

### ASSOCIATED CONTENT

Figure SM-1. XRD studies of spent catalyst used in acid pH (that determined by the presence of MAc and FAc)

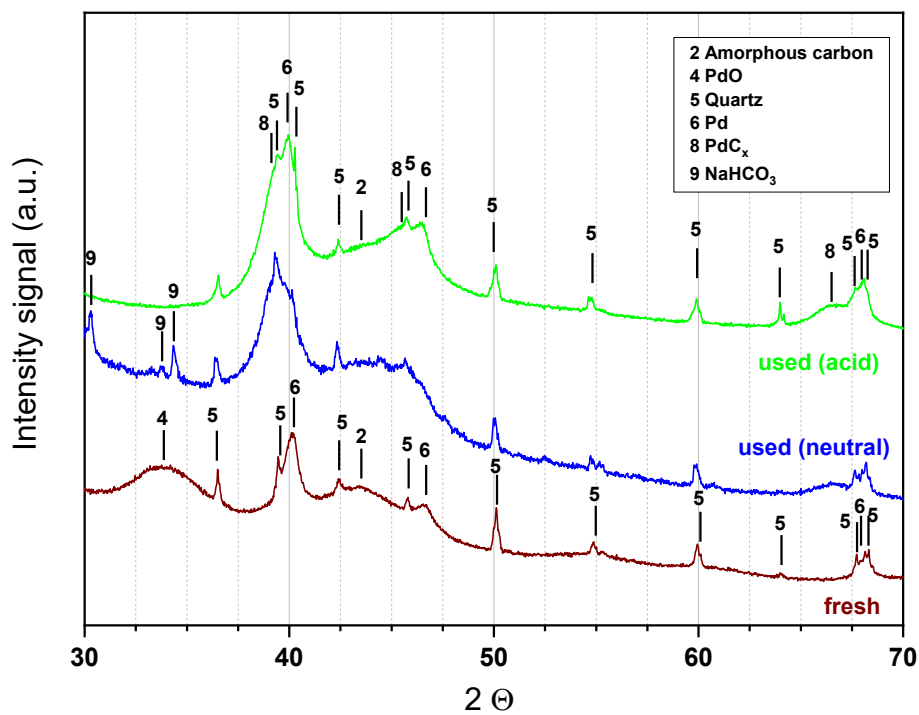


Figure SM2.

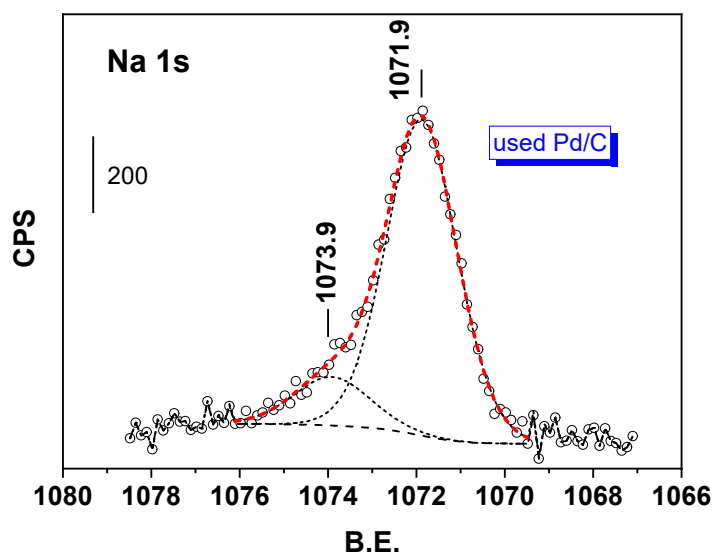


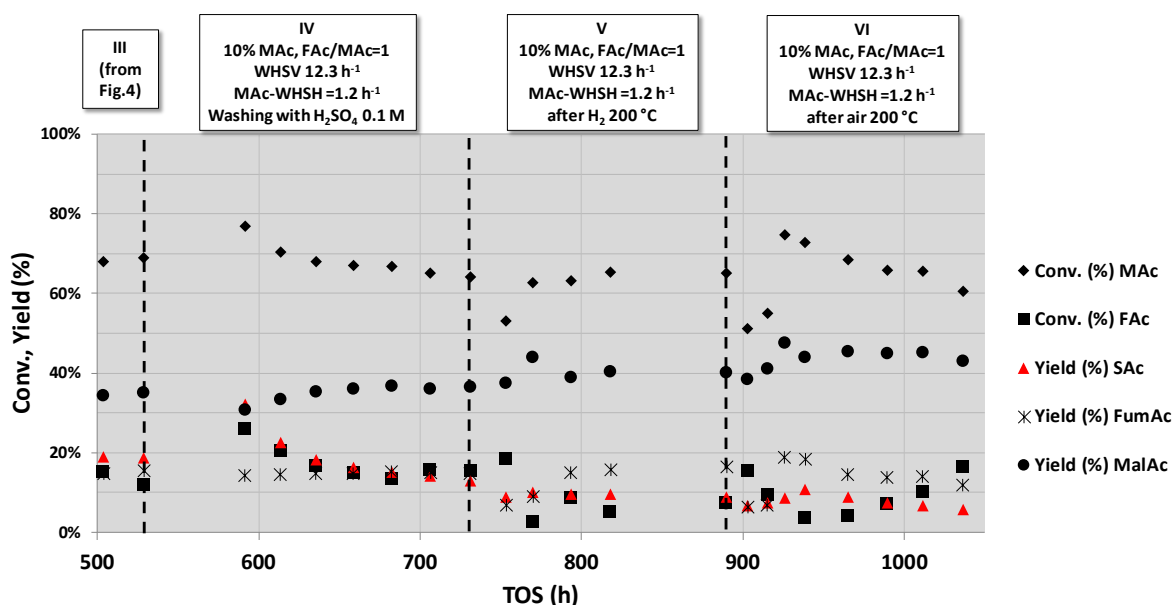
Figure SM2. Na 1s core level of the used catalyst (used catalyst corresponds to that downloaded after the period VI of Figure 1).

**Figure SM-3. Attempts of regeneration on the catalyst used with acid medium.**

Figure SM-3 summarises the investigation regarding the attempts to regenerate the spent catalyst used with MAC and FAc under natural pH. Similar treatments to those described for the catalyst used with neutralized feedstock were tried. The experiments actually were conducted after the period III represented in the Figure 4, that is why the periods of this figure goes from IV to VI.

- H<sub>2</sub>SO<sub>4</sub> 0.1 M treatment

The results under the heading of period IV represent the catalytic performance of the catalyst after being treated overnight with 0.1 mL/min<sup>-1</sup> of H<sub>2</sub>SO<sub>4</sub> 0.1 M at 100 °C (before and after flowing the sulfuric acid solution, H<sub>2</sub>O was flown until the solution collected was at neutral pH). This is a similar treatment to that used in Figure 10 but using more concentrated H<sub>2</sub>SO<sub>4</sub> (0.1 M vs. 0.01 M) and higher temperature conditions (100 °C vs. 50 °C). The Figure SM-3 shows a transient recovery of the activity at the beginning of period IV, that is also translated to the SAc yield, varying from 15 % at the end of period III to 32 % at the beginning of period IV. Apparently, this rinsing treatment removes, or refresh, some acid sites. Anyway, this regeneration is very limited and the MA yield is still very far from that achieved with the fresh catalyst before the accelerated deactivation during period II in Fig. 4 (80 % vs. 32 %). Moreover, this recovery is very short and the catalyst, again, continuously deactivates (following the trend of the period III of Fig. 4), reaching a SAc yield close to 15 % after 202 h on stream. In conclusion, using higher concentrated H<sub>2</sub>SO<sub>4</sub> and higher temperature regeneration conditions than those applied to the neutralised case did not result in a significant



**Figure SM-3.** Effect on catalytic properties of treatment intended at regenerating the catalytic (periods IV, V and VI). The experiment is the continuation of Fig. 4, consequently the period III visible at the beginning of the Fig. represents the final period III of Fig. 4. Common reaction conditions: catalyst loading 0.1 g, pressure = 1.01 MPa, 10 wt % MAC, T = 150 °C and mol FAc/MAC = 1.

regeneration of the catalyst either.

- H<sub>2</sub> treatment (period V)

Once the period IV was over, the catalyst was subjected to a treatment with a H<sub>2</sub> flow (period V). The details of this treatment were those described previously for the Figure 11. During this period, the SAc yield (red triangles data) was quite similar to that observed at the end of period IV, confirming the lack of performance of the H<sub>2</sub> treatment to reactivate the spent catalyst.

- O<sub>2</sub> treatment (period VI)

After this period V, the catalyst was subjected to a mild calcination treatment under air (the details of the treatment are those given when discussing the figure 1). The results of this period VI clearly show that the calcination under air did not result either in the regeneration of the catalyst.

Figure SM-4. XRD studies of catalyst used with neutralised acid feed and after treatment with air and H<sub>2</sub> (reflections marked as 5 are for quartz, 6 are for Pd<sup>0</sup> and 8 for PdC<sub>x</sub>)

When discussing these XRD, we will focus on the Pd reflections, marked as 6 (Pd<sup>0</sup>) and 8 (PdC<sub>x</sub>) in the patterns. The rest of the reflections have been discussed in the main article. Both treatments result in the increase of the intensity of the Pd<sup>0</sup> peaks at the expense of the removal of the PdC<sub>x</sub> ones (8). Interestingly, PdO reflections were also detected in the O<sub>2</sub> treated sample.

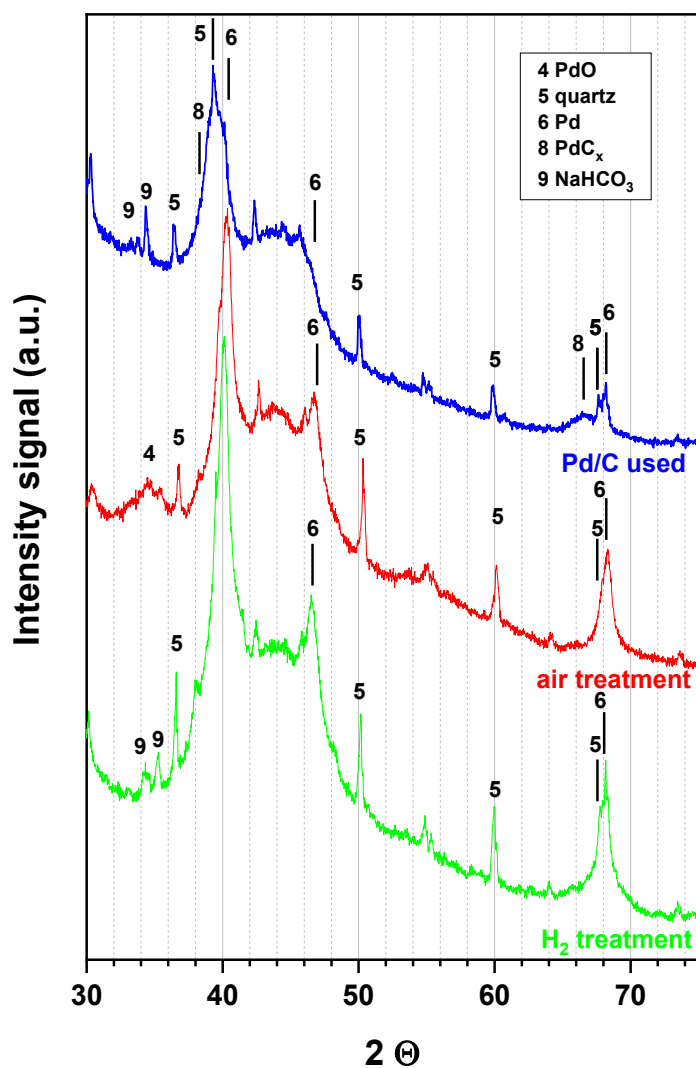
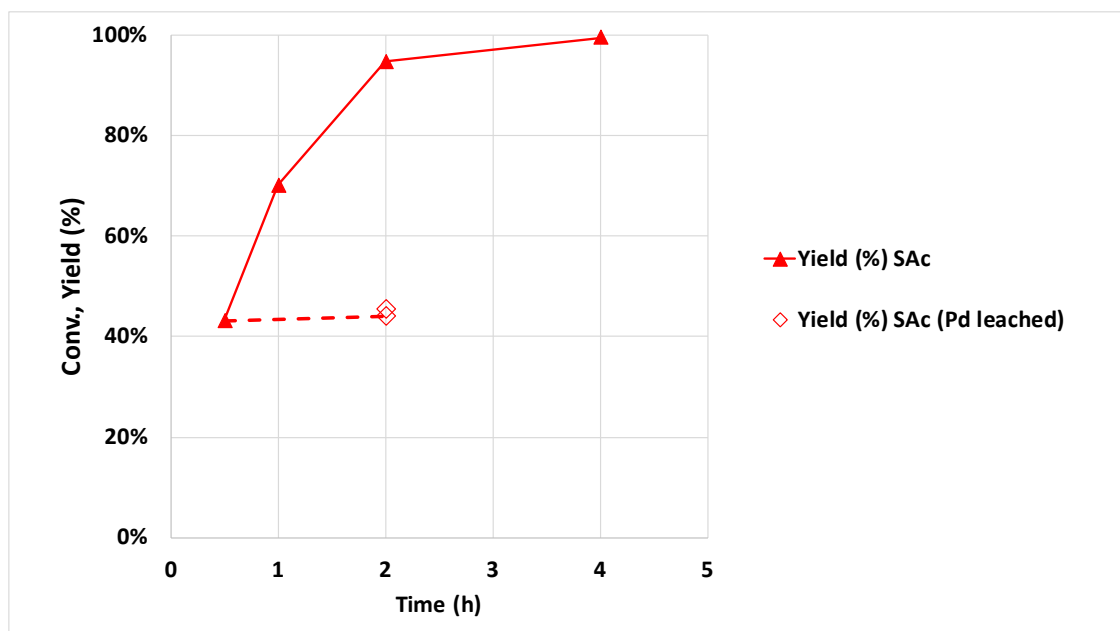


Figure SM-5. Kinetics of formation of SAc conducted in a batch reactor (full red triangles) and contribution of Pd species leached to the reaction mixture (empty red diamond). Reaction conditions: 5 wt% of MAc, 1 wt. % of catalyst, mol FAc/MAC = 1, 10 bar of N<sub>2</sub>, 150 °C.



The red full triangles in the Figure SM-5 represent the kinetic of formation of SAc under the reaction conditions indicated in the caption. The red empty diamonds are the catalytic activity obtained after 0.5 h of reaction with the solid and once the solid was removed from the reaction mixture and the liquid filtrate put back in the reactor, is additionally subjected to 1.5 h under the same reaction conditions (overall reaction time = 2 h). Two repetitions of the same experiment were conducted. It is clearly seen that the yield of SAc so obtained does not increase with respect to that obtained with the solid catalyst after 0.5 h of reaction, demonstrating that the homogeneous contribution of the Pd species leached to the liquid phase is negligible compared to the heterogeneous contribution coming from the solid Pd/C catalyst.

The chemical analysis of Pd leached to the reaction mixture after the first 0.5 h of reaction was found to be < 0.1 mg/L. This is quite a low Pd concentration what explains the negligible homogeneous contribution of leached Pd species.

(Only for comparison purposes and assuming that the concentration of Pd leached in the downstream reaction mixture of Figure 3 (acid case) is 0.1 mg/L and considering that ca. 8 L of solution was flown through the reactor, around 0.8 mg of Pd can be assumed to be removed from the catalyst at the end of the experiment of Figure 3. This represents 16 % of the Pd initially loaded in the reactor. Although lower than that determined by chemical analysis comparing both the fresh and used catalyst of Figure 3 (58 % of Pd leaching), is still in the same order of magnitude. We have to bear in mind that larger MAc and FAc concentration and higher temperatures than that of Figure SM-5 were used in some periods of Figure 3, so larger leaching rates should be expected for Figure 3 experiments).