The liquid-phase oxidation of cyclohexanone with oxygen, catalysed by Keggin-type polyoxometalates. A cleaner alternative to the current industrial process for adipic acid synthesis.

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Introduction

One current industrial production of adipic acid is based on the oxidation of KA Oil (a mixture of cyclohexanol and cyclohexanone) with nitric acid. This synthetic approach was developed during the 40's but several technological improvements have been adopted with positive results on energy consumption, final quality of the product, safety and environmental impact of the process. In any case, the study of an alternative synthetic pathway in which air is the oxidising agent is still a fascinating challenge of the modern chemistry with the potential industrial application due to the savings resulting from the elimination of nitric acid production and recovery plant. Furthermore, the process co-produces N_2O, a pollutant gas that has to be abated before emissions of tail gases into the atmosphere.

Different catalytic systems have been reported for the oxidation of KA Oil with air [1,2]. In the present work we describe the catalytic performance of P/Mo-based Keggin-type polyoxometalates for the liquid-phase oxidation of cyclohexanone to adipic acid with oxygen.

Materials and Methods

The reaction was carried out in a pressurized vessel (P ranging from 1 to 4 bar), with continuous feed of air or O_2, while the liquid phase being loaded in a batch-wise mode. The experiments were carried out either in the absence of solvent, or with different relative amounts of H_2O and other organic protic solvents. The temperature of reaction was varied between 70 and 120°C. The analysis method was set up in order to have the composition of both the liquid phase and the gaseous effluent stream.

Results and Discussion

Figure 1 reports the effect of the reaction time on the cyclohexanone conversion and on the selectivity to the reaction products, at 70°C and 4 bar. The catalyst used was a Keggin-type polyoxometalate, having composition $H_4PMo_{11}VO_{40}$, soluble in the reaction medium. The products were adipic acid, glutaric acid, succinic acid and carbon dioxide. An increase of the reaction time led to the progressive increase of the reactant conversion. A linear relationship between the two parameters implies the absence of relevant catalyst deactivation phenomena. The initial selectivity to adipic acid was close to 50%; this indicates the presence of parallel reactions of oxidative degradation of cyclohexanone, leading to the formation of the undesired by-products. An increase of the reactant conversion led to a slight decrease of the selectivity to adipic acid, because of the presence of consecutive reactions of degradation. Reaction temperatures higher than 70°C led to an increase of the conversion, with however a considerably lower selectivity to adipic acid. Also, the variation of pressure from 1 to 4.8 bar caused an increase of cyclohexanone conversion, due to both the higher residence time of O_2 and its higher concentration in the liquid-phase; unexpectedly, the higher conversion was accompanied by a better selectivity to adipic acid (Table 1). This effect was attributed to a variation of the oxidation level of the polyoxometalate under reaction conditions, as a consequence of the variation of oxygen concentration in the liquid phase. The importance of the polyoxometalate redox characteristics on catalytic performance was confirmed by checking the initial performance of pre-reduced catalysts.

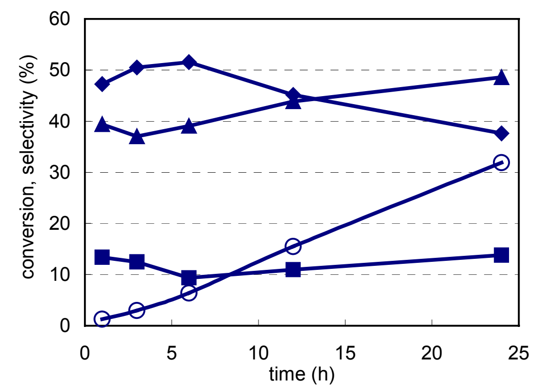

Figure 1. Effect of the reaction time on the catalytic performance. T 70°C, P 4 bar. Solvent: water. Catalyst $H_4PMo_{11}VO_{40}$. Cyclohexanone conversion (O), selectivity to adipic acid (◆), to glutaric + succinic acids (■) and to CO_2 (▲). The selectivity to glutaric and succinic acids includes the co-formation of CO_2.

Table 1. Effect of pressure on the catalytic performance. Other conditions as in Figure 1.

T (°C), P (bar)	CyONE conv, %	Adipic Acid select, %	Glut + Suc Acids, select, %	CO_2 select, %
70, 1	3.6	48	4	48
70, 2	4.5	49	7	44
70, 4.8	9.9	56	10	34

Significance

The industrial significance of the work is related to the need for an environmentally more friendly process for adipic acid production. Keggin-type polyoxometalates are versatile systems that effectively catalyze the reaction of cyclohexanone oxidation with oxygen.

References

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