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

Paola Anguita,[a] Jesús Manuel García-Vargas,[a] Sonia Gil,[a*] Anne Giroir-Fendler[a*]

[a]*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, C_3H_6 and NO reaction mechanism, an in-situ DRIFTS study using $NO+O_2$ and $NO+C_3H_6+O_2$ at 250ºC was carried. Obtained results showed that the higher and lower C_3H_6 reaction rates of K and Na catalysts is related to the nitrate species interaction with carbonaceous intermediates associated to the NO reduction via SCR-C_3H_6. 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 CO_2 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[1]. These impurities had an important effect on catalytic performances and durability of current after-treatment systems[2]. 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-Al_2O_3 DOCs catalysts, both fresh and poisoned with Na, K and Ca, were synthetized by impregnation[3] and characterized by several techniques: ICP, BET, XRD, TEM, H_2-TPR and XPS. Catalytic tests were carried out using 50 mg of catalysts and a reactant mixture containing $[NO] \approx 500$ ppm, $[CO] \approx 300$ ppm, $[C_3H_6] \approx 300$ ppm, $[CO_2] \approx 5$ vol.%, $[O_2] \approx 10$ vol.%, $[H_2O] \approx 3.5$ vol.% and He as carrier gas (GHSV = 135000 h^{-1}). Temperature was increased and decreased by a ramp of 5ºC min^{-1} from 80ºC up to 600ºC. 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 $NO+O_2$ and $NO+C_3H_6+O_2$ as gas mixtures at 250ºC.

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 250ºC of $NO+O_2/He$ and $NO+C_3H_6+O_2/He$ (Figure 1) mixtures were evaluated. The formation of NO_2 in the gas phase during $NO+O_2$ exposure promoted the formation of nitrates adsorbed species, especially when alkali impurities were present, due to its electro-donator 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 C_3H_6 oxidation. Furthermore, isocyanate and cyanide bands were found, as an evidence of interaction between propene surface species and nitrates, involved in the NO_x reduction by propene[4]. In agreement with our previous catalytic results[5], 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 C_3H_6 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-C_3H_6. 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 C_3H_6 oxidation.

Table 1. Catalytic activity results (*(mol g_{PGM}^{-1} s^{-1})·10^5).

Catalyst	Reaction rate* C_3H_6 (210ºC)	Reaction rate* NO (250ºC)
PtPd	4.318	6.015
0.5% K - PtPd	9.059	5.052
1.6% Na - PtPd	0.296	2.408
1.5% Ca - PtPd	9.354	1.705

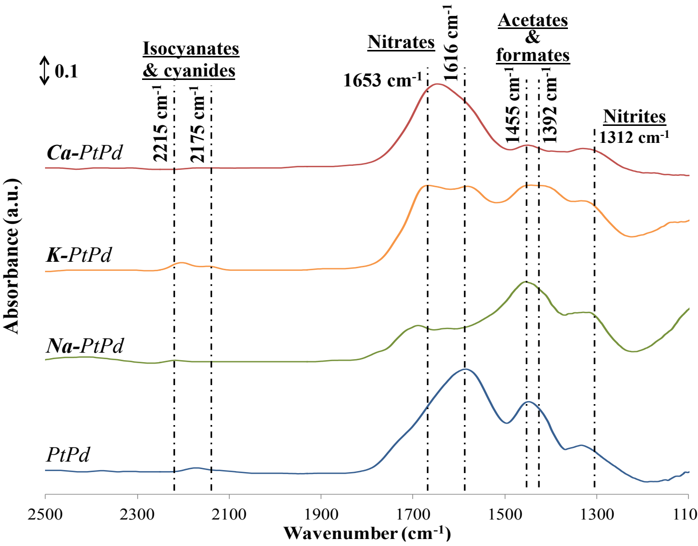

Figure 1. DRIFT spectra of adsorbed species in following $NO+C_3H_6+O_2$ at 250ºC.

4. Conclusions

NO-TPD and DRIFT 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 raison of the lower NO reaction rate of Ca-poisoned catalyst; 2) the formation of acetate and formate intermediates associated to the C_3H_6 oxidation and 3) the possible interaction between formed isocyanate/cyanide and nitrate surface species involved on NO reduction via SCR-C_3H_6, 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 NO_2.

References

1. G. Cavataio, H. Jen, D. Dobson, J. Warner, SAE Technnical Paper, 2009-01-2823 (2009).
2. M. Lance, A.Wereszcack, T. Topps, R. Ancimer SAE Int. J. Fuels Lubr. 9 (2016) 683-694.
3. M. Haneda, K. Suzuki, M.Sasaki, H. Hamada, M. Ozawa, Appl. Catal. A 475 (2014) 109-115.
4. X. Auvray, L. Olsson, Appl. Catal. B 168 (2015) 342-352.
5. P. Anguita, J.M. García-Vargas, F. Gaillard, E. Iojoiu, S. Gil, A. Giroir-Fendler, Appl. Catal. B (2017) (submitted).