Optimizing the performance of catalytic traps for hydrocarbon abatement during the cold-start of a gasoline engine

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Abstract

A key target to reduce current hydrocarbon emissions from vehicular exhaust is to improve their abatement under cold-start conditions. Herein, we demonstrate the potential of factorial analysis to design a highly efficient catalytic trap. The impact of the synthesis conditions on the preparation of copper-loaded ZSM-5 is clearly revealed by XRD, N₂ sorption, FTIR, NH₃-TPD, SEM and TEM. A high concentration of copper nitrate precursor in the synthesis improves the removal of hydrocarbons, providing both strong adsorption sites for hydrocarbon retention at low temperature and copper oxide nanoparticles for full hydrocarbon catalytic combustion at high temperature. The use of copper acetate precursor leads to a more homogeneous dispersion of copper oxide nanoparticles also providing enough catalytic sites for the total oxidation of hydrocarbons released from the adsorption sites, although lower copper loadings are achieved. Thus, synthesis conditions leading to high copper loadings jointly with highly dispersed copper oxide nanoparticles would result in an exceptional catalytic trap able to reach superior hydrocarbon abatement under highly demanding operational conditions.

Keywords: catalytic traps, factorial design, cold-start emissions, Cu-ZSM-5.

1. Introduction

Nowadays, the transport sector contributes significantly to air pollution and climate change [1, 2] and on-road transportation is considered as a key issue for the next decade [3, 4]. Currently, due to catalyst improvements the most significant part of the total emissions during a trip, especially for short trips (<10 km), takes place during the cold-start [5]. The emissions in this period of gasoline engines are typically associated with fuel enrichment to avoid misfires due to condensation effects on the cylinder walls. Part of this extra fuel does not participate in the combustion process, increasing the engine-out carbon monoxide and hydrocarbon (HC) emissions during cold-start operation. Moreover, the widespread use of three way catalyst (TWC) in modern gasoline vehicles implies disproportionally high levels of gaseous pollutants at the tailpipe during cold-start operation, when the catalyst's temperature is not high enough to ensure an efficient conversion of pollutants [6].

To curb these emissions, the incorporation of an inorganic nanoporous material to act as a catalytic trap prior to the TWC, is one of the most promising solutions. The adsorbent must be able to capture the HCs at low temperatures and to retain them up to the optimal catalyst operating temperature is reached. Zeolites have been found to be the preferred adsorbent material and their effectiveness in retaining exhaust HC at low temperatures is well documented [7-10]. Their properties can be tuned to design bifunctional solids [11], adsorbing HCs on zeolites at low temperatures and subsequently oxidizing the adsorbed HCs over the active catalytic sites as they are released at higher temperatures. Therefore, important parameters are the adsorption capacity and catalytic combustion efficiency of the trap and TWC light-off temperature. Previous results [12-14] showed that ZSM-5 zeolites could be a promising material as HC trap. It has also been observed that propene retention under cold-start conditions

could be improved by ion-exchange with different metals [15, 16] and copper has been proved to create selective adsorption points for HC abatement under cold-start conditions [17]. A direct correlation was observed between the degree of copper-exchange and the trapping efficiency [16, 18, 19]. However, there are many different methods and conditions to introduce copper in ZSM-5 zeolite [16-18, 20-23] and no systematic study has been performed in order to establish the conditions required to obtain optima HC traps from copper-loaded ZSM-5 zeolites.

The present investigation is primarily aimed to optimize the synthesis conditions of copper-loaded ZSM-5 zeolites to improve the capacity as HC cold-start traps under high demanding experimental conditions. This will be performed via a 2^5 full factorial experimental design using MINITAB® 16.1.1 software (trial version) [24].

2. Experimental

2.1. Preparation of copper-loaded zeolites

A commercial ZSM-5 zeolite (CBV 3024 E, Zeolyst International, nominal Si/Al ratio = 15, NH_4 -form) was converted to the protonic form by calcination at 450°C for 6 h in static air (ramp rate = $5^\circ\text{C}\cdot\text{min}^{-1}$).

Copper introduction was achieved by treating the zeolites (3 g) in stirred aqueous solutions of copper precursor under several temperature, time and pH conditions. These conditions were chosen based on previously reported results [16-18, 20-23] on the preparation of Cu-ZSM-5 zeolites. The precursors were copper nitrate (99% Sigma Aldrich) or copper acetate (98% Sigma Aldrich) and the concentration was selected between 1 or 100 mM (16.6 cm^3 per gram of zeolite). The pH of the solution was adjusted at either 2 or 6 by addition of ammonium hydroxide (32 wt% Sigma Aldrich) solution (1 M) prior to heating under reflux at either 25 or 100°C for either 6 or 24 h.

Subsequently, the copper-loaded samples were filtered, washed, dried at 105°C for 13 h, and finally calcined at 550°C for 4 h (ramp rate = 1°C·min⁻¹). The preparation conditions of all the samples are shown in Table 1. It must be noted that depending on the synthesis conditions several processes accounting for ion-exchange, impregnation and deposition-precipitation could take place although a proper relationship between the synthesis procedure and the different factors is hidden due to the occurrence of simultaneous processes, *i.e.* precipitation and dissolution, during the synthesis [25]. The acid ZSM-5 zeolite is coded H-ZSM-5. Copper-containing catalysts are coded Cu-ZSM-5(x) where x corresponds with the number of sample determined randomly by the factorial design software to minimize possible systematic errors during the synthesis process.

2.2. Characterization

X-ray diffraction (XRD) patterns were measured with a Bruker D8 Advance series II diffractometer using monochromatic Cu-K α radiation ($\lambda = 0.1541$ nm). The textural characterization of the zeolites was carried out by means of the adsorption of N₂ at -196°C (Autosorb 6, Quantachrome). Surface area was calculated using the BET equation (S_{BET}). The copper content in the solids was measured by inductively coupled plasma-optical emission spectroscopy (ICP-OES), in a Jobin Yvon 2000 instrument. Secondary electron images (SEM) were acquired using a SEM Inspect F50 microscope. Transmission electron microscopy (TEM) images were acquired using a FEI Technai F30 microscope. Infrared spectroscopy was performed using a Bruker Vertex 70 spectrometer. Temperature-programmed desorption of ammonia (NH₃-TPD) was measured by using a Micromeritics Pulse Chemisorb 2700 instrument. The amount of coke formed during the cold-start test (CST) was determined by thermogravimetric

analysis (TGA). Details of the experimental procedures can be found in the Supporting Information.

2.3. Simulated Cold-Start Tests

CST experiments were carried out in the experimental system shown in Figure 1. It was comprised of a fixed-bed reactor (ID = 0.52 cm; 0.06 g of sample) externally heated. Flow rates of all gases were controlled by mass flow controllers. Steam was generated in an auxiliary reactor with temperature control, and was introduced into the main stream to simulate automotive “cold-start conditions”.

Prior to each test the zeolite was pretreated *in situ* at 500°C for 30 min in a flow of argon. In the course of the simulated CSTs, the reactor temperature was increased from 30°C to 500°C at 50°C·min⁻¹, and held at this temperature for a further 30 min. The temperature was measured by a thermocouple located at the top of the catalyst bed. The inlet gas composition initially used for CST experiments was 0.010% v/v propene, 0.0087% v/v toluene, 1.0% v/v oxygen, 10% v/v water in Ar leading to a total flow of 100 cm³ STP·min⁻¹ and a gas hourly space velocity of 100000 h⁻¹. After that, in order to check the effect of CO₂ addition in the cold-start process and to assess the reusability of the catalytic traps, three consecutive CSTs were performed once the reactor was cooled down using the same space velocity under the presence of 0.010% v/v propene, 0.0077% v/v toluene, 1.0% v/v oxygen, 10% v/v water and 10% v/v CO₂ in Ar. Aliquots of the outlet stream were analyzed on line using a quadrupole spectrometer (Omnistar, Pfeiffer Vacuum). The following masses were monitored: m/z = 40 for argon, 42 for propene, 91 for toluene, 32 for oxygen and 18 for water. m/z = 55 and 56, related to oligomer formation [26, 27] and m/z = 44 and m/z = 28 related to CO₂ and

CO formation, respectively, were also followed during the experiment. The efficiency of the trap for CST (hereafter denoted as efi_{CST}) was defined in Equation 1:

$$\text{efi}_{\text{CST}} = \frac{\text{treated HCs}}{\text{total inlet HCs}} \cdot 100 \quad (1)$$

where treated HCs (propene and toluene) are calculated by integration of the signal curves and total inlet HCs as the product of flow, concentration and reaction time.

2.4. Experimental design

In order to evaluate factors that influence efi_{CST} , a two level five factors full factorial experiment, 2^5 was designed. The minimum number of experiment runs that has to be carried out for a two level factorial design is $2^5 = 32$ runs. Five factors such as concentration of the copper precursor, time, temperature, pH and copper precursor type were selected. Each factor was studied at two levels. Table 1 shows these factors and levels.

MINITAB® 16.1.1 software was used to analyze the experimental data, in order to measure the effect of various factors on efi_{CST} . The design determined which factors have important effects on a response as well as how the effect of one factor varied with the level of the other factors.

3. Results

3.1. Catalyst performance

Figure 2 shows the CST profiles for Cu-ZSM-5(16) and Cu-ZSM-5(17) zeolites. The performance of the remaining solids is shown in Figure S1. In all cases, during the first minutes of the CST, the signal of HCs was kept close to zero due to either physical adsorption or chemical interactions between the HCs and the adsorbent surface [18]. As the temperature of the system increased, the adsorption was no longer favored and the

CST profile showed HC evolution peaks, firstly for propene and later for toluene. Eventually, the HCs signal started to decrease due to the occurrence of catalytic combustion as supported by a lower HC concentration than the initial one and the appearance of CO₂ signal. It is worth to point out that samples obtained with the highest concentration of copper salt produced a complete oxidation of HC at temperatures higher than 250°C and their signals dropped to zero. On the other hand, for the original zeolite as well as those samples obtained at the lowest copper salt concentration, full HC conversion was not achieved.

efi_{CST} and CO₂ releasing temperature of all the samples are shown in Table 2. efi_{CST} for the parent H-ZSM-5 zeolite was lower than those values observed for copper-loaded samples, which is consistent with previous findings [17]. In addition, efi_{CST} obtained for samples prepared at 1 mM was remarkably lower than those using 100 mM, regardless precursor, pH, temperature and time. Regarding CO₂ releasing temperature, it must be noted that this value has been estimated from the cycle in the absence of CO₂. A proper discerning between the CO₂ related to the catalytic combustion and the CO₂ in the main gas flow in the following cycles was prevented due to the relatively high CO₂ concentration (10% v/v). However, the catalytic combustion seemed to occur at similar temperatures in both cases as observed from the HC evolution through the CST. It can be observed that the catalytic trap Cu-ZSM-5(16) showed the highest efi_{CST} of *ca.* 94% with low CO₂ releasing temperature, which was a very remarkable result. .

On the other hand, the stability of the samples was experimentally evaluated by deactivation %, *i.e.* the differences between efi_{CST} in the first and in the third cycle under the presence of CO₂. In most of the samples, a deactivation phenomenon was detected after three cycles (see Table 2). Moreover, it was also generally observed that the performance of all the zeolites declined when CO₂ is incorporated as model

compound into the model gas stream probably due to a competitive adsorption over the active sites. Finally, it is worth commenting that replicate runs were carried out for Cu-ZSM-5(11) and Cu-ZSM-5(16) samples, showing similar efi_{CST} (80.0% vs 82.1% and 93.9% vs 93.6% for Cu-ZSM-5(11) and Cu-ZSM-5(16), respectively) which was within acceptable experimental error.

3.2. Experimental design

3.2.1. Full factorial model

A linear regression model was fitted for the experimental data using the least square technique implemented in MINITAB. The model coefficients for efi_{CST} , the effects and standardized effects of the factors and interactions are shown in Table 3 where A, B, C, D and E denote temperature, aging time, concentration, pH and type of precursor, respectively. The significance of the data is judged by its p-value being closer to zero. For this model, a 95% confidence level was chosen which means that the p-value should be less than or equal to 0.05 for the effect to be statistically significant [28]. Therefore, variable concentration and three interaction terms (concentration and pH, temperature and pH, time and pH) are the most significant parameters with p-values of 0.00, 0.022, 0.033 and 0.034, respectively.

The absolute value of the estimated effect determines its relative strength over the response. The higher the value of the effect, the higher the influence over the response. From the analysis of the factors described previously, precursor concentration had the highest effect on efi_{CST} . It was found that the linear variable concentration and interaction term concentration and pH had a positive effect on efi_{CST} . This means that with the increase of these factors efi_{CST} increased. Contrarily, interaction term temperature and pH and time and pH had a negative effect. Thus, with the increase of

these variables efi_{CST} decreased. The efficiency of all the samples, efi_{CST} calculated, was calculated with the regression equation obtained using the coefficients displayed in Table 3. The low value of standard deviation (5.33) between the experimental and the calculated results showed that the regression equation adequately represented the actual relationship between the response and significant variables. The calculated values were found to be very close to the experimental results as it can be observed from Table 2. High value of R^2 (98.1%) and R^2 (adjusted) (89.9%) indicated a high dependency and correlation between the observed and the calculated values of the response. Thus, this model was a sufficient basis for the interpretation of the obtained relationships between the different factors and efi_{CST} . The maximum experimental efi_{CST} (93.9%) was adequately calculated by the mathematical model (94.7%) and corresponded to Cu-ZSM-5(16). Finally, it is worth mentioning that the stability of the samples evaluated by means of the experimental deactivation (%) was unsuccessfully correlated with the synthesis conditions.

3.2.2. Student's *t*-test

Student's *t*-test was carried out to determine whether the calculated main and interaction effects were significantly different from zero [28]. Pareto plot in Figure 3 visually represents the absolute values of the standardized effects of the main factors and the effects of the interaction factors. A reference line corresponding to the *t*-value for a 95% confidence level was drawn to indicate that the factors which extend past this line were potentially important. It can be seen from Figure 3 that concentration had the greatest effect on efi_{CST} . Moreover, the combination of pH and concentration, time and pH and temperature and pH were also statistically significant.

3.2.3. Analysis of variance (ANOVA)

In order to determine the significant main and interaction effects of factors influencing efi_{CST} , an analysis of variance was performed. The sum of squares (SS) and mean square of each factor (MS), and F-value, defined as the ratio of the respective mean square effect and the mean square error, are shown in Table 4. Since for a 95% confidence level, 1 degree of freedom and 32 factorial tests $F_{0.05,1,32}$ is equal to 4.15, all the effects with F-values higher than 4.15 were significant. According to the obtained F-value and p-value (Table 3), the effect of concentration, time and pH, pH and concentration and temperature and pH seemed to be statistically significant on efi_{CST} .

One important assumption for the statistical analysis of data from experiments is that the data come from a normal distribution. The normality of the data can be checked by plotting a normal probability plot of the residuals. If the points fall fairly close to a straight line, then the data are normally distributed. As observed from Figure S2 (a) the data from the experiments came from a normally distributed population. Moreover, Figure S2 (b) plots the residuals vs. the fitted values (calculated response). The residuals were randomly distributed around zero *i.e.* the errors had a constant variance.

According to the student's t-test and F-test, the effect of concentration and several interaction effects which were statistically non-significant compared to the other effects were discarded and the model was recalculated by eliminating the effect of non-significant factors. High value of R^2 (92.9%) and R^2 (adjusted) (90.9%) indicated a high dependency and correlation between the observed and the calculated values of response. Table 5 shows the analysis of variance for the reduced model. The lack of fit associated with the elimination of some factors resulted in an F-value of 1.34. This value was lower than the tabulated $F_{0.05,8,32} = 2.24$. However, a statistical significance of these factors in the model could not be ruled out.

3.2.4. Contour plot

Contour plot is the projection of the response surface as a two-dimensional plane. This analysis gives a better understanding of the influence of variables and their interaction on the response. To investigate the interactive effect of pH and time on efi_{CST} for both precursors, the hold values of the remaining factors were set at 62.5 °C and 100 mM. For copper nitrate precursor, it is clear that an increase of the pH led to an increase of efi_{CST} (see Figure 4 (a)). Moreover, for a pH value higher than *ca.* 4.5, an increase of the pH turned into higher efi_{CST} regardless the aging time. On the other hand, the effect of the copper acetate precursor is shown in Figure 4 (b). It can be observed that pH had a minor influence on efi_{CST} , thus obtaining similar values for the entire range.

3.3. Sample properties

The phase purity and crystallinity of the samples was verified by XRD. Sharp reflections, corresponding to the MFI structure [29], were observed in all cases (see Figure 5). Slightly decreased reflection intensities were observed for copper-loaded zeolites at low angles confirming the occupancy of distinct sites in the channel system of the ZSM-5 zeolite. Additionally, reflections at 36° and 39° in Cu-ZSM-5(11), Cu-ZSM-5(16) and Cu-ZSM-5(19) samples evidenced the formation of monoclinic CuO (ICSD PDF-number: 01-073-6023 45-937). These reflections could be related to detectable crystallites of CuO with $d \geq 3$ nm and/or high copper content in the samples [23]. The absence of these peaks did not discard the presence of CuO in the solids since it could still be present either as amorphous and/or well dispersed small particles in the external or in the channels of the zeolite, as previously observed [17]. These reflections appeared distinctly in the samples with more decreased reflection intensities.

The copper loading, porous properties and coke content of the samples are compiled in Table 6. Analysis by means of ICP-OES revealed a highly differentiated copper content depending on the concentration of the copper salt used. For samples obtained with a high concentration of copper nitrate, the Cu content ranged from 0.87 to 10.22 wt%, being the latter value related to the complete incorporation of copper species under these conditions, either as Cu-exchanged cations or as CuO nanoparticles. When using copper acetate as precursor, similar copper loadings were achieved regardless the pH value (2.37 ± 0.50 wt%). Therefore, full incorporation of copper was not accomplished and the occurrence of different equilibrium processes seemed to be taking place. On the other hand, the samples prepared by using 1 mM copper precursor concentration had similar copper loadings (0.11 ± 0.01 wt%). As seen in Figure S3, Supporting Information, the conventional H-ZSM-5 exhibited a type I isotherm with a limited uptake of N₂ at higher relative pressures, typical of a purely microporous material. Similar N₂ isotherms were found after copper-exchange, although the BET surface area was generally reduced (Table 6). As expected, the reduction was more significant for those samples with the highest copper loading. Moreover, coke formation ranging from 5.7 to 10.9 wt% was detected after four consecutive cycles (Table 6).

Figure 6 shows representative SEM images of fresh Cu-ZSM-5(16) and both fresh and used (in four consecutive CSTs) Cu-ZSM-5(17) zeolite. These zeolites were prepared under the same conditions, except for the copper precursor: Cu-ZSM-5(16) was prepared using copper nitrate, whereas Cu-ZSM-5(17) was prepared using copper acetate. Both zeolites exhibited comparable morphology although some differences could be pointed out. In the case of Cu-ZSM-5(16) some particles (lighter grey colored particles) of distinct rod-like morphology were visible in areas of the external surface of the larger zeolite crystals, which could be related to the copper oxide phase detected by

XRD. On the other hand, these particles were not identified in Cu-ZSM-5(16), neither for the fresh nor for the used sample.

TEM images of the fresh Cu-ZSM-5(16) zeolite (Figure 7 (a,b)), evidenced a heterogeneous dispersion of copper oxide (lighter grey to white colored spots), with particles of similar shape to those visible in the SEM images in addition to smaller-size nanoparticles decorating the external surface of the zeolite. Thus, a wide particle size distribution ranging from 2 to 20 nm was attained. Contrarily, in the case of Cu-ZSM-5(17) zeolite (Figure 7c), TEM micrographs revealed a homogeneous dispersion of copper oxide nanoparticles of 2.5 ± 0.5 nm. It is noteworthy that the large copper oxide particles identified for Cu-ZSM-5(16) were not observed in this sample. In addition, differences neither in the dispersion of the copper oxide particles nor in the particle size were noticed after use (Figure 7d).

FTIR spectra in the hydroxyl stretching region of the different catalytic traps are reported in Figure 8. The band corresponding to bridging hydroxyls at Brønsted acid sites (3610 cm^{-1}), the band arising from isolated terminal silanol groups (3740 cm^{-1}), and the broad contribution associated with silanol nests (centered at *ca.* 3450 cm^{-1}), were apparent as expected for the H-ZSM-5 zeolite [30]. In the higher copper precursor concentration Cu-loaded sample, the interaction of copper with the hydroxyl groups resulted in decreased band intensities. This was most noticeable for the Brønsted acid hydroxyls, which disappeared almost entirely, supporting the incorporation of copper in ion-exchange sites. No significant changes compared to the parent H-ZSM-5 zeolite were evidenced by FTIR for the lower copper-loaded samples.

NH₃-TPD was used to further characterize the strength of accessible acid sites in the catalysts (Figure 9). Due to the conditions used, all the samples displayed a desorption peak below 150°C related to weakly physisorbed ammonia. At higher temperatures, two

characteristic desorption peaks centered at *ca.* 180°C and 370°C were distinguished for the protonic zeolite and most of the samples characterized. For samples obtained with both the highest copper nitrate concentration and the highest pH value, peaks appear around 270°C and 545°C and the original peak around 370°C becomes less noticeable. In fact, the significant decrease of this original desorption peak was consistent with the high exchange degree of Brønsted acid sites in these samples. The creation of distinct adsorption sites at high copper loading in copper-containing ZSM-5 zeolites has been previously reported [31-33]. Conversely, this feature was not appreciated when using copper acetate as precursor (see Cu-ZSM-5(1) and Cu-ZSM-5(17)), regardless temperature, pH and precursor concentration, likely related to their lower copper content.

4. Discussion

Previously, it was demonstrated that the amount of copper in ion-exchange positions and the presence of CuO particles on the external surface of the zeolite crystals were both key parameters determining the performance of these solids as catalytic traps [18]. In addition, high dispersion of copper oxide nanoparticles has been previously probed to create distinct adsorption sites at high copper loading in ZSM-5 zeolites that favor their application as HC traps [33]. Herein, an experimental factorial design analysis has been performed in order to optimize the synthesis process towards optima catalytic traps with both high copper-exchange degree and well-dispersed CuO nanoparticles, responsible of the catalytic activity.

The results of the experimental factorial design analysis showed that the precursor concentration was the factor that mainly influenced efi_{CST} , which increased when this factor increased. Moreover, pH was also a key factor influencing efi_{CST} when using

copper nitrate precursor, whilst this pH effect was not observed for copper acetate. Accordingly, those solids prepared under these optima conditions, showed the best performance among all the solids with efi_{CST} values higher than 90%.

For all these optima samples, FTIR spectra showed high degrees of ion-exchange, which was an initial request for HC abatement at low temperature. Additionally, full HC catalytic combustion was achieved for all these samples at high temperature, although optima samples prepared using nitrate precursor generally showed lower CO_2 releasing temperature. ICP-OES analysis showed that samples prepared using copper nitrate at optima conditions exhibited remarkably higher copper loadings than those using the acetate counterpart. However, samples from copper nitrate presented larger copper oxide particles with rod-like crystal morphology visible on the external surface of zeolite particles, which were absent in the copper acetate analogue. In this case, an improved homogeneous dispersion of copper oxide nanoparticles of 2.5 ± 0.5 nm was attained. Thus, high efficiency for propene and toluene (model hydrocarbons) removal were obtained at high copper loadings (9-10 wt%) for samples Cu-ZSM-5(16) and Cu-ZSM-5(26) prepared using copper nitrate. On the other hand, a number of samples prepared using copper acetate (Cu-ZSM-5(17), Cu-ZSM-5(20), Cu-ZSM-5(23) and Cu-ZSM-5(27)) with a much lower copper content, e.g., around 2.5 wt%, showed also a high performance. This behavior was probably associated to an enhanced homogeneous dispersion of copper nanoparticles when using copper acetate as precursor as it has been observed by TEM. These facts seemed to point out that high copper loadings and an improved homogeneous dispersion of copper oxide nanoparticles appeared to be the most desirable features to design a highly efficient catalytic trap, since a greatly amount of catalytic sites would be provided for the total oxidation of HCs released from the adsorption sites.

Regarding the stability of the samples, the low number of CSTs prevented a direct correlation between the deactivation phenomenon and the synthesis conditions to be established. In general, low copper-loaded materials (< 0.14 wt%) generally exhibited a relevant deactivation degree. Indeed, these solids were very similar to the parent H-ZSM-5 zeolite as stated by the characterization results, which also evidenced a deactivation phenomenon upon cycling. In all cases, the deactivation phenomenon was consistent with the presence of coke ranging from 5.7 to 10.9 wt% proved by TGA analysis, which is a well-known problem observed for this type of materials when applied for NO_x abatement [34]. Thus, both blockage of the adsorption or catalytic sites due to coke formation, or their loss due to the migration of copper species could originate the deactivation observed, although the occurrence of sintering could not be confirmed by TEM. However, it should be highlighted that sample with the highest copper loading hardly showed deactivation after three consecutive cycles although comparable coke formation occurred and value about 8 wt% were observed. Then, a higher number of cycles should be carried out before reaching any definitive conclusion.

5. Conclusions

Abatement of hydrocarbon emissions under cold-start conditions has been studied. A factorial design analysis was performed to optimize the synthesis conditions towards high efficient catalytic traps. Within the five factors comprising the study, the concentration of copper precursor has been proved to have the most significant influence in the synthesis of highly efficient traps. This factor exhibited a positive effect and a high concentration of precursor improved the removal of hydrocarbons. The optimum synthesis conditions were found for the sample Cu-ZSM-5(16) as 100 mM,

25°C, 24 hours, nitrate precursor and pH 6. The use of high copper loadings together with an improved homogeneous dispersion of CuO nanoparticles appeared to be the most desirable features to design a highly efficient catalytic trap. Regarding the stability of the samples, those samples with the highest copper loading hardly showed deactivation after three consecutive cycles.

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Table 1. Experimental factors and levels investigated in the experiment and characterization data of the samples.

Sample	Conc [mM]	Temp [°C]	Time [h]	pH	Precursor
H-ZSM-5					
Cu-ZSM-5(20)	100	100	6	2	Acetate
Cu-ZSM-5(10)	100	100	6	2	Nitrate
Cu-ZSM-5(26)	100	100	6	6	Nitrate
Cu-ZSM-5(27)	100	100	6	6	Acetate
Cu-ZSM-5(1)	100	100	24	2	Acetate
Cu-ZSM-5(18)	100	100	24	2	Nitrate
Cu-ZSM-5(11)	100	100	24	6	Nitrate
Cu-ZSM-5(14)	100	100	24	6	Acetate
Cu-ZSM-5(5)	100	25	6	2	Nitrate
Cu-ZSM-5(15)	100	25	6	2	Acetate
Cu-ZSM-5(19)	100	25	6	6	Nitrate
Cu-ZSM-5(23)	100	25	6	6	Acetate
Cu-ZSM-5(3)	100	25	24	2	Nitrate
Cu-ZSM-5(13)	100	25	24	2	Acetate
Cu-ZSM-5(16)	100	25	24	6	Nitrate
Cu-ZSM-5(17)	100	25	24	6	Acetate
Cu-ZSM-5(12)	1	100	6	2	Acetate
Cu-ZSM-5(32)	1	100	6	2	Nitrate
Cu-ZSM-5(22)	1	100	6	6	Acetate
Cu-ZSM-5(30)	1	100	6	6	Nitrate
Cu-ZSM-5(2)	1	100	24	2	Nitrate
Cu-ZSM-5(6)	1	100	24	2	Acetate
Cu-ZSM-5(28)	1	100	24	6	Nitrate
Cu-ZSM-5(9)	1	100	24	6	Acetate
Cu-ZSM-5(8)	1	25	6	2	Nitrate
Cu-ZSM-5(24)	1	25	6	2	Acetate
Cu-ZSM-5(21)	1	25	6	6	Nitrate
Cu-ZSM-5(29)	1	25	6	6	Acetate
Cu-ZSM-5(4)	1	25	24	2	Nitrate
Cu-ZSM-5(25)	1	25	24	2	Acetate
Cu-ZSM-5(7)	1	25	24	6	Acetate
Cu-ZSM-5(31)	1	25	24	6	Nitrate

Table 2. CO₂ releasing temperature, experimental and calculated values of efi_{CST} .

Sample	CO ₂ releasing temperature [°C] ^a	efi_{CST} experimental [%] ^b	Deactivation experimental [%] ^c	efi_{CST} calculated [%] ^d
H-ZSM-5	270	42.2	7.62	-
Cu-ZSM-5(20)	209	91.6	7.84	91.7
Cu-ZSM-5(10)	175	84.4	6.53	85.1
Cu-ZSM-5(26)	92	93.0	0.83	90.7
Cu-ZSM-5(27)	192	90.5	1.84	91.9
Cu-ZSM-5(1)	209	87.2	1.13	88.7
Cu-ZSM-5(18)	184	89.5	5.20	88.1
Cu-ZSM-5(11)	193	80.0	0.54	83.9
Cu-ZSM-5(14)	130	92.4	3.42	89.4
Cu-ZSM-5(5)	195	75.2	1.51	77.2
Cu-ZSM-5(15)	175	84.3	-1.83	84.5
Cu-ZSM-5(19)	206	85.8	-1.63	88.3
Cu-ZSM-5(23)	183	93.5	7.45	91.8
Cu-ZSM-5(3)	224	80.2	3.91	82.7
Cu-ZSM-5(13)	223	85.9	5.87	84.1
Cu-ZSM-5(16)	88	93.9	0.38	94.7
Cu-ZSM-5(17)	217	91.4	4.03	89.9
Cu-ZSM-5(12)	241	56.2	5.86	52.2
Cu-ZSM-5(32)	216	54.8	11.8	58.0
Cu-ZSM-5(22)	168	47.1	0.80	49.6
Cu-ZSM-5(30)	234	56.6	10.6	54.8
Cu-ZSM-5(2)	191	77.7	6.59	76.0
Cu-ZSM-5(6)	219	64.9	15.8	67.4
Cu-ZSM-5(28)	241	48.9	-0.61	49.1
Cu-ZSM-5(9)	228	52.1	16.5	51.2
Cu-ZSM-5(8)	231	56.4	9.60	53.4
Cu-ZSM-5(24)	233	51.5	-2.51	55.3
Cu-ZSM-5(21)	190	59.7	9.38	61.2
Cu-ZSM-5(29)	219	64.5	12.4	62.2
Cu-ZSM-5(4)	307	60.6	12.2	62.0
Cu-ZSM-5(25)	209	60.3	21.1	58.1
Cu-ZSM-5(7)	209	53.4	9.17	54.1
Cu-ZSM-5(31)	250	48.6	0.55	48.7

^afor the cycle without CO₂, ^bfor the first CST under the presence of CO₂, ^ccalculated by $(\text{efi}_{\text{CST,C1}} - \text{efi}_{\text{CST,C3}})/\text{efi}_{\text{CST,C1}} \cdot 100$ (cycles under the presence of CO₂), ^dcalculated applying the regression equation.

Table 3. Estimated effects and coefficients for the 2^5 design.

Term	Net effect	Coefficient	p-value
Constant		72.3	
A	1.42	0.71	0.480
B	1.43	0.72	0.476
C	30.4	15.2	0.000
D	-0.63	-0.32	0.749
E	-1.29	-0.65	0.518
A $\times$ B	1.01	0.50	0.613
A $\times$ C	0.99	0.50	0.617
A $\times$ D	-5.18	-2.59	0.033
A $\times$ E	1.76	0.88	0.387
B $\times$ C	-1.04	-0.52	0.600
B $\times$ D	-5.17	-2.58	0.034
B $\times$ E	0.37	0.18	0.851
C $\times$ D	5.79	2.90	0.022
C $\times$ E	-2.94	-1.47	0.169
D $\times$ E	-1.02	-0.51	0.608
A $\times$ B $\times$ C	-3.77	-1.88	0.092
A $\times$ B $\times$ D	-0.69	-0.35	0.725
A $\times$ B $\times$ E	-0.76	-0.38	0.702
A $\times$ C $\times$ D	0.59	0.30	0.763
A $\times$ C $\times$ E	-0.99	-0.50	0.617
A $\times$ D $\times$ E	-0.37	-0.18	0.851
B $\times$ C $\times$ D	3.51	1.75	0.112
B $\times$ C $\times$ E	0.77	0.38	0.697
B $\times$ D $\times$ E	-2.56	-1.28	0.224
C $\times$ D $\times$ E	1.48	0.74	0.462

Standard error coefficient for all cases = 0.94. A is temperature [°C], B is time [h], C is concentration [mM], D is pH and E is precursor.

Table 4. Analysis of variance.

Term	Degrees of freedom	Sum of squares [SS]	Mean square [MS]	F-Value
A	1	16.1	16.1	0.57
B	1	16.4	16.4	0.58
C	1	$7.39 \cdot 10^3$	$7.39 \cdot 10^3$	260
D	1	3.19	3.19	0.11
E	1	13.4	13.4	0.47
A $\times$ B	1	8.10	8.10	0.29
A $\times$ C	1	7.90	7.90	0.28
A $\times$ D	1	215	215	7.56
A $\times$ E	1	24.7	24.7	0.87
B $\times$ C	1	8.72	8.72	0.31
B $\times$ D	1	213.4	214	7.52
B $\times$ E	1	1.09	1.09	0.04
C $\times$ D	1	269	269	9.45
C $\times$ E	1	69.3	69.3	2.44
D $\times$ E	1	8.30	8.30	0.29
A $\times$ B $\times$ C	1	114	114	4.00
A $\times$ B $\times$ D	1	3.85	3.85	0.14
A $\times$ B $\times$ E	1	4.58	4.58	0.16
A $\times$ C $\times$ D	1	2.82	2.82	0.10
A $\times$ C $\times$ E	1	7.90	7.90	0.28
A $\times$ D $\times$ E	1	1.09	1.09	0.04
B $\times$ C $\times$ D	1	98.4	98.4	3.46
B $\times$ C $\times$ E	1	4.73	4.73	0.17
B $\times$ D $\times$ E	1	52.3	52.3	1.84
C $\times$ D $\times$ E	1	17.6	17.6	0.62
Error	6	170	28.4	
Total	31	$8.74 \cdot 10^3$		

A is temperature [°C], B is time [h], C is concentration [mM], D is pH and E is precursor.

Table 5. Analysis of variance of the reduced model.

Term	Degrees of freedom	Sum of squares [SS]	Mean square [MS]	F-Value
C	1	$7.39 \cdot 10^3$	$7.39 \cdot 10^3$	287
A $\times$ D	1	215	215	8.33
B $\times$ D	1	214	214	8.29
C $\times$ D	1	269	269	10.4
Residual error	23	328	14.3	
Lack of fit	8	249	31.1	1.34
Pure error	16	370	23.1	
Total	31	$8.74 \cdot 10^3$		

A is temperature [°C], B is time [h], C is concentration [mM] and D is pH.

Table 6. Characterization data of the samples.

Sample	Cu content^a [wt%]	S_{BET}^b [m²·g⁻¹]	Coke^c [wt%]
H-ZSM-5	-	434	8.03
Cu-ZSM-5(20)	2.49	410	-
Cu-ZSM-5(10)	1.39	426	-
Cu-ZSM-5(26)	9.91	285	-
Cu-ZSM-5(27)	2.43	394	-
Cu-ZSM-5(1)	2.67	303	6.92
Cu-ZSM-5(18)	1.45	373	-
Cu-ZSM-5(11)	8.63	275	6.70
Cu-ZSM-5(14)	3.33	334	-
Cu-ZSM-5(5)	1.19	323	-
Cu-ZSM-5(15)	1.87	411	-
Cu-ZSM-5(19)	10.2	273	6.85
Cu-ZSM-5(23)	2.36	311	-
Cu-ZSM-5(3)	0.87	398	8.87
Cu-ZSM-5(13)	1.92	452	-
Cu-ZSM-5(16)	9.02	265	8.55
Cu-ZSM-5(17)	1.85	412	5.71
Cu-ZSM-5(12)	0.13	395	-
Cu-ZSM-5(32)	0.11	396	-
Cu-ZSM-5(22)	0.11	466	-
Cu-ZSM-5(30)	0.10	380	-
Cu-ZSM-5(2)	0.11	336	-
Cu-ZSM-5(6)	0.11	398	-
Cu-ZSM-5(28)	0.11	408	-
Cu-ZSM-5(9)	0.12	391	-
Cu-ZSM-5(8)	0.09	461	-
Cu-ZSM-5(24)	0.13	407	-
Cu-ZSM-5(21)	0.11	391	-
Cu-ZSM-5(29)	0.11	426	-
Cu-ZSM-5(4)	0.11	425	-
Cu-ZSM-5(25)	0.14	420	-
Cu-ZSM-5(7)	0.11	422	8.70
Cu-ZSM-5(31)	0.08	426	11.0

^aMeasured by ICP-OES. ^bBET method. ^cMeasured from TGA experiments.

Figure captions

Figure 1. Diagram of test system.

Figure 2. Simulated CSTs for different HC traps, Cu-ZSM-5(16) (a), Cu-ZSM-5(17) (b). 1st cycle: black dotted line. Three following cycles: 1st cycle: black; 2nd cycle: green; 3rd cycle: light grey dotted line. Conditions shown in the text.

Figure 3. Pareto chart for standardized effects.

Figure 4. Contour plot for efi_{CST} vs. pH and time for (a) copper nitrate and (b) copper acetate precursor.

Figure 5. XRD patterns of the selected HC traps (u designates used sample). Marked reflections at $2\theta = 36$ and 39° arise from CuO.

Figure 6. SEM images of Cu-ZSM-5(16) (a), Cu-ZSM-5(17) (b) and Cu-ZSM-5(17) used (c) samples.

Figure 7. TEM images of Cu-ZSM-5(16) (a, b), Cu-ZSM-5(17) (c) and Cu-ZSM-5(17) used (d) samples.

Figure 8. FTIR spectra in the hydroxyl stretching region of the selected HC traps.

Figure 9. NH_3 -TPD profiles of the selected HC traps.

Figure 1

Figure 2

(a)

(b)

Figure 3

Figure 4

(a)

(b)

Figure 5

Figure 6

Figure 7

Figure 8

Figure 9