ISGC 2019
May 13th - 17th

N°798 / PC
TOPIC(s) : Industrial chemistry / Chemical engineering

Elimination of coke in an aged hydrotreating catalyst via non-thermal plasma process

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PURPOSE OF THE ABSTRACT

Elimination of coke in an aged hydrotreating catalyst via non-thermal plasma process
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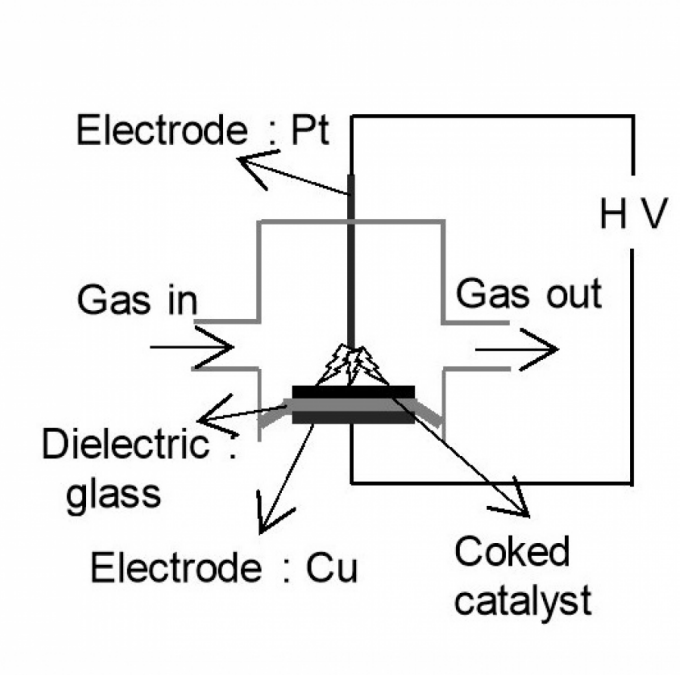
The hydrodesulfurization (HDS) process is one of the most important processes used in a refinery to remove sulfur-containing compounds due to worldwide environmental policies and the requirement to limit the sulfur content in gasoline and diesel fuels at 10 ppm. The most widely employed catalyst for hydrodesulfurization process is cobalt-molybdenum supported on alumina after a sulfidation step leading to the formation of the so-called ?CoMoS active phase? where cobalt is decorating the edges of MoS2 slabs [1]. Despite efforts made, the catalyst deactivation, due to coke accumulation in the pores of the catalyst, is a problem of great and continuing concern. The most widely used method for catalyst activity recovery is the oxidative regeneration using diluted air. The experimental conditions used were optimized and particularly in terms of temperature as it must not exceed 500°C, however the formation of crystallized species known to be refractory to sulfidation, such as CoMoO4 or CoAl2O4 is often observed [2]. As a result the removal of coke deposits using a classical oxidation treatment only leads to partial restoration of activity to a level of 70-90% when a level of more than 95% is required.

Consequently there are needs to propose new strategies to perform catalyst regeneration. Among alternative processes, we showed that non-thermal plasma was successfully used to regenerate completely a coked zeolite at room temperature with a low energy consumption [3]. In the present study the removal of coke from an aged industrial hydrodesulfurization catalyst, was investigated, which to the best of our knowledge has never been reported before.

The aged catalyst was introduced into the plasma reactor as a thin wafer, using DBD non-thermal plasma with a pin to plate geometry (Fig1). After 130 minutes of plasma treatment, with P=30W, 70% of coke was removed while more than 40% of sulfur was still present. Characterizations of catalyst at different location of the wafer show that coke was more easily removed at the center, closed to the pin electrode where the electric field is more intense. The Raman analysis performed at the center of the wafer after 130 minutes of plasma treatment (30W) exhibits fluorescence, while the characteristic bands of carbon structure D-band(1350 cm-1) and G-band (1600 cm-1) are visible at the periphery of the disk, confirming that carbon is more easily removed at the center of the wafer. The presence of CoMoO4 phase has not been observed by XRD analysis while the formation of an unexpected phase was highlighted. It corresponds to the family of Keggin HPA PMo12O40 3-, which could be an interesting precursor of catalyst for HDS process. These results show that plasma treatment under an oxidant media could be an interesting alternative regeneration method of the coked HDS catalyst.

FIGURES



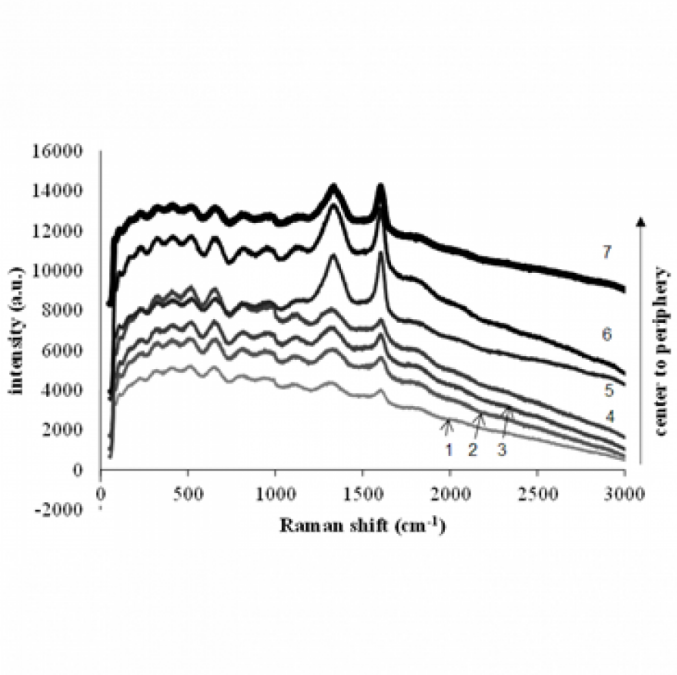


FIGURE 1
Pin to plate DBD reactor

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FIGURE 2
Raman spectra of the catalyst at different location of the wafer, after plasma treatment

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KEYWORDS
Non thermal Plasma | Hydrotreating Catalyst | Catalyst Regeneration | coke

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