also, CuO cluster can adsorb.

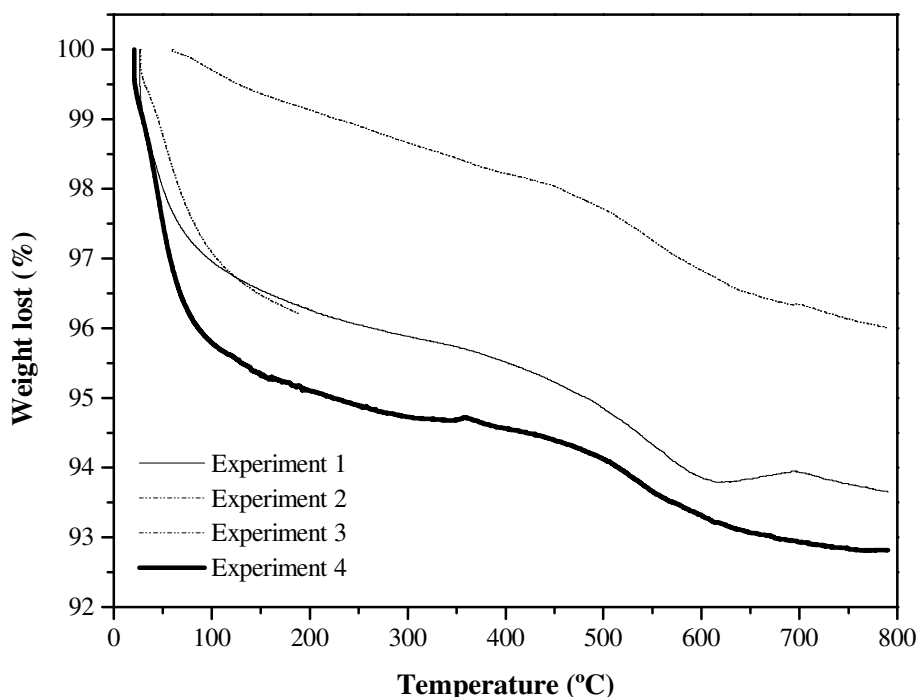


Figure 3. TGA profiles for catalysts Cu3.3-5.4.

Table 3. Weight lost percentage corresponding to temperature range 30 – 120 °C.

Samples	Experiment 1	Experiment 2	Experiment 3	Experiment 4
Fe-PILC	6.05	5.31	2.01	2.77
Cu3.3-5.4	3.15	2.99	0.70	5.15
Cu4.8-7.0	3.54	2.78	0.95	7.95
Cu6.2-9.0	3.33	2.72	1.09	7.48
Cu6.5-10.5	2.87	2.59	0.88	7.23

3.2. Hydrothermal stability.

From the point of view of industrial application, it is interesting to study the reversibility of the NO conversion when water is removed from the feed stream. Therefore, after testing the catalytic activity of the catalysts in absence and presence of water, regeneration of the catalysts was carried out under a helium flow of 100 mL/min for 10 h at 180 °C. All the catalysts showed the same behaviour. Figure 4 shows the results for the sample Cu6.2-9.0. It can be observed that the deactivation

was reversible, so that when water is removed from the feed, NO conversion is completely recovered.

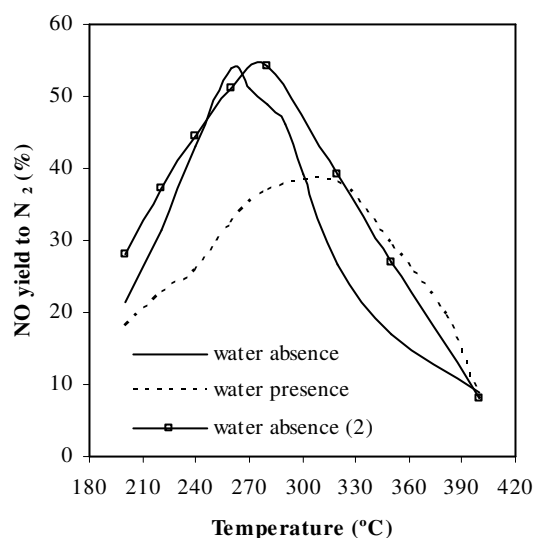


Figure 4. Reversibility study over sample Cu6.2-9.0. Reaction conditions: NO = C₃H₆ = 1 000 ppm, O₂ = 5 wt %, H₂O = 10 %, He = balance, catalyst = 0.25 g, and total flow rate = 125 mL/min.

On the other hand, hydrothermal stability of catalysts Cu6.2-9.0 was examined under simulated wet conditions for 48 h at 260 °C (temperature corresponding to maximum NO conversion under dry conditions) (Figure 5). Moreover, nitrogen adsorption runs were carried out on catalysts after reaction tests under wet conditions to check textural characteristics with the aim of verifying whether metal sintering or damage in the support has occurred (Table 4). Catalysts showed hydrothermal stability after 48 h on stream, and their textural properties were not modified under wet conditions.

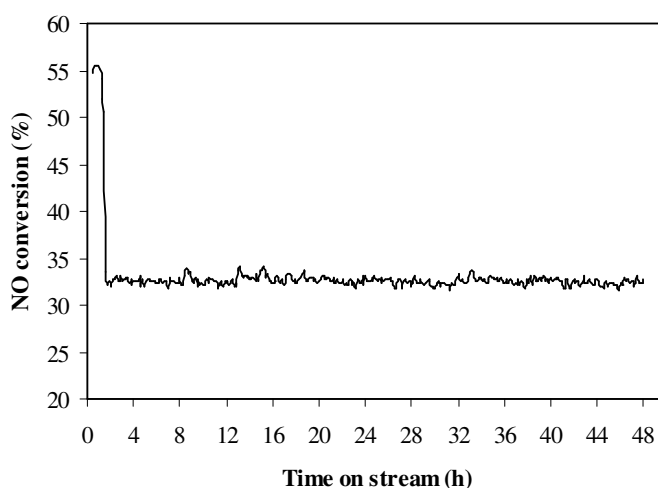


Figure 5. NO conversion to N₂ in the presence of water over the catalyst Cu6.2-9.0 as a function of time at 260 °C. Reaction conditions: NO = C₃H₆ = 1 000 ppm, O₂ = 5 wt %, H₂O = 10 %, He = balance, catalyst = 0.25 g, and total flow rate = 125 mL/min.

Table 4. Micropore area and volume values.

Muestras	S _{int} (m ² /g) ^a	V _{μp} (cm ³ /g) ^b	S* _{int} (m ² /g) ^a	V* _{μp} (cm ³ /g) ^b
Cu3.3-5.4	211	0.123	209	0.120
Cu4.8-7.0	177	0.105	177	0.100
Cu6.2-9.0	158	0.100	156	0.100
Cu6.5-10.5	147	0.097	146	0.092

^a Micropore area obtained from the t-plot method (S_{int}).

^b Micropore volume obtained from the t-plot method (V_{μp}).

*Values under wet reaction conditions (10 % H₂O).

4. Conclusions

Cu ion exchanged iron pillared clays were tested for the HC-SCR of NO in the presence of water. It was observed that water inhibited the catalytic activity of the samples. NO and C₃H₆ adsorption on Cu²⁺ sites was inhibited by water. However, the most important negative effect was the inhibition of propene adsorption over CuO clusters. Therefore, the promotional effect of CuO aggregates obtained in absence of water was lost under wet conditions.

It was observed that inhibition by water was fully reversible and catalysts showed hydrothermal stability after 48h on stream. Their textural properties were not modified under wet conditions.

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