Green process of adipic acid synthesis from cyclohexanone and cyclohexene over Dawson-type polyoxometates

R.M.Guerroudj[2,3], L.Dermeche[1, 2], L. Mouheb[1,2], T.Mazari[1,2], S. Benadji[2] and C.Rabia[2]

[1] Laboratoire de Recherche de Chimie Appliquée et de Génie Chimique, Hasnaoua I, Université Mouloud Mammeri B.P.17 RP, 15000 Tizi-Ouzou.
[2] Laboratoire de Chimie du Gaz Naturel, Faculté de Chimie, Université des Sciences et de la Technologie Houari Boumediene (USTHB), BP 32, El-Alia, 16111 Bab-Ezzouar, Alger, Algeria
[3]Centre de Recherche Scientifique et Technique en Analyse Physico-chimique CRAPC, BP 384, Zone Industrielle Bou-Ismail, RP 42004 Tipaza, Algeria

Phone number: 213 797241240 and e-mail : leila.dermeche@ummto.dz

1. Introduction – World production of adipic acid is increasing with its growing demand for nylon synthesis and other applications. Its industrial production is based on the oxidation of a mixture of cyclohexanone and cyclohexanol (known as KA oil) using an excess of concentrated nitric acid in presence of Cu/V catalyst. KA-oil was obtained from cyclohexane oxidation in the presence of air. However, the reduction of HNO_3 generates a large amount of greenhouse gases. Among them, N_2O is the most dangerous [1-3]. An alternative to this process is the use of H_2O_2 as oxidant and polyoxometalates (POMs) as catalyst. POMs have the advantage of possessing acid and oxidative properties that can be controlled according with the constituent elements and the requirements of the reactions. The aim of this study is to substitute the pollutant and corrosive nitric acid by hydrogen peroxide, in the presence of Dawson-type POMs in the adipic acid production, according to a green protocol.

2. Experimental - Dawson-type polyoxometalates as formula $K_6P_2W_{12}Mo_6O_{62}$, α1-$K_{10}P_2W_{12}Mo_5\square O_{61}$, α1-$K_8P_2W_{12}Mo_5SnO_{61}$ and α-$Cs_4SnP_2W_{12}Mo_6O_{62}$ were synthesized and characterized by FTIR, ^{31}P NMR and UV-Vis spectroscopies and DRX. Their catalytic performance was examined in the adipic acid synthesis reaction from cyclohexanone and cyclohexanone/cyclohexanol mixture at 90°C and cyclohexene at 70°C in the presence of hydrogen peroxide. The reaction products analysis was performed by HPLC.

3. Results and Discussion - The IR analysis showed that all salts have the characteristic vibration bands of the Dawson anion. The ^{31}P NMR confirmed the purities and the Dawson-type structure. UV-Visible spectroscopy revealed that the tin substituted POMs are partially reduced. The XRD analysis demonstrated that the crystal structure depends on the chemical composition of the POM.
The reactivity of POMs in adipic acid synthesis showed that, in the oxidation of cyclohexanone at 90°C, $Cs_4SnP_2W_{12}Mo_6O_{62}$ is the most active with an AA yield equal to 61%. $K_6P_2W_{12}Mo_6O_{62}$ is the most efficient with 47% AA yield from the equimolar mixture cyclohexanol/cyclohexanone. From cyclohexene oxidation at 70°C, the highest AA yield is 32% obtained with $K_{10}P_2W_{12}Mo_5\square O_{61}$. The HPLC analysis showed the total conversion of the substrate, the purity of the adipic acid and the selectivity of $Cs_4SnP_2W_{12}Mo_6O_{62}$ favorable to adipic acid formation.

4. Conclusions - The adipic acid synthesis in the presence of the POM-H_2O_2 system is a promising alternative to that using nitric acid, which could replace the industrial synthesis method, which is a source of air pollution.

5. References

[1] D.D. Davis, in: W. Gerhartz (Ed.), vol. A1, 5th edn., Wiley, New York, 1985, pp. 270–272.
[2] Castellan, A., Bart, J.C.J., Cavallaro, S. (1991). *Catal. Today*., 9(3): 285-299
[3] Castellan, A., Bart, J.C.J., Cavallaro, S. (1991). *Catal. Today*., 9(3) 255-283