Molecular simulation design of a multisite solid for the abatement of cold start emissions


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Supplementary Information

Details of computer modeling and experimental techniques, preparation of samples, XRD pattern, TEM images, Thermogravimetric analyses, Hydrocarbon simulated cold start tests

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1.- Computer modeling

1.1.- Computational details

Within the software Accelrys® Materials Studio 5.0 [1] (MS software), most of the zeolite structures listed in the “atlas of zeolite framework types” are available. The MFI framework was imported from MS database. From this structure, several Si atoms were changed by Al and, in addition, the Cu²⁺ and H⁺ atoms were inserted. Al atoms were first placed by following the Lowenstein rules in the most probable position T12, followed by T6 when T12 positions were not available [2,3]. Cation positions were optimized using the “Locate task” of the SORPTION module, by means of the Canonical Monte Carlo simulated annealing algorithm [4]. This tool provides a good approximation of global energy minimum by lowering the temperature of the system [5]. Cation loading simulation conditions are shown in Table S1. The PCFF force-field [6] was utilised and, according to literature [7], the charges applied were +2.05 e⁻ for Si, +1.75 e⁻ for Al, +1 e⁻ for H, +2 e⁻ for Cu and -1.025 e⁻ for oxygen close to Si and -1.2 e⁻ for O close to Al, which results in a neutral system. Framework structure is assumed to be rigid since framework flexibility is generally negligible when loading small molecules [8]. Three different cases were studied and the optimized unit cells (u.c.) are...
compiled in Figure S1: A) copper exchange zeolite (2 Cu\(^{2+}\) per u.c., CuZSM-5); B) proton exchange zeolite (5 H\(^+\) per u.c., HZSM-5) and, C) a copper and protons exchange zeolite (1 Cu\(^{2+}\) and 3 H\(^+\) per u.c., CuHZSM-5). The Si/Al ratios of these solids are 22.75, 15 and 15 respectively. The preferential positions of Al atoms and cations (Figure S1) are in the intersections of straight and sinusoidal channels in the MFI structure showing a slight shift to the straight channels in accordance with previous literature data [2, 3, 9-12].

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**Table S1.** Cation Loading simulation conditions.

Propene and toluene molecule geometries were optimized using the “Geometry optimization” task of the FORCITE module, which applies classical molecular mechanics calculations to minimize the total energy of a given geometry. The PCFF force-field [6] was used. For water molecule the SPC/E model has been chosen with charges 0.848 e\(^-\) for oxygen atoms and 0.424 e\(^-\) for hydrogen atoms [13, 14].

**Figure S1.** Optimized u.c. used for the simulations (x-y view). Red lines represent oxygen, black lines represent silicon, pink balls are aluminium, grey are copper cations and blue are protons.
To calculate the equilibrium adsorption capacity of the gas mixture, the “Fixed Pressure” task of the SORPTION module from MS Software was used, by means of the Grand Canonical Monte Carlo (GCMC) ensemble. In this method, the gas molecules are loaded into the zeolite structure as a function of the gas fugacity at fixed bulk pressure and temperature. In the GCMC calculations, the PCFF force-field [6] was used for both gas-gas and gas-solid interactions as described above. Under this premises, the adsorption of the mixture 0.01 kPa of propene, 0.01 kPa toluene and 10 kPa water at 30 ºC in the three solids described above was studied. Simulation conditions are shown in Table S2.

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Sample interval

| Exchange | 2.000  | |
| Conformer | 1.000 | |
| Rotate | 1.000 | 5 deg |
| Translate | 1.000 | 1 Å |
| Regrowth | 0.100 | |

**Table S2.** Fixed pressure adsorption simulation conditions

1.2.- Results and discussion

Due to the high reactivity of the system at relatively low temperatures, alkenes rapidly undergo isomerization, oligomerization, or other reactions. All these reactions make difficult to extract reproducible data from experiments. Therefore, theoretical simulations are indispensable for gaining insight into the adsorption of alkenes in zeolites [15]. Physisorption is the first step of all the processes named above, in the case of acid ZSM-5 characterized by the formation of a π-complex, *i.e*, the interaction
between the acid proton and the π-electrons of the C=C double bond. In this regard, we applied the powerful method [16] Grand Canonical Monte Carlo (GCMC) theoretical simulations to explore the implications of changing extraframework protons by copper cations in the electrostatic environment and the spatial availability of the gas molecules in the remaining space of the zeolite. This enables the description of the adsorption step in a multisite solid, important for the subsequent modeling of the catalytic system.

The results obtained for the physisorption of the gas mixture are presented in the following section. As it can be seen in figures S2, S3 and S4, the distribution of model molecules, propene, toluene and their mixtures, are highly dependent on the extra-framework cation positions. In the case that copper cations are totally exchanged in the structure (Figure S2) propene molecules show a higher probability distribution close to the copper atoms; while toluene molecules are located at the intersections where copper cations are not available. When propene and toluene mixtures are studied, a similar probability distribution is observed since there is not competitive adsorption between them. If only protons are exchanged in the structure (Figure S3) propene molecules, as single model compound, are mainly observed at the intersections. Similarly, toluene molecules are also located at the intersections. In binary mixtures, it is observed that the toluene molecules move the propene ones from the intersections into the sinusoidal channels, due to the competition for the adsorption sites in the intersections. In the case that copper atoms and protons are exchanged simultaneously (Figure S4) propene molecules are situated at both the intersections and the straight channels, while toluene molecules are observed at the intersections, preferentially where protons are exchanged. When propene-toluene mixtures are studied in partially exchanged copper zeolites, selective adsorption is taking place. As a general conclusion, it is observed that propene molecules are highly attracted by copper cations while toluene molecules show more affinity for protons.

Since water is present in a high concentration, it is important to assess the interaction with the zeolite to design a multisite efficient adsorbent. In Figures S5, results obtained through the simulations of water in the different structures are shown. Water molecules tend to locate close to the copper cations when both Cu^{2+} and H^+ are present in the structure. However, when considering Cu^{2+} totally exchanged in the structure, water is uniformly distributed through all the structure, while if only H^+ are present in the structure as extra-framework cation, the water molecules tend to locate mainly at the intersections.

Next, we describe the behaviour of the different structures considered in this work in contact with the mixture of propene and toluene in presence of water. In all cases, water molecules showed higher adsorption probability in the same sites as when they were the only molecules in the structure. Propene, toluene and their mixture are distributed in the structure in different ways depending on the cations that are present. When Cu^{2+} are the only cations present in the structure, Figure S6, water adsorption is taking place at the three different types of adsorption sites. However, if only H^+ are exchanged as extra-framework cations, water is situated in all the channel intersections, which could block the diffusion of the HC molecules to the adsorption sites, see Figure S7. When both Cu^{2+} and H^+ are present in the structure, Figure S8, whilst propene molecules are observed in straight and sinusoidal channels, toluene molecules are preferentially situated at the intersections of sinusoidal and straight channels where extra-framework copper cations are not exchanged.
Figure S2. Probability distribution of propene, toluene and propene-toluene mixtures obtained through the simulations for the MFI structure Si/Al=22.75 completely exchanged with Cu^{2+} cations. A. Propene; B. Toluene and C. Binary mixture.
Atoms:
- Cu²⁺
- Al
- Si
- O

Adsorbates:
- toluene
Atoms:
- Cu²⁺
- Al
- Si
- O

Adsorbates:
- propene
- toluene
**Figure S3.** Probability distribution of propene, toluene and propene-toluene mixtures obtained through the simulations for the MFI structure Si/Al=15 completely exchanged with H⁺ cations. A. Propene; B. Toluene and C. Binary mixture.

Atoms:
- : H⁺
- : Al
- : Si
- : O

Adsorbates:
- : propene

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**Figure S4.** Probability distribution of propene, toluene and propene-toluene mixtures obtained through the simulations for the MFI structure Si/Al=15 simultaneously exchanged with Cu$^{2+}$ and H$^+$ cations (1 copper cation and 3 protons per u.c.). A. Propene; B. Toluene and C. Binary mixture.
Atoms: H⁺, Cu²⁺, Al, Si, O
Adsorbates: propene, toluene
Figure S5. Probability distribution of water molecules obtained through the simulations for a MFI structure. A. Cu$^{2+}$ exchanged (Si/Al=22.75), B. H+ exchanged (Si/Al=15) and C. Cu$^{2+}$ and H+ exchanged 1:3 atom ratio per.u.c. (Si/Al=15).

Atoms: Cu$^{2+}$, Al, Si, O

Adsorbates: water
Atoms:
- H⁺
- Cu²⁺
- Al
- Si
- O

Adsorbates:
- water
Figure S6. Probability distribution of propene-toluene-water mixtures obtained through the simulations in a MFI structure Si/Al=22.75 exchanged with Cu$^{2+}$ cations.
Figure S7. Probability distribution of propene-toluene-water mixtures obtained through the simulations in a MFI structure Si/Al=15 exchanged with H⁺.
**Figure S8.** Probability distribution of propene-toluene-water mixtures obtained through the simulations in a MFI structure Si/Al=15 exchanged with H$^+$ and Cu$^{2+}$ cations.

[Images showing probability distribution with labels for atoms and adsorbates]
2.- Experimental

2.1.- Preparation of the samples
HZSM-5 was obtained by calcination of a commercial sample of ZSM-5 (ammonium form; Si/Al=15; from Zeolyst International) at 450 ºC during 6 hours (5 ºC/min). CuHZSM-5 solid was prepared from HZSM-5 by an ion-exchange method as follows: HZSM-5 (6 g) was mixed with an aqueous solution (100 mL) of copper nitrate (Cu(NO$_3$)$_2$·3H$_2$O) (concentration 3.45·10$^{-3}$ M), and the mixture was heated in a thermostatic bath under stirring at 77 ºC during 18 hours. The slurry obtained was filtered, washed with distilled water and dried at 110 ºC for 12 hours. Finally, the material obtained was calcined at 550 ºC for 4 hours (1 ºC/min). The amount of Cu in the sample was 0.7 wt. %.

2.2.- XRD
Solids prepared were characterized by X-ray diffraction (XRD), using a SEIFERT 2002 power diffractometer with a Cu-K$_\alpha$ radiation. The scanning rate was 2º/min in the 5-50º angle range. The diffractograms before and after ion-exchanged process are similar (see figure S9), indicating that no crystallinity change has occurred.

Figure S9. XRD diffractograms of the samples HZSM-5 and CuHZSM-5.

2.3.- TEM
Transmission Electron Microscopy (TEM) was performed on a JEOL (JEM-2010). A small amount of the sample was positioned on a carbon microgrid supported on nickel. The zeolite size and morphology before and after ion-exchange are similar (see Figure S10)
2.4.- Thermogravimetric analyses
Thermogravimetric analyses were used to determine the amount of coke deposited on the zeolite. Thus, the weight change of the zeolites during the oxidation was measured. The sample was heated to 900 °C at a rate of 80 ºC/min under air flow (250 ml/min). The weight loss between 200 and 900 °C was attributed to coke burning. Measurements for each sample were repeated at least three times. The results for HZSM-5 zeolite and CuHZSM-5 are 12 wt. % and 6.5 wt. % respectively.

2.5.- Hydrocarbon simulated cold start tests.
The inlet gas composition used for HC adsorption experiments was 100 ppmv propene, 90 ppmv toluene, 1% v/v oxygen, 10% v/v water and Ar balance. CO and CO₂ gases were also incorporated in preliminary studies to see the effect on the HC trap performance. Interestingly, it was observed that catalytic combustion of CO started above 200 °C, temperature at which the TWC is able to carry out its role as catalytic converter. Moreover, neither CO nor CO₂ affected the trap performance of CuHZSM-5 materials. Thus, CST experiments were carried out by using a model gas mixture composed of propene, toluene, oxygen and water vapour. Steam was generated in an auxiliary reactor with temperature control, and was introduced into the main stream using Ar as carrier gas. All gas flows were fixed using mass flow controllers. The experiments were run in a fixed bed reactor (diameter = 0.457 cm; gas flow 30 ml/min; 0.20 g of sample) externally heated and coupled to a Mass Spectrometer. The following signals 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 were also followed during the experiment. It is worth to highlight that only traces of these signals were detected. During the simulated cold start test, the reactor temperature was increased from 30 °C to 600 °C at 50 °C/min, keeping the maximum temperature for 30 minutes. In order to study the zeolites ageing, consecutive cold start tests were performed once the reactor temperature was cooled down. In order to study the catalytic
behaviour of CuHZSM-5, the evolution of CO$_2$ was studied following m/z 28 and 44. It
is observed the increase in CO$_2$ concentration at 550 ºC related to HC combustion (see
Figure S11).

**Figure S11.** Simulated cold start test for CuHZSM-5 zeolite, CO$_2$ evolution.
Conditions: 100 ppmv propene, 90 ppmv toluene, 1% v/v O$_2$, 10% v/v H$_2$O and Ar
balance. GHSV= 10000 h$^{-1}$. Blue line: Temperature evolution, red line: CO$_2$ evolution.

3.- References