

# HIGHLY POROUS HYBRID ZIRCONIUM PHOSPHONATES BY NON-HYDROLYTIC SOL-GEL METHODS

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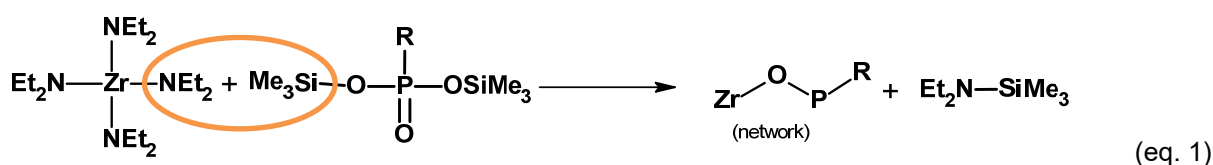
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## ABSTRACT:

Organic-inorganic hybrid materials are attractive heterogeneous catalysts and catalyst supports.<sup>1</sup> They combine the inorganic network stability with properties brought by the organic building blocks, i.e., controlled hydrophobicity, and improved hydrothermal stability. The combination of such a hybrid with catalytically active metal may lead to successful catalyst material.<sup>2</sup> Zirconium phosphonates are promising Lewis acidic catalysts, but their conventional preparation (hydrothermal methods) yield usually microporous layered structures.<sup>3</sup> Non-hydrolytic sol-gel process can be applied to obtain amorphous mesoporous 3D structures.<sup>4</sup>

We proposed a synthetic route to zirconium phosphonates based on the reaction of Zr dialkylamides with trimethylsilyl phosphonates (eq. 1)<sup>2</sup> with both terminal and bridging organic groups (Me, <sup>t</sup>Bu, Ph, ethylene, phenylene, xylylene). The nature of organic substituents in phosphonates played a significant role in final product porosity. The surface area reached up to 700 m<sup>2</sup> g<sup>-1</sup>. Pore sizes were usually in the mesoporous range (2.5 nm) even without templates. The degree of condensation ranged from 65 to 85 %. Thus, there were still ~25 % of residual reactive groups on the xerogel surface available for post-synthetic grafting.

Structure and acidity of zirconium phosphonates were thoroughly characterized by solid-state NMR spectroscopy. The high atomic homogeneity was verified by IR spectroscopy and STEM-EDS. The degree of condensation was determined gravimetrically and by TG-DSC. ICP-OES confirmed the Zr:P ratios, which were ranging from 0.5 to 1. Catalytic activity of Zr sites was confirmed in a batch mode on a model reaction: aminolysis of styrene oxide.



## References

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