



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



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HIGHLIGHTS

- Optima synthesis conditions for hydrocarbon removal were determined by factorial design.
- Improved hydrocarbon retention was achieved for highly exchanged copper zeolites.
- CuO nanoparticles catalyzed the total oxidation of trapped hydrocarbons.
- Copper acetate precursor favored higher dispersions of CuO nanoparticles.
- Maximum propene removal efficiency from the optimization procedure was 93.9%.

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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.

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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 disproportionately 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

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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 2⁵ 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, NH₄-form) was converted to the protonic form by calcination at 450 °C for 6 h in static air (ramp rate = 5 °C 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 and 100 mM (16.6 cm³ 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

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

(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 Fig. 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 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 100,000 h⁻¹. After that, in order to check the effect of CO₂ addition in the

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