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Cyclohexanone oxidation over Dawson polyoxometalate catalysts in the presence of the hydrogen peroxide

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Hydrogen peroxide, powerful oxidant, besides being easy to handle compared to molecular oxygen and air, is also known for its clean environment because of its reduction leading only to the water formation. In organic synthesis, H_2O_2, was used in the Baeyer-Villiger reaction and the alkenes epoxide in the presence of harmful solvents as chloroform and acetonitrile and charge transfer agents as cetylpyridinium bromide or chloride. In this work, H_2O_2 was used for the cyclohexanone oxidation at 90°C, without solvent addition and in the presence of Dawson type polyoxometalates (POMs) as formula α- and β-$K_6P_2W_{18}O_{62}$ (α- and β-P_2W_{18}), α-$K_6P_2Mo_6W_{12}O_{62}$ ($P_2Mo_6W_{12}$) and α-$K_7P_2Mo_5VW_{12}O_{62}$ ($P_2Mo_5VW_{12}$). The observed reaction products are adipic (A), glutaric (G), succinic (S), levulinic (L), 6-hydroxyhexanoic (HH), methoxy-6-oxohexanoic (MOH) acids and unidentified products (X). The catalytic results showed that the cyclohexanone conversion is very high (94-99%), whatever the POM composition. The distribution and selectivity of the products are sensitive to both composition and the symmetry of the POM. Thus, α-P2W18 mainly favors the formation of adipic acid (45% of selectivity) and β-P_2W_{18} to that of 6-hydroxyhexanoic acid (74% of selectivity). $P_2W_{12}Mo_6$ is the most selective to adipic acid (59% of selectivity) and $P_2W_{12}Mo_5V$ to levulinic acid (54% of selectivity). In the cyclohexanone oxidation, the high activity of the POM may be due to the role played by H_2O_2. The latter would behave as a precursor of peroxo-POM species, generated by the reaction of POM with hydrogen peroxide. These species could be the active species for the formation of carboxylic acids.