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To be cited as: *ChemCatChem* 10.1002/cctc.201800419

Link to VoR: http://dx.doi.org/10.1002/cctc.201800419

A Journal of
ChemPubSoc Europe

WILEY-VCH www.chemcatchem.org

Cyclohexane oxidation to adipic acid under green conditions: a scalable and sustainable process.

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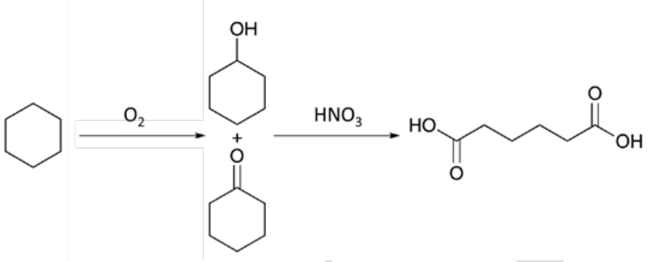
Abstract:

This work reports a 1 mol scale catalytic process to synthesize adipic acid directly from cyclohexane in solvent free conditions using air as oxidant. Catalysts based on vanadium phosphorous oxides were prepared, characterized and tested. They showed good activity and remarkably high selectivity to adipic acid in comparison to other already known heterogeneous catalysts. The use of solvent free conditions permits the easy separation of the product from the reactant mixture, which is very important from the industrial point of view. The process can be used at industrial scale for sustainable adipic acid synthesis.

Currently, one of the main challenges of the chemical industry is the development of new sustainable and "green" processes taking into account the numerous environmental issues that affect our planet. Consequently, there is a renewed interest in the production and use of chemicals obtained through environmentally friendly technologies. Adipic acid (AA) is an aliphatic dicarboxylic acid with high volume of production and it is primarily used as starting reagent in the preparation of nylon-6,6 polyamide, fibres, plasticizers, food additives and many other applications [1]. Global production of adipic acid is around 2900 ktons/year and the demand continues to grow around 2%/year with non-nylon applications growing faster than the nylon sector [2]. Industrially, adipic acid is synthesized by a two-step process involving oxidation of cyclohexane to a mixture of cyclohexanol and cyclohexanone (the so-called KA oil) further oxidised by HNO_3 to the final acid (Scheme 1).



Scheme 1. Schematic representation of the current industrial method for cyclohexane oxidation.

This process is seriously harmful for the environment and leads to a huge mark on the global warming. Indeed, the nitrous oxide (N_2O) produced in this process is an unavoidable stoichiometric waste that is commonly considered as a major factor of the global warming and ozone depletion [3]. Moreover, it is also responsible for acid rains and smog. Every years more than 400,000 metric tons are emitted into the atmosphere, which corresponds to about 5–8 % of the worldwide N_2O production [3].

When developing a new process, which eventually could be used at industrial scale, the choice of the starting reagent is crucial. Such a process requires a starting material, which is widely available, economically viable and suitable for green reaction conditions (namely liquid phase oxidation, solvent free conditions, use of air as oxidant and avoiding the use of any free radicals initiators). Such a substrate would permit to obtain a product with a competitive cost as compared with to the traditional process. For these reasons cyclohexane (CH) was chosen as the starting molecule as it is a largely available chemical with a competitive cost.

Here, we reported on the synthesis of the adipic acid using heterogeneous catalysts based on vanadium phosphorous oxides. As prepared catalysts were tested in the oxidation of cyclohexane, without any solvent and under mild conditions (T<150°C, 13-25 bars of air).

As reported in the literature [4], the oxidation of cyclohexane carried out in solvent-free conditions, using air as oxidant and without the presence of free radicals initiators does not permit to reach high level of conversion (Table 1), due to the difficulty in the activation of the aliphatic ring of the alkane. In particular, it is worth to note that the maximum cyclohexane conversion (57%) was obtained after a long time of reaction (16 h) without the formation of significant amounts of adipic acid [5-7] as could be seen from Table 1. 65% of selectivity to adipic acid was reached in the case of Fe-AlPO-31 but only after 24 hours of reaction and at a very low CH conversion (7%).

Table 1. Literature results [5-7] obtained in solvent-free conditions using air as oxidant and without free radicals initiators.

Catalyst	T (°C), P (bar), time (h)	Reaction rate^{a} / CH conversion (%)	Main product selectivity (%)
Co-AlPO-5	130, 15, 16	8 / 11	KA Oil 80
Co-AlPO-36	130, 15, 16	42 / 57	KA Oil 83
Fe-AlPO-31	100, 15, 24	3 / 7	AA 65
Fe-AlPO-5	100, 15, 24	2 / 5	KA Oil 77
Fe-AlPO-5	130, 15, 24	4 / 7	KA Oil 51, AA 31

[a] [$mmolCH*gcat^{-1}*h^{-1}$]

In this work, heterogeneous catalysts consisting in supported vanadium-phosphorus mixed oxides (VPO), which are known as being excellent oxidation catalysts for n-butane conversion to maleic acid, were developed. The first step was the synthesis of the $VOHPO_4{\cdot}0.5H_2O$ precursor, obtained by refluxing a mixture of vanadium pentoxide and phosphoric acid in isobutanol for 6 hours. In a second step, the precursor was supported on several supports (CeO_2, Fe_3O_4, H-mordenit and Y-goethite) then calcined at 500 °C for 4 hours under static air. The precursor used in the preparation of VPO catalysts was analysed by

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means of XRD to verify its structure (data not shown here). The results confirmed the presence of the characteristic diffraction peaks of the $VOHPO_4 \cdot 0.5H_2O$ precursor validating in the same time the synthesis method.

The first catalytic screening was performed at 120°C using 5 wt% VPO supported on different supports (CeO_2, Fe_3O_4, H-mordenite, Y-and goethite (FeO(OH)). The catalytic results are shown in Table 2. It could be seen that a remarkably high reaction rate was achieved in the case of VPO and VPO/CeO_2 catalyst, which was then chosen for further studies. Several parameters such as temperature, pressure and time of the reaction were studied. Blank tests performed with the support and without catalyst clearly indicated the important role of VPO as an active phase in the cyclohexane oxidation to adipic acid. The effect of the pressure was studied in the 13-25 bar range, but no significant variations in term of conversion and products selectivity was observed. Tests at different temperatures were performed at 100 °C, 120°C, 135 °C and 150 °C keeping constant the others reaction parameters (time and pressure) in order to improve the catalytic activity of the VPO-based catalysts.

Table 2. The reaction was carried out with 13 bar of air, air flow of 120 mL/min, 120 °C, 15 mg of catalyst, 20 mL of cyclohexane and 4 h of reaction time, ammol of cyclohexane (CH) converted/(gram of catalyst)*(time) [mmolCH*gcat-1*h-1]. b Selectivity to: KA Oil (mixture cyclohexanol/cyclohexanone), adipic acid (AA), c No catalyst was used, d Cyclohexane conversion in %.

Catalyst	Reaction rate[a]	Selectivity[b] [%] KA Oil	AA
blank test[c]	<1[d]	99	0
VPO/CeO_2	**24**	**93**	**6**
VPO/Fe_3O_4	4	98	0
VPO/H-mordenite	4	98	0
CeO_2	2	99	0
VPO	12	95	2

The results obtained after 4 h of reaction are shown in Figure 1. As expected the catalytic activity is strongly influenced by the temperature of the reaction. No activity was observed at 100 °C. At 135 °C the rate of reaction reached 63 mmolCH*gcat-1*h-1 while an increase of the temperature to 150 °C brings the reaction rate to the maximum value of 162 mmolCH*gcat-1*h-1.

The highest selectivity to cyclohexanol, that is the primary product of oxidation, was obtained at 120°C (80%). At 135 °C and 150°C the cyclohexanol selectivity were respectively 69% and 43%, which suggests that at higher temperatures the further oxidation of cyclohexanol to secondary products prevails. Indeed cyclohexanone selectivity increased from 11% to 15% at 135 °C, but remained almost constant at 150 °C. In addition, the selectivity to adipic acid reached the maximum also at higher temperature. As shown in Figure 2 selectivity of 25% to AA was obtained at 150 °C. It is worth to note that the tests at higher temperature (170 °C), showed the presence of several decomposition products, which were insoluble in both, water and organic solvents and therefore impossible to analyse via GC or HPLC.

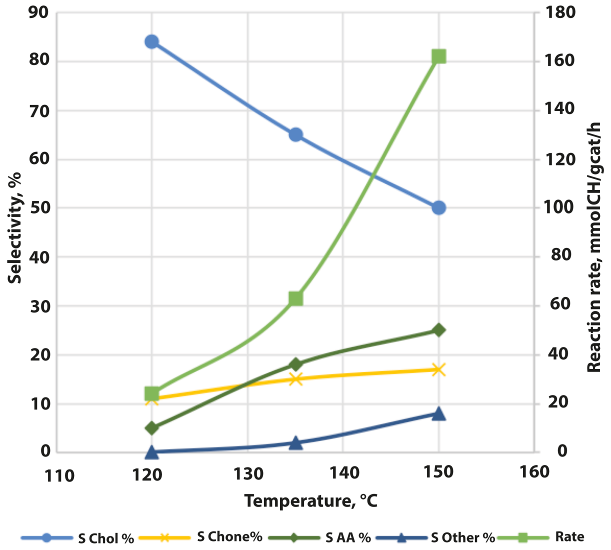

Figure 1. Effect of the temperature on the catalytic performance of VPO/CeO2. Conversion of CH (X) and products selectivity (S) at 120 °C, 135 °C, 150 °C.

The effect of the time of reaction (4 and 10 hours) was also investigated in the range 100-135 °C. The results are given in Table 3.

Table 3. Effect of the time of reaction at 100 °C, 120 °C and 135 °C, using VPO/CeO_2. [a]temperature of the reaction (°C). [b]time of reaction (h). [c]Conversion of cyclohexane (CH). [d]Selectivity to KA oil (cyclohexanol (Chol) + cyclohexanone (Chone)), adipic acid (AA) and other (glutaric acid (GA) and succinic acid (SA)).

		X[c] %	Selectivity[d] %		
T[a]	t[b]	CH	KA Oil	AA	Other
100	4	0	0	0	0
	10	1	99	0	0
120	4	2	93	6	0
	10	5	83	13	4
135	4	4	78	18	2
	10	12	51	35	11

The tests confirmed that even after 10 h of reaction the catalyst is inactive at 100 °C (not shown). Moreover at high temperature (>150 °C) many by-products such as: formic acid cyclohexyl ester, acetic acid cyclohexyl ester, pentanoic acid cyclohexyl ester, butyrolactone, hexanoic acid, acetic acid, 2-cyclohexen-1- one, formic acid, butanoic acid cyclohexyl ester and hexanoic acid ethyl ester were identified.

It is clear that an increase in the time of the reaction increases the cyclohexane conversion. Indeed, 12% conversion was reached at 135 °C after 10 hours of reaction. In terms of AA selectivity, the best performance was also obtained at 135 °C (35%). This temperature seems to enhance the activity of the catalyst without favouring the formation of by-products, as observed at 150 °C. An increase in time of the reaction at 135 °C leads also to higher selectivity to secondary products such as cyclohexanone and adipic acid. This trend suggests that the oxidation of CH to CHOL is the rate-determining step and this is proved also by the low cyclohexane conversion reached after 10 hours. Once the concentration of the cyclohexanol starts to increase it can be oxidised more easily to cyclohexanone and adipic acid, leading to higher selectivity to these two products

Catalysts based on vanadium phosphorous oxides (VPO) supported on ceria have been tested for direct oxidation of cyclohexane to adipic acid under green conditions. This catalytic system is able to activate the cyclohexane ring at relatively low temperature, low pressure of air and without the use of any free radical initiators. Moreover, it shows a good activity in terms of cyclohexane conversion and adipic acid selectivity, especially in comparison with the results reported in the literature for similar conditions. In particular high reaction rates and good adipic acid selectivity were obtained. Further studies are in progress in order to improve the catalytic system based on vanadium phosphorous oxides and also to better understand the reaction pathway.

Experimental Section

Synthesis of the $VOHPO_4 \cdot 0.5H_2O$ precursor:
The appropriate amounts of vanadium oxide (≈6g) and phosphoric acid (≈8.3g) (P/V ratio 1.1) were added into a three-neck round-bottom flask with 125 mL of isobutanol. The solution was then heated under reflux at 100°C for 16h. The final blue solid was filtered and washed with acetone (3x100mL) and dried in the oven overnight (90°C).

Preparation of the supported VPO/CeO_2 (5% wt):
The appropriate amount of vanadium precursor was dispersed in few millilitres of ethanol and the solution was dropped on cerium oxide until the mud point was reached. The wet solid was then dried in the oven (100°C) and the operation repeated till all the solution containing the VPO species was adsorbed on ceria. Subsequently the catalyst was calcined under static air atmosphere at 500 °C for 4 hours with a temperature rate of 20 °C/min.

X-ray diffraction:
The X-ray analysis was carried out by using Bruker D8 Advance diffractometer operated at an accelerating voltage of 40 kV and an emission current of 40 mA with Cu radiation.

Catalytic tests:
20 mL of cyclohexane and 15 mg of catalyst were introduced into a Teflon vessel installed inside of the reactor system. At the beginning the temperature of the reflux condenser started to cool down at the minimum temperature of -10 °C, once the temperature was reached the pressure was increased with an airflow to the set point value. Only when the pressure was constant the stirring system started to work and the vessel temperature started to increase until the desired value, this step is important to avoid the evaporation of the volatile cyclohexane. Airflow of 120 mL/min of oxygen was used in order to work in semi-batch conditions. At the end of reaction 0.5 mL of the final liquid solution was withdraw with a micropipette and kept for the GC analysis (Shimadzu GC2010 Plus AF, FID detector, ZB-WAX plus column), and then a certain amount of water (20-30 mL) was added in order to extract the other products for HPLC analysis (Shimadzu UFHPLC, Rezex ROA Organic acid column, trifluoroacetic acid as eluent with the total flow rate of 0.5 mL/min). The catalyst was filtered and the two final solutions, organic and aqueous solution separated.

Acknowledgements

The REALCAT platform is benefiting from a state subsidy administrated by the French National Research Agency (ANR) within the frame of the ‘Future Investments’ program (PIA), with the contractual reference ‘ANR-11-EQPX-0037’. The European Union, through the ERDF funding administered by the Hauts-de-France Region, has co-financed the platform. Centrale Lille, the CNRS, and Lille 1 University as well as the Centrale Initiatives Foundation, are thanked for their financial contributions to the acquisition and implementation of the equipment of the REALCAT platform.

Keywords: Adipic acid • $VOPO_4$ • heterogeneous catalysis • green oxidant • solvent free

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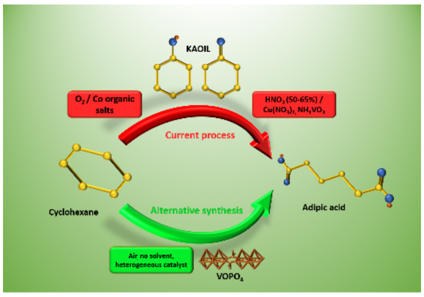

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