In situ DRIFT study of biodiesel impurities influence on Diesel Oxidation Catalysts surface adsorption properties

Paola Anguita, Jesús Manuel García-Vargas, Sonia Gil, Anne Giroir-Fendler

*Université de Lyon, Lyon, F-69003, France, Université Claude Bernard Lyon 1, Villeurbanne, F-69622, CNRS, UMR 5256, IRCELYON, 2 avenue Albert Einstein, Villeurbanne, F-69622, France.
*Corresponding author: anne.giroir-fendler@ircelyon.univ-lyon1.fr; sonia.gil@ircelyon.univ-lyon1.fr

Abstract: Na, K, Ca-biodiesel impurities impact on surface properties of diesel oxidation catalyst was evaluated by NO-Temperature Programmed desorption (TPD) and Diffuse Reflectance Fourier Transform Infrared Spectroscopy (DRIFTS). To clarify the intermediate species involved in the CO, C₃H₆ and NO reaction mechanism, an in-situ DRIFTS study using NO+O₂ and NO+C₃H₆+O₂ at 250°C was carried. Obtained results showed that the higher and lower C₃H₆ reaction rates of K and Na catalysts is related to the nitrate species interaction with carbonaceous intermediates associated to the NO reduction via SCR-C₃H₆. However, NO reaction rate decreased due to the stronger nitrates adsorption on Ca-poisoned catalyst.

Keywords: Diesel Oxidation Catalyst, in-situ DRIFTS, biofuel impurities effects.

1. Introduction

The more restrictive government regulations for gas emissions from mobile and stationary sources (Euro VI emission standards and CO₂ emissions limits by Kyoto protocol) promoted the continuous improve of existing after-treatment systems and the use of renewable fuels like biodiesel. However, the use of biodiesel as a biofuel, especially B100, expose after-treatment systems to kilograms of impurities (Na, K and Ca), which came from liquid-phase synthesis of biodiesel and automotive lubricant oils. These impurities had an important effect on catalytic performances and durability of current after-treatment systems. Particularly, the CO, hydrocarbon (HC) and NO oxidation capacity of commercial Diesel Oxidation Catalysts (DOCs) can be reduced by biodiesel and lubricant impurities, which is critical parameter to ensure the correct operation of subsequent after-treatment chain. Competitive adsorption of NO, CO and HC and redox properties are one of the most important factors affecting the DOCs catalytic behavior, which could be widely modified by these impurities. Nevertheless, there is relatively few scientific data available that satisfactorily describe the effects of biofuels on catalyst properties and catalytic behavior, which hinders the identification of its reaction intermediates and the design of more efficient DOCs catalysts. Therefore, the main goal of this study is to better understand the biofuel impurities effects on active adsorption sites of DOCs catalysts by in-situ Diffuse Reflectance Fourier Transform Infrared Spectroscopy (DRIFTS) in order to elucidate the reaction pathway induced by current biofuel impurities.

2. Experimental

PtPd/CeZr/La-Al₂O₃ DOCs catalysts, both fresh and poisoned with Na, K and Ca, were synthetized by impregnation and characterized by several techniques: ICP, BET, XRD, TEM, H₂-TPR and XPS. Catalytic tests were carried out using 50 mg of catalysts and a reactant mixture containing [NO] ≈ 500 ppm, [CO] ≈ 300 ppm, [C₃H₆] ≈ 300 ppm, [CO₂] ≈ 5 vol.%, [O₂] ≈ 10 vol.%, [H₂O] ≈ 3.5 vol.% and He as carrier gas (GHSV = 135000 h⁻¹). Temperature was increased and decreased by a ramp of 5°C min⁻¹ from 80°C up to 600°C. Moreover, in order to better understand the effects of biofuel impurities on surface catalyst properties, the adsorption/desorption on fresh and poisoned catalysts was studied separately by use of TPD and DRIFTS. To further clarify the mechanism of such a heterogeneous reaction, an in-situ DRIFTS investigation was carried using NO+O₂ and NO+C₃H₆+O₂ as gas mixtures at 250°C.

3. Results and discussion

Firstly, three desorption peaks were detected by NO-TPD analyses for the fresh catalyst, while only two desorption peaks at slightly higher temperatures were found in presence of Na, K and Ca impurities, being the NO desorbed amount higher in the case of Ca-poisoned catalyst. These results evidenced the
modifications of NO adsorption active sites by biofuel impurities. Besides, DRIFTS spectra obtained after NO adsorption for the fresh and poisoned catalysts showed the formation of new adsorption sites after addition of alkali impurities, which could be related to the basic character of these species; in agreement with the higher NO desorption temperatures and NO desorbed found by NO-TPD. In addition, adsorption at 250°C of NO+O2/He and NO+C3H6+O2/He (Figure 1) mixtures were evaluated. The formation of NO2 in the gas phase during NO+O2 exposure promoted the formation of nitrates adsored species, especially when alkali impurities were present, due to its electron-donor role that increase interaction with NO, according to their modified redox properties (not shown). Otherwise, in presence of propene, acetate and formate species were formed on catalysts surface, which are intermediates on C3H6 oxidation. Furthermore, isocyanate and cyanide bands were found, as an evidence of interaction between propene surface species and nitrates, involved in the NO2 reduction by propene4. In agreement with our previous catalytic results5, the intensity of the bands associated to the carbonaceous intermediate species was lower in the case of Na-poisoned catalyst than that of the fresh catalyst, as lower was the C3H6 reaction rate found on catalytic tests for this catalyst (Table 1). On the contrary, K-poisoned catalyst evidenced a higher intensity of intermediate species bands related with NO reduction via SCR-C3H6. However, in the case of Ca-poisoned catalyst the lower NO reaction rate seems to be more related to the higher adsorption strength of nitrate species than existent carbonaceous intermediates for C3H6 oxidation.

Table 1. Catalytic activity results (*mol gcat-1 s-1)·105).

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Reaction rate* C3H6 (210°C)</th>
<th>Reaction rate* NO (250°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PtPd</td>
<td>4.318</td>
<td>6.015</td>
</tr>
<tr>
<td>0.5% K - PtPd</td>
<td>9.059</td>
<td>5.052</td>
</tr>
<tr>
<td>1.6% Na - PtPd</td>
<td>0.296</td>
<td>2.408</td>
</tr>
<tr>
<td>1.5% Ca - PtPd</td>
<td>9.354</td>
<td>1.705</td>
</tr>
</tbody>
</table>

4. Conclusions

NO-TPD and DRIFTS spectra allowed to elucidate the creation of new adsorption sites of NO in form of nitrates on alkali-poisoned catalysts, which confirm that the biofuel impurities had a significant effect on catalyst active adsorption sites. Moreover, the modified pathway reactions involved on poisoned-DOCs catalysts were revealed, including: 1) the higher formation of nitrate surface species compared to the fresh catalyst, which is the main reason of the lower NO reaction rate of Ca-poisoned catalyst; 2) the formation of acetate and formate intermediates associated to the C3H6 oxidation and 3) the possible interaction between formed isocyanate/cyanide and nitrate surface species involved on NO reduction via SCR-C3H6, which was higher in the case of K-poisoned catalyst than Na-poisoned catalysts, which explain their higher propene conversion in detriment of NO oxidation to NO2.

References