Spectroscopic characterization of supported rhenium oxide catalysts for olefin metathesis: effect of additives.

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Olefin metathesis is a reaction which finds very important industrial applications in petrochemical intermediates, polymers and specialty chemicals [1]. Among the heterogeneous catalysts, rhenium oxide dispersed over γ–alumina (Re_2O_7/Al_2O_3) proved to be very interesting, due to the high activity and selectivity under mild reaction conditions. Nevertheless, the catalytic activity increases quasi-exponentially with the rhenium content and is unfortunately very low at low coverage. A promising route to improve the catalytic performance in the region of low rhenium loadings is the incorporation of other metal oxide as additives (such as V_2O_5, MoO_3 and WO_3 [2]). We observed a similar catalytic improvement pre-treating the γ–Al_2O_3 support with a transition metal chloride ($TiCl_4$, $FeCl_3$).

In order to clarify the interaction of rhenium oxide with the support, we investigated the effect of additives on supported rhenium oxide catalysts. Comparing the FT-Raman spectra of the Re_2O_7/Al_2O_3 catalyst with and without additives, similar isolated monografted tri-oxo species were evidenced in both cases. Otherwise, in the modified Re_2O_7/Al_2O_3 catalyst a slight increase in the Re=O stretching barycentre toward higher frequencies was observed (fig. 1), indicating a reinforcement of the Re=O bond and reflecting an increase in acidity of the Re^{VII} centres.

With the aim of confirm this evidence, the catalysts were characterised by FT-IR spectroscopy of adsorbed pyridine, one of the most commonly used probe molecule to study the surface acidity of heterogeneous catalysts [3]. A further increase in surface Lewis acidity with respect to the unmodified Re_2O_7/Al_2O_3 catalyst was in fact observed (fig. 2), confirming the determining role of Lewis acidity in promoting the catalytic activity of surface rhenium sites.

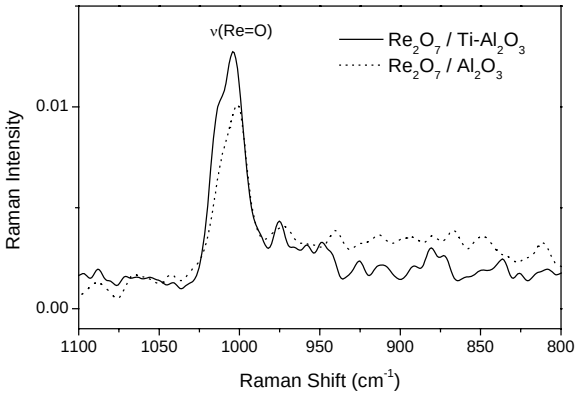

Fig. 1 – FT-Raman spectra.

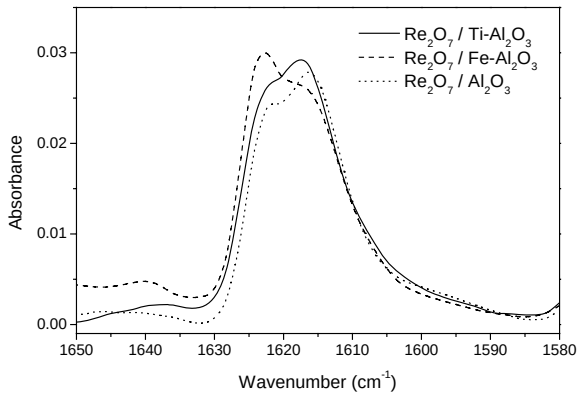

Fig. 2 – FT-IR spectra of adsorbed pyridine.

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