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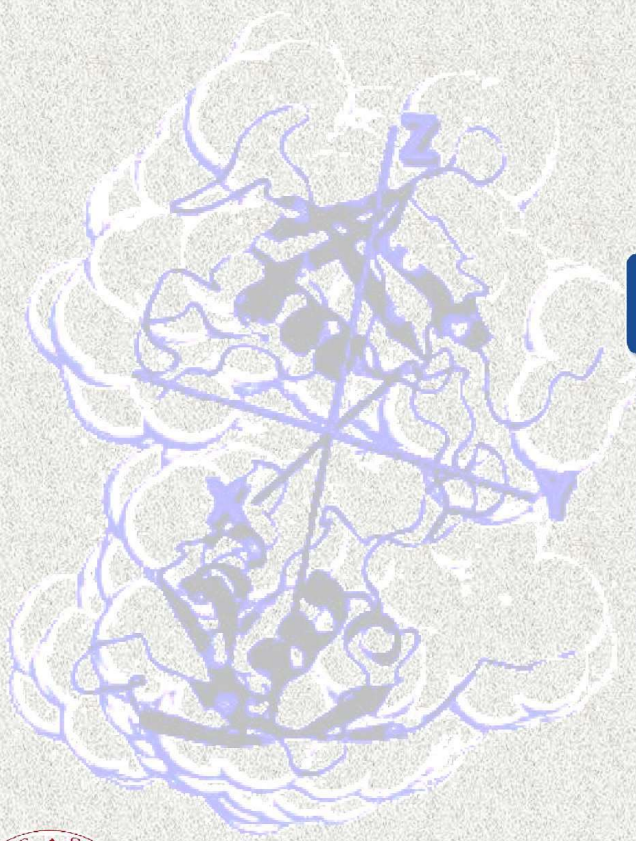

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SELECTIVE HYDROGENATION OF 2-METHYL-3-BUTYN-2-OL ON Pd CATALYSTS

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In the frame of the heterogeneous catalysis, it is well known that size and shape effects play a primal role in driving activity and selectivity [1] and sometimes in giving structure-sensitive reactions [2]. Recently, *Crespo-Quesada et al.* [3] reported that the 2-methyl-3-butyn-2-ol (MBY) selective reduction on palladium is strongly influenced both by the metal planes – namely, {100} and {111} – and by the reaction site topologies involved in the hydrogenation while the adsorption energies drove the catalytic kinetics. In fact, triple to double-bond reduction seemed to occur four times faster on surface sites with respect to edge or corner sites. Conversely, double to single-bond reduction seemed to occur almost exclusively on edge sites. Moreover, {100} and {111} planes would seem to be more active in the triple-bond and double-bond hydrogenation, respectively. In order to understand and, hopefully, drive these structure-sensitive effects Density Functional Theory (DFT) calculations were performed. A Pd_{30} cluster was employed as the model for the catalyst. This was cut from a *fcc* palladium fragment, to obtain both (100) and (111) faces (see Figure 1). Different sites and binding modes were considered to describe either the MBY or 2-methyl-3-buten-2-ol (MBE) interaction and hydrogenation, occurring on the palladium surface. Kinetic studies on MBY and MBE hydrogenation over the Pd_{30} cluster showed very close activation energy values, irrespective of the surface species considered. On the contrary, the MBY and MBE adsorption energies on the different sites of the palladium faces and the corresponding structural changes were peculiar to the different adsorbed species and plane sites and could be easily connected to the activation of the unsaturated bonds hence to the reactivity of the differently adsorbed species. These results, finally, confirmed the already claimed structure sensitivity of the title reaction and, moreover, the higher reactivity of MBY with respect of MBE, which was also observed [3].

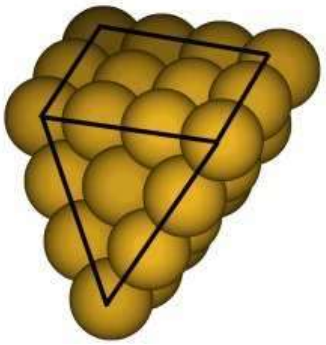

Figure 1. Pd_{30} cluster, showing both the (100) and (111) faces

[1] Duca, D.; Barone, G.; Varga, Zs. *Catal. Letters*, **2001**, *72 (1-2)*, 17–23.
[2] Bond, G. C. *Metal-Catalysed Reaction of Hydrocarbons*, Springer NY, 2005.
[3] Crespo-Quesada, M.; Yarulin, A.; Jin, M.; Younan, X.; Kiwi-Minsker, L. *J. Am. Chem. Soc.*, **2011**, 133 *(32)*,12787–12794.