

# Optimization of nanostructured materials for hydrocarbon abatement during the cold-start period of gasoline vehicles

B. Puértolas Lacambra (2014)

*Departamento de Energía y Mediambiente (Grupo de Investigaciones Medioambientales). Instituto de Carboquímica (ICB-CSIC), 50018 Zaragoza, Spain.*

*Supervisors: T. García Martínez (Instituto de Carboquímica, ICB-CSIC) and M. V. Navarro López (Instituto de Carboquímica, ICB-CSIC).*

## Objectives and novelty

Air pollution poses a major environmental concern worldwide. In metropolitan areas, motor vehicle exhaust contributes a major source of contaminants. More restrictive legislations regarding automotive emissions resulting in a remarkable decrease in the amount of pollutants associated to new vehicles. With current three-way catalysts (TWC), a recognized challenge in preventing these emissions is the lack of treatment capacity of hydrocarbons (HC) and CO under cold-start conditions. Fresh catalysts start to operate at ca. 170 °C, but aged catalysts light-off at ca. 200-225 °C. These catalysts need between 60 to 120 seconds to reach these temperatures and during this time, about 50 to 80% of unburned HCs and around 80% CO are emitted. To curb the HC emissions, the incorporation of an inorganic nanoporous material to act as a HC trap prior to the TWC, is one of the most promising solutions. Zeolites are often considered as HC trap materials due to their stability under a variety of conditions. Different zeolites and zeotypes, with varying pore dimensionality and pore network connectivity, have been studied as adsorbents for HC emission control during the cold-start period. However, none of the reported materials have demonstrated the necessary characteristics of a HC trap under very demanding operational conditions. In this sense, a priority goal is to find an adsorbent that fulfills this requirement.

Regarding CO emissions during the cold-start phase, there are only a few studies in the literature that aim to control this hazardous pollutant. The absence of effective catalysts for CO oxidation at low temperatures and resistant to sintering up to temperatures as high as 800 °C represents a true challenge and will offer new opportunities if the activity during the cold-start and stability at normal operation are assured. An inherent problem for nanoparticulate catalysts is their well-documented lack of stability under highly demanding operational conditions. Supported and unsupported metal nanoparticles show rapid particle growth, especially at elevated reaction temperatures. For many industrially important catalytic applications, such as automobile exhaust control, reaction temperatures typically exceed 600 °C, and thermal stability of the catalysts becomes a crucial issue.

In this regard, a feasible solution for the complete elimination of these pollutants is presented by the development of the adequate technologies. Considering the expected increasing restrictions on the future legal frame, the development of realistic technologies for the abatement of these pollutants seems essential to reduce the impact of current gasoline engines.

## Results

A Cu-ZSM-5 zeolite was used as HC trap. In this

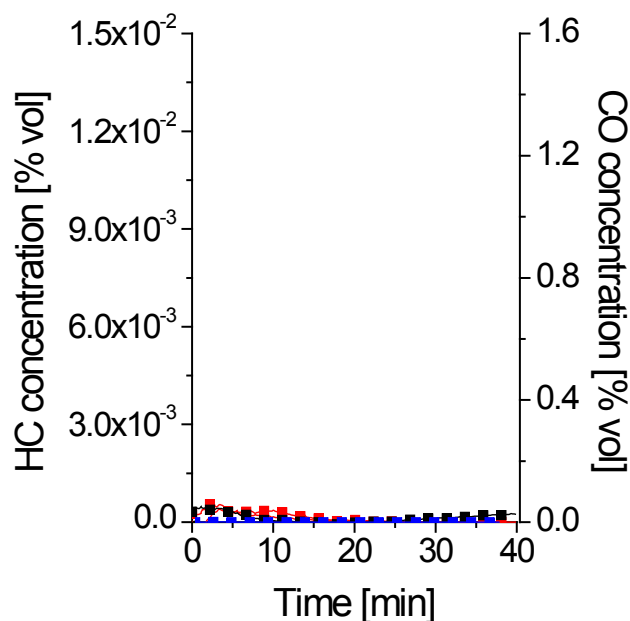
solid, the partial substitution of protons in ion exchange positions by copper cations made ZSM-5 an ideal material as HC trap under simulated cold-start conditions at a space velocity of 10K h<sup>-1</sup>. The presence of copper species was also demonstrated to play an important role in the behavior of the trap by means of the catalytic combustion of hydrocarbons. The oxidation of the model hydrocarbons (propene and toluene) once they were desorbed was probed to contribute to the improvement of their removal efficiency.

An experimental factorial design subsequently revealed that the concentration of the copper precursor used in the synthesis was the factor that influenced the most the efficiency of the hydrocarbon trap during the overall CST. Thus, HC removal efficiency increased when increased the precursor concentration. High concentrations of copper nitrate precursor led to a heterogeneous distribution of copper oxide nanoparticles ranged from 2-20 nm whereas the use of copper acetate precursor guided to an improved homogeneous dispersion of copper oxide nanoparticles of 2.5 ± 0.5 nm. Thus, high copper loadings together with an improved homogeneous dispersion of copper oxide nanoparticles appeared to be the most desirable features to design a highly efficient hydrocarbon trap.

To meet these requirements, a hierarchical zeolite was designed. The results obtained pointed out that a copper-loaded hierarchical zeolite had an ideal behavior as hydrocarbon trap at higher space velocities (60K h<sup>-1</sup>). A larger external surface, arising from the introduction of intracrystalline mesopores, coupled with the preserved intrinsic crystallinity and acidic properties of the conventional H-ZSM-5, led to an enhanced accessibility of copper sites located in ion exchange positions and to an increased dispersion of copper oxide species. These structural features translated into a stable bifunctional catalyst that was able to perform as an ideal trap under very demanding operational conditions.

Regarding the development of a CO oxidation catalyst, the material employed consisted of gold supported on a Ti-Si-O mesoporous material. This mesoporous Ti-Si-O material was prepared by a wet impregnation of titanium using an ethanolic solution of titanium (IV) oxyacetylacetonate on a nanoparticulated bimodal mesoporous silica denoted as UVM-7. The resulting material showed gold nanoparticles with a narrow size distribution around 3.0 nm, homogeneously dispersed over the Ti-Si-O support. The gold nanoparticles maintained their diameter at ca. 3.0 nm at calcination temperatures up to 800 °C. The observed exceptional thermal stability of gold nanoparticles on metal oxide modified UVM-7 was illustrated by several high-temperature catalytic applications, such as CO oxidation during

the cold-start period of an engine, its capacity as three-way catalyst and its application in the methane catalytic combustion. The results for the simultaneous reduction of HC and CO by the copper-loaded hierarchical zeolite and the CO oxidation catalyst are presented in Figure 1.



**Figure 1.** Experimental performance of CO oxidation catalyst and HC catalytic trap in the simultaneous reduction of HC and CO emissions of a model gas exhaust. Red lines represent propene, black lines represent toluene and blue lines represent CO. Conditions: 0.01% v/v propene, 0.0077% v/v toluene, 1.6% v/v CO, 1% v/v oxygen, 10% v/v water and Ar balance, temperature increase up to 600 °C at 50 °C·min<sup>-1</sup>. GHSV = 200K and 30K h<sup>-1</sup> for the CO oxidation catalyst and the HC trap, respectively.

## Conclusions

A feasible proposal for the complete abatement of HC and CO has been developed. The use of the HC trap together with the CO oxidation catalysts exhibited 100% HC and CO removal after three consecutive cycles at high demanding operational conditions. Hydrocarbon abatement has been addressed by the optimization of the design of a copper-loaded hierarchical ZSM-5 zeolite whereas the handling of the CO emissions during the cold phase of an engine was dealt with the development of a highly active and stable CO oxidation catalyst.

## Related publications

[1] Navarro MV, Puértolas B, García T, Murillo R, Mastral AM, Varela-Gandía FJ, Lozano-Castelló D, Cazorla-Amorós D, Bueno-López A, Experimental and simulated propene isotherms on porous solids, *Appl. Surf. Sci.*, 2010; 256, 5292-5297.

[2] Puértolas B, López MR, Navarro MV, López JM, Murillo R, García T, Mastral AM, Modelling of the breakthrough curves obtained from the adsorption of propene in inorganic microporous solids, *Adsorpt. Sci. Technol.*, DOI: 10.1260/0263-6174.28.8-9.761.

[3] Puértolas B, Navarro MV, López JM, Murillo R, Mastral AM, García T, Recent solutions for the abatement of hydrocarbon emissions during the cold start of light vehicles, *Recent Patents on Chemical Engineering*, 2011; 4, 36-52.

[4] Puértolas B, Navarro MV, López JM, Murillo R, Mastral AM, García T, Modelling the heat and mass transfers of propane onto a ZSM-5 zeolite, *Sep. Purif. Technol.* 2012; 86, 127-136.

[5] Puértolas B, Navlani-García M, López JM, García T,

Murillo R, Mastral AM, Navarro MV, Lozano-Castelló D, Bueno-López A, Cazorla-Amorós D, Molecular simulation design of a multisite solid for the abatement of cold start emissions, *Chem. Comm.*, 2012; 48, 6571-6573.

[6] Puértolas B, López JM, Navarro MV, García T, Murillo R, Mastral AM, Varela-Gandía FJ, Lozano-Castelló D, Bueno-López A, Cazorla-Amorós D, Abatement of hydrocarbons by acid ZSM-5 and BETA zeolites under cold-start conditions, *Adsorption*, 2013; 19, 357-365.

[7] Navlani-García M, Puértolas B, Lozano-Castelló D, Cazorla-Amorós D, Navarro MV, García T, CuH-ZSM-5 as hydrocarbon trap under cold start conditions, *Environ. Sci. Technol.* 2013; 47, 5851-5857.

[8] Navlani-García M, Varela-Gandía FJ, Bueno-López A, Cazorla-Amorós D, Puértolas B, López JM, García T, Lozano-Castelló D, BETA zeolite thin films supported on honeycomb monoliths with tunable properties as hydrocarbon traps under cold-start conditions, *ChemSusChem*. 2013; 6, 1467-1477.

[9] Puértolas B, García Andújar L, García T, Navarro MV, Mitchell S, Pérez-Ramírez J, Bifunctional Cu/H-ZSM-5 zeolite with hierarchical porosity for hydrocarbon abatement under cold-start conditions, *Appl. Catal., B*. 2014; 144-145 (2014) 161-170.