New insights on the interaction of trimethylphosphine oxide with zeolite acid sites

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Introduction

³¹P NMR chemical shifts of trimethylphosphine oxide (TMPO) have been suggested as reliable and practical acidity scale for solid acid catalysts.¹ Such conclusion arises from two established ideas: i) the interaction of TMPO with Brønsted and Lewis acid sites, gives rise to ³¹P chemical shifts in distinct ranges; ii) the ³¹P chemical shifts of TMPO interacting with Brønsted acid sites is directly proportional to its acid strength, i.e. higher ³¹P chemical shifts indicate higher acid strength. We have pointed out previously that the ³¹P chemical shift range of TMPO-adsorbed materials is more complex than what has been previously reported. For example, we have shown that the interaction of TMPO with H-[B]ZSM-5 Brønsted and Lewis acid sites, result in ³¹P chemical shifts within the same range.³ Recently, we proposed that the ³¹P chemical shift range assigned to the interaction of TMPO with Brønsted acid sites, encode information beyond acid strength, including the stabilization of neutral (TMPO−H) and (TMPOH) ions pairs, whose amount and geometry depends on the pure structure.³ In this work, we try to disentangle possible ³¹P chemical shift assignments by carefully loading known amounts of TMPO onto H-ZSM-5 zeolites, using 1D and 2D solid-state NMR experiments combined with DFT computational methods.

Results

Effect of TMPO-loading

Figure 2. ³¹P high-power decoupling (HPDEC) and cross-polarization (CPMAS) NMR spectra of HZSM-5 samples loaded with 2 mg of TMPO before and after being exposed to air moisture. 2D ³¹P-¹H HETCOR MAS NMR data can be used to provide an unambiguous assignment of the ³¹P resonances.

Conclusions

Three ³¹P resonances at 88, 77 and 65 ppm are assigned to TMPO interacting with Brønsted acid site. Each chemical shift reflects a distinct degree of protons transfers, i.e. acid proton is closer to TMPO and farther from the zeolite framework.

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References


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