

Hydrocarbon Storage on Small-Pore Cu-Zeolite SCR Catalyst

Ashok Kumar, Krishna Kamasamudram and Aleksey Yezerets
Cummins Inc

ABSTRACT

In this study we investigated the interaction of short- and long-chain hydrocarbons (HCs), represented by propene (C_3H_6) and n-dodecane ($n-C_{12}H_{26}$), respectively, with a state-of-the-art small-pore Cu-Zeolite SCR catalyst. By varying HC adsorption conditions, we determined that physisorption was the primary mechanism for some minor HC storage at low temperatures ($< 200^\circ C$), while chemical transformation was involved in more substantial HC storage at higher temperatures ($200-400^\circ C$). The latter was evidenced by the oxygen-dependent and thermally-activated nature of the storage process, and further confirmed by the carbon-rich composition of the deposits.

The nature of HC-derived deposits of different origins and amounts was further probed using the standard SCR reaction at kinetically challenging conditions (at $200^\circ C$), as well by ammonia adsorption/desorption experiments. The resulting observations indicate that the carbonaceous deposits originating from long-chain HCs accumulate solely on the outer surface of the zeolite crystallites, while short-chain HCs can access both the external surface and the pores.

The stored HCs can be readily removed in the form of CO , CO_2 , and H_2O by an oxygen-rich mixture at elevated temperatures or by using NO_2 as an oxidant at lower temperatures.

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1. INTRODUCTION

Zeolite-based catalysts have emerged as a technology of choice for converting NO_x to N_2 in diesel engine exhaust gas using NH_3 as a reductant, via a process called Selective Catalytic Reduction (SCR). It is well known that zeolites can store hydrocarbons (HCs) [1,2,3,4]. Several exhaust gas conditions could potentially lead to the exposure of the SCR catalyst to HCs, for example relatively low exhaust temperatures during extended vehicle idling, cold start conditions, and even DPF regeneration events. In a typical on-highway aftertreatment system, the degraded performance of upstream oxidation catalysts (e.g., DOC) can also lead to HC slip to the downstream SCR catalyst. The stored HCs can have a detrimental effect on the SCR catalyst performance and durability, through HC-poisoning and by creating opportunities for uncontrolled exothermic events in the case of the rapid oxidation of the accumulated HC deposits [1].

The recent discovery of small-pore transitional metal-exchanged zeolite catalysts, which are commonly believed to be immune to the accumulation of long-chain HCs and consequently to poisoning by them, opened an avenue to minimize such catalyst deactivation [1,2,3,4]. However our results, discussed in this paper, indicated that measurable amounts of long-chain HC can store even on small-pore Cu-

zeolite catalysts under certain conditions, having a limited detrimental impact on catalyst performance. This observation led us to revisit the impact of both small and large HCs on small-pore Cu-zeolite SCR catalyst.

In this study, propene (C_3H_6) and n-dodecane ($n-C_{12}H_{26}$) were used as model species for short- and long-chain HCs, respectively, to quantify the HC storage and its impact on the performance of a commercial small-pore Cu-zeolite SCR catalyst under various exhaust gas conditions. Furthermore, the mechanism, location, and the nature of stored HCs were explored.

2. EXPERIMENTAL DETAILS

2.1. Experimental Setup and Conditions

A state-of-the-art small-pore Cu-zeolite SCR catalyst, supported on 300 cpsi cordierite substrate, was used in this study. The zeolite belonged to the structural family of chabazite (CHA), with a pore opening of $3.8\text{\AA}$. A cylindrical sample of 1 inch diameter and 3 inch length was cored from a larger SCR catalyst brick. A wrap made up of quartz material was used to hold the core in the quartz reactor tube. The quartz wrap was treated at $650^\circ C$ for 2 h, prior to the evaluations, in an oven to remove potential carbon-containing

compounds, which can interfere with CO, CO₂, and HC measurements.

The experimental data were collected using a bench flow reactor system with transient measurement capability, the details of which can be found elsewhere [5]. Synthetic exhaust gas was supplied to the catalyst sample at a total flow rate of 26 slpm, resulting in the gas hourly space velocity (GHSV, or more frequently referred as SV) of approximately 40,000 h⁻¹. All the gas lines were temperature-controlled at 190°C in order to avoid the adsorption of H₂O, NH₃, or HCs. Water and n-dodecane were injected into the heated synthetic exhaust gas through fine capillaries connected to Teledyne ISCO pumps. CO₂ was not fed with the simulated exhaust gases in this study to enable quantification of CO₂ produced during HC oxidation. Prior to an experiment, a catalyst core was de-greened in a baseline feed mixture (containing 10% O₂ and 8% H₂O in N₂), at 650°C for 2 h. Composition of reactants and products were analyzed using MKS Multigas 2030 FTIR. Experimental conditions are summarized in the Table (1).

Table 1. Experiment conditions used in this study

Catalyst	1 inch diameter x 3 inch long commercial Cu-zeolite SCR
Sample State	De-greened at 650°C for 2 h in base feed
Base Feed	10% O ₂ and 8% H ₂ O in N ₂ , Space Velocity = 40 kh ⁻¹
HC Storage	n-C ₁₂ H ₂₆ (~1000 ppm C ₁) or C ₃ H ₆ (~1000 – 5000 ppm C ₁) in base feed for 0.5 – 24 h at T=100 – 450°C with 50°C interval
TPO	HC storage temperature to 600°C with 10°C/min Ramp followed by 1 h at 600°C
SCR Reaction	200 ppm NO, 200 ppm NH ₃ at 200°C for 2 h in base feed

When referring to HC storage in this work, we do not imply molecular adsorption of the original species, but rather any combination of their adsorption and reactive transformation, for example via partial oxidation, polymerization, or coking. The amount of HC storage was determined using the sum of the cumulative amounts of HC desorbed, as well as CO and CO₂ evolved during the subsequent temperature programmed oxidation (TPO) experiments. These values were translated into the HC mass loading at the beginning of the TPO experiment, by assuming the C/H stoichiometry of the parent hydrocarbon.

2.2. Experimental Methodology

In order to quantify the HC storage, either long-chain or short-chain HCs were metered at a fixed inlet concentration and at a constant temperature to the reactor for a prescribed

time. This step was followed by the removal of HCs in the presence of oxygen using a temperature programmed oxidation (TPO) up to 600°C with a ramp rate of 10°C/min. For example, as illustrated in Figure 1, 1000 ppm C₁ of n-C₁₂H₂₆ reactant was introduced at 350°C for 1 h. During this step, a small fraction of n-C₁₂H₂₆ was continuously converted to CO and CO₂, while the remaining n-C₁₂H₂₆ could contribute to the HC storage. The storage step was not used for quantifying the amount of HC captured by the catalyst due to a low rate of disappearance, which would lead to a large integral error. Rather, the quantification was based on integrating the amounts of HCs, CO and CO₂, measured during the above TPO step.

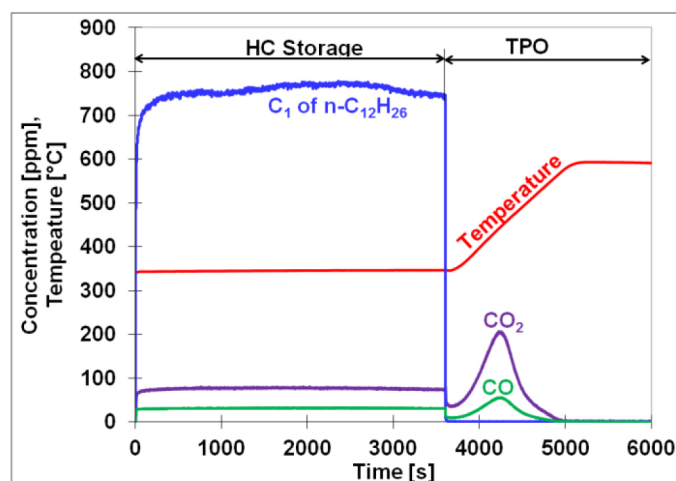


Figure 1. Example of HC storage experiment with 1000 ppm C₁ of n-C₁₂H₂₆ feed at 350°C for 1 h followed by a TPO up to 600°C

3. RESULTS AND DISCUSSION

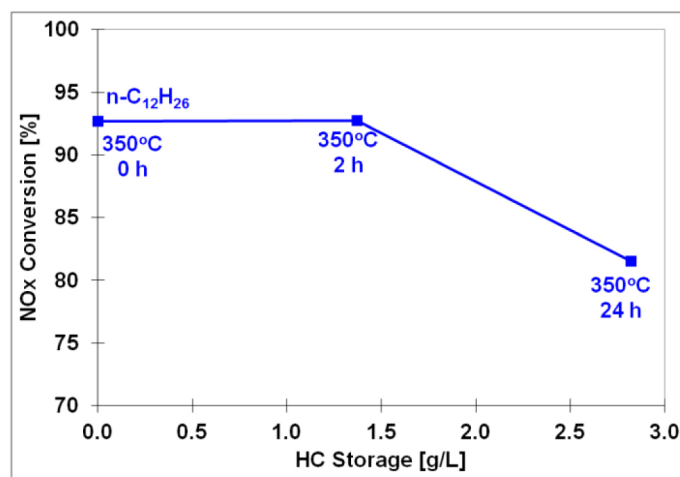


Figure 2. Impact of stored HC, derived from exposure of n-C₁₂H₂₆ at 350°C, on NOx conversion

Steady-state NO_x conversion over Cu-zeolite, before and after n-C₁₂H₂₆ exposure at 350°C for 2 h and 24 h under lean conditions is shown in Figure 2. Contrary to the expectations, NO_x conversion over the catalyst, exposed to this long-chain HC for 24 h, was substantially reduced. Subsequently, significant amount of HCs were found on this catalyst sample. This finding, which will be discussed in further detail in Section 3.1.3, provided an impetus for a systematic study of the mechanism of HC storage and the nature and location of the stored species, which became the focus of this work.

3.1. Long-Chain HC Storage

In the following sections, the process of n-dodecane storage on the small-pore Cu-zeolite SCR catalyst was first investigated by varying parameters such as temperature, time, and presence of oxygen during the storage. Subsequently, the nature of the stored species was considered, based on the kinetics of their adsorption and oxidative removal, their elemental composition, and their impact on such practically important catalyst functions and NH₃ adsorption/release and SCR activity.

3.1.1. Effect of HC Storage Temperature

In the following set of experiments, we have applied the same experimental methodology as described in the previous section, to a broader temperature range. In particular, the HC storage experiment was carried out with 1000 ppm C₁ of n-C₁₂H₂₆ at temperatures between 100 and 450°C for 1 h, and immediately followed by a TPO to quantify the amount of HCs storage (Figure 3a). The total amount of storage featured a bi-modal profile vs. temperature. In the range below ~200°C, the total storage was very low, and declined with increasing temperature. Please note that this trend, albeit not very pronounced on the plot given its scale, was substantially beyond the experimental uncertainty. Also, as evidenced by the TPO, at these temperatures HC storage occurred predominantly without chemical transformations, as the majority of desorbed species consisted of n-C₁₂H₂₆.

At the same time, much larger HC storage was observed at the temperatures above ~ 300°C. It peaked around 350-400°C, due to the high conversion of HC to CO_x (= CO + CO₂) at the elevated temperatures over this catalyst. It is interesting to note that the majority of HCs stored at these conditions have been removed in the form of CO_x, with virtually no molecularly desorbed n-dodecane.

Thus, it appears that at low temperatures very small quantities of n-C₁₂H₂₆ can adsorb molecularly and weakly, presumably via a physisorption on the external surface of the zeolite particles, while at elevated temperatures much larger quantities of dodecane can get stored on this catalyst, presumably via some reactive transformations. In order to better understand the nature of these transformations, we have conducted a series of additional experiments, with the HC exposure temperature being fixed at 350°C, where the largest HC storage was observed.

We would also like to point out here, that the ratio of CO and CO_x (Figure 3b) was virtually identical among all the experiments described in this paper. It hints that similar kind of carbon containing species was stored during HC storage. Further, on a different experiment (not shown here), we observed the onset of CO oxidation above 400°C on this catalyst. Therefore, the ratio, CO/CO_x, measured was not perturbed by CO oxidation.

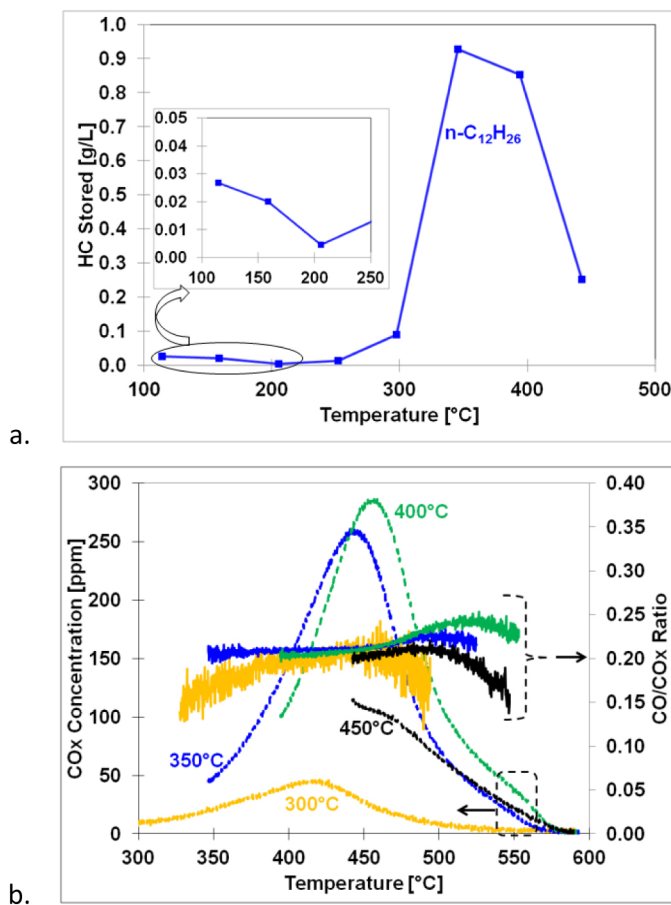


Figure 3. Effect of temperature on HC storage, a. total HC storage with 1000 ppm C₁ of n-C₁₂H₂₆ for 1 h, b. CO_x evolution profiles and CO/CO_x ratio during TPO after HC storage

3.1.2. Effect of O₂ Concentration

In order to verify the impact of potential reactive transformations on the HC storage on this catalyst, the additional set of experiments was performed under inert and oxidizing conditions. In particular, HC storage at 350°C for 1 h was carried out in the presence of 0 and 10% O₂, followed by a TPO. Figure 4a shows that there were no measurable quantities of CO, CO₂ or n-dodecane detected during the TPO after the HC exposure in the absence of O₂. On the other hand, TPO after n-C₁₂H₂₆ exposure in the presence of 10% O₂ (Figure 4b) showed 1.1 g/L of HC storage.