

# Modification of catalyst supports: phosphate and malonic acid adsorption on $\gamma$ - $\text{Al}_2\text{O}_3$

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The first preparation step of a hydrotreating catalyst consists in the deposition of metallic precursors in solution onto a solid support,  $\gamma$ - $\text{Al}_2\text{O}_3$ . This mandatory impregnation step is known to be crucial for the final catalytic activity as the support plays an important role on the surface speciation of active species precursors. Indeed, due to its pH buffer effect, it modifies the impregnation solution speciation and it can also be dissolved and react with metallic precursors in solution [1]. Industrially, inorganic or organic dopants such as phosphorus or malonic acid are used to enhance the catalytic performance: they can be added before, during or after the impregnation step. In order to rationalize the impact of pre-impregnated dopants on  $\gamma$ - $\text{Al}_2\text{O}_3$  on the catalytic activity, it is first necessary to determine precisely their adsorption modes and their anchoring surface sites on the surface. Hence, a modification by adsorption of phosphorus and malonic acid at different loadings has been performed and the surface chemistry was finely characterized by a multi-technique approach and modelled using a  $\gamma$ - $\text{Al}_2\text{O}_3$  solid/liquid interface model [2].

With an increasing phosphorus coverage, the isoelectric point IEP (electrokinetic measurements) shifts towards lower values, characteristic of a covalent adsorption. This information on the surface charge combined to the identification of the surface sites involved (FTIR) allows us to model the surface complexes formed and highlights a two steps adsorption process. First, at low phosphorus coverage ( $< 1.3$  at  $\text{P}/\text{nm}^2$ ), a monodentate complex adsorbs on  $\mu_1$ - $\text{Al}_\text{IV}$ -OH (110). Once all these surface sites are consumed by the formation of the complex, a precipitation process occurs at higher coverage (Figure 1A). Regarding the malonic acid adsorption, a singular behaviour is put in evidence by the electrokinetic measurements. Indeed, a plateau is observed indicating a neutralization of the surface charge by the covalent adsorption of a neutral complex. In a complementary way, IR spectroscopy was used to determine the complex geometry and adsorption sites involved. Finally, a surface complexation model was built to fit the neutralization plateau and determine the surface complex and the adsorption sites involved (Figure 1B).

The good agreement with the experimental data provides valuable information which will allow a better understanding of the impact of a modified surface on the speciation of metallic precursors during impregnation and finally, on the catalytic activity.

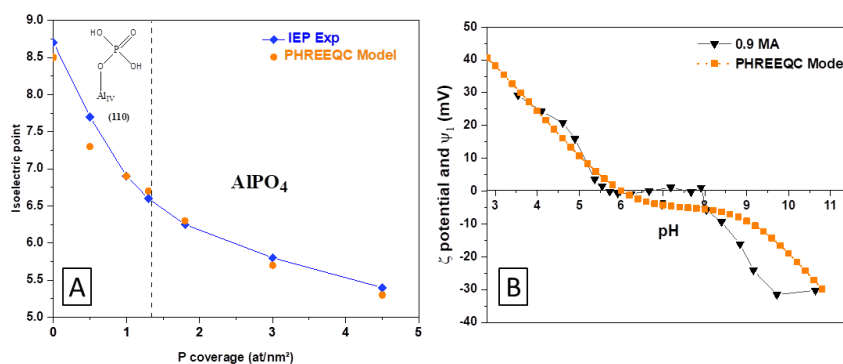


Fig. 1. (A) Evolution of the IEP as a function of phosphorus content (at/nm<sup>2</sup>) for monodentate complex adsorption and surface precipitation adsorption involving  $\mu_1$  sites on (110) alumina facets compared to experimental data. (B) Evolution of the  $\zeta$  potential as a function of pH for alumina modified by malonic acid compared to experimental data

## Reference :

[1] X. Carrier, J. F. Lambert, M. Che. J. Am. Chem. Soc. 119, 10137-10146 (1997)

[2] M. Corral Valero, B. Prelot, G. Lefèvre, Langmuir 35, 12986-12992 (2019)