COMMUNICATION

ChemComm
www.rsc.org/chemcomm

A highly efficient oxidation of cyclohexane over VPO catalysts using hydrogen peroxide

Unnikrishnan R. Pillai and Endalkachew Sahle-Demessie*

National Risk Management Research Laboratory, Sustainable Technology Division, MS 443, United States Environmental Protection Agency, Cincinnati, Ohio 45268, USA. E-mail: Sahle-Demessie.Endalkachew@epa.gov; Fax: 011-513-569-7677

Received (in Corvallis, OR, USA) 21st June 2002, Accepted 10th July 2002
First published as an Advance Article on the web 22nd August 2002

A highly efficient oxidation of cyclohexane to cyclohexanol and cyclohexanone is accomplished over calcined vanadium phosphorus oxide (VPO) catalysts in a relatively mild condition using hydrogen peroxide under a nitrogen atmosphere.

Oxidation of the relatively inert C–H bond of hydrocarbons constitutes one of the most desirable but challenging reactions.[1] Of particular importance is the oxidation of cyclohexane due to the large demand for its oxidized products such as cyclohexanone and cyclohexanol, which are important raw materials for the production of adipic acid and caprolactam.[2] The present commercial process for cyclohexane oxidation is carried out at around 150 °C and 1–2 MPa pressure affording ~4% conversion and 70–85% selectivity to cyclohexanone and cyclohexanol.[3] The greater demand for these oxidation products and the high-energy intensity of the present process warrant a replacement with a more effective catalytic process. The increased environmental concerns in recent years call for benign oxidants such as molecular oxygen or hydrogen peroxide.[4] Na-GeX molecular sieve has been the most stable and active catalyst reported so far where hydrogen peroxide was used as the oxidant.[5] Other notable catalysts include titanium containing mesoporous materials such as TS-1, Ti-MCM-41 and metal containing AlPO redox molecular sieves.[6–8] However, most of them show a cyclohexane conversion $\leq$20%.[9]

Vanadium phosphorus oxide (VPO) catalysts are known for high activity for the vapor phase *n*-butane oxidation to maleic anhydride.[10] However, it has not been sufficiently explored for the cyclohexane oxidation. Herein we report a highly efficient oxidation of cyclohexane over calcined VPO catalyst in an environmentally benign oxidation protocol involving aqueous hydrogen peroxide in nitrogen atmosphere.

VPO catalyst with a P/V ratio of 1.1 was prepared according to a procedure described elsewhere.[10] XRD spectra of the catalyst after calcination showed high intensity peaks characteristic of the presence of $(VO)_2P_2O_7$ phase and also low intensity peaks characteristic of the $VOPO_4$ phase.[10] This shows that the vanadium in the calcined catalyst sample was predominantly in the V^{4+} state with a small amount of V^{5+} species.

The results of cyclohexane oxidation[†] over calcined VPO catalysts in the presence of a nitrogen atmosphere has been compared with that in the presence of air, other oxidants such as *tert*-butyl hydroperoxide (TBHP), various solvents as well as heating patterns (Table 1). Approximate turnover numbers (TON) were determined on the assumption that all the vanadium in the catalyst sample was in the form of $(VO)_2P_2O_7$. A highly efficient and unprecedented quantitative oxidation of cyclohexane to cyclohexanol and cyclohexanone could be accomplished at 65 °C over VPO catalysts in acetonitrile solvent using H_2O_2 under a N_2 atmosphere (Table 1, entries 1–4). TON as high as 400 could be achieved (entry 1) which is better than many of the catalyst systems reported earlier. The reaction was equally successful even at a ten fold higher (143 mmol) scale (Table 1, entry 4). The reaction was much slower in the presence of air (entry 6) and when the reaction mixture was heated slowly (entry 5). Acetone has also been found to be a favorable solvent for the oxidation (entry 8). The reaction, however, was slow in methanol (entry 9) and 1, 4-dioxane (entry 10) while no noticeable conversions were observed in the presence of dichloromethane (CH_2Cl_2) and also in the absence of any solvent. TBHP was not found to be as efficient as H_2O_2. No significant acid formation was detected in any of the products ($\leq$5%) as determined by HPLC. To the best of our knowledge, this kind of very high conversion for cyclohexane is unusual and is being reported for the first time.

The catalyst, however, was found to be soluble in the reaction mixture forming a homogeneous solution and therefore not recoverable by filtration for recycling. Nevertheless, the reaction could be successfully carried out repeatedly by the addition of new batches of substrate along with the solvent and oxidant to the previous reaction mixture containing the products

Table 1 Cyclohexane oxidation over VPO catalysts[a]

Entry	Conditions	H_2O_2/ substrate (mmol)	Solvent (10 ml)	Duration/h	Conversion (%)	Selectivity (%) Cyclohexanol	Cyclohexanone	TON
1[b]	N_2/heat-I	4	Acetonitrile	8	70	37	63	308
				20	91	36	64	400
2	N $_2$/heat-I	4	Acetonitrile	4	70	49	51	154
				8	84	50	50	185
3	N_2/heat-I	2	Acetonitrile	8	46	53	47	101
4[c]	N_2/heat-I	4	Acetonitrile (100 mL)	4	70	44	56	154
5	N_2/heat-II	4	Acetonitrile	8	66	41	59	145
6	Ai/heat-I	4	Acetonitrile	8	67	50	50	147
7[d]	N_2/heat-I	4 (TBHP)	Acetonitrile	8	25	27	73	55
8	N_2/heat-I	4	Acetone	8	85	39	61	187
9	N_2/heat-I	4	Methanol	8	20	73	27	44
10	N_2/heat-I	4	1,4-Dioxane	8	25	70	30	55

[a] Cyclohexane (14.3 mmol), catalyst (10 mg), solvent (10 mL), H_2O_2 (57 mmol), 65 °C, stirrer. [b] Catalyst (5 mg). [c] Cyclohexane (143 mmol), solvent (100 mL), H_2O_2 (570 mmol), 65 °C, stirrer. [d] *tert*-butyl hydroperoxide (57 mmol). Heat-I = pre-heated heating mantle where the reaction vessel was placed on a mantle pre-heated to the reaction temperature. Heat-II = post-heated heating mantle where the reation vessel was slowly heated to the reaction temperature.

DOI: 10.1039/b206044b

Table 2 Recyclability of VPO catalysts for cyclohexane oxidation

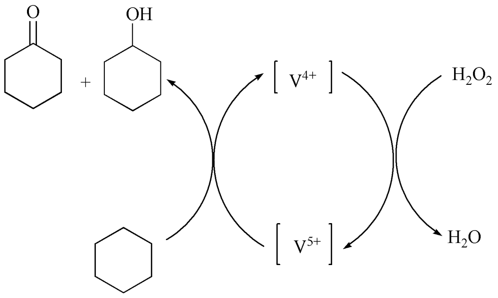
Entry	Conditions	Reaction cycle	Duration/h	Conversion (%)	Selectivity (%) Cyclohexanol	Cyclohexanone	TON
1[a]	N_2/heat-I	1	20	> 95	42	58	> 209
2[b]	N_2/heat-I	2	8	76	48	52	167
			20	> 95	46	54	> 209
3[b]	N_2/heat-I	3	8	47	44	56	103
			20	84	39	61	185
4[c]	N_2/heat-I	2	8	50	54	46	110
			20	97	30	67	213
5[a]	N_2/heat-II	1	20	95	42	58	209
6[b]	N_2/heat-II	2	8	45	46	54	99
			20	92	47	53	202
7[a]	Air/heat-I	1	20	79	51	49	174
8[b]	Air/heat-I	2	4 8	40	47	53	88
			20	56	59	41	123

[a] Cyclohexane (14.3 mmol), catalyst (10 mg), acetonitrile (10 mL), H_2O_2 (57 mmol), 65 °C, stirrer. [b] By adding cyclohexane (14.3 mmol), acetonitrile (10 mL) and H_2O_2 (57 mmol) to the previous reaction mixture after 20 h of reaction. [c] Same as *b* but after removing the products from the previous reaction mixture by vacuum distillation.

or after removing the products by vacuum distillation (Table 2). The recycling activity was higher for the reaction conducted in nitrogen than that in the presence of air (compare entries 1 and 2 with entries 7 and 8 in Table 2). The activity and TON decreased in successive batches; however, extending the reaction time could complete the reaction.

The calcined VPO catalysts showed vanadyl pyrophosphate ($(VO)_2P_2O_7$) as the predominant phase present in addition to some $VOPO_4$ phase. P/V ratios in the precursor higher than stoichiometric stabilize the $(VO)_2P_2O_7$ phase from re-oxidation in the reactant atmosphere as well as during calcination in air at high temperatures.[11] It has been suggested that VPO catalysts may be terminated by a distorted vanadyl pyrophosphate structure,[12] which may result in the generation of more Lewis (V^{4+}) and Brönsted (P–OH) acid sites on the catalyst surface. It is also reported that maximum catalytic performance requires a certain degree of disorder in the VPP lattice.[13,14] X-Ray photoelectron spectroscopy (XPS) studies have shown that catalysts calcined at lower temperatures (< 750 °C) contain superficial V^{5+} species and ^{31}P NMR studies have shown that V^{5+} microdomains are located on the surface of the VPO catalysts and isolated V^{5+}sites are located in sublayers of the vanadyl pyrophosphate structure.[15]

The cyclohexane oxidation pathway over VPO catalysts, therefore, appears to be a reversible V^{4+}/V^{5+} redox mechanism as illustrated in Scheme 1.[16] Excess phosphorus at the surface stabilizes the pyrophosphate framework so that the appearance of V^{5+} sites, which are essential to the V^{4+}/V^{5+} redox mechanism, will be reversible. This also explains why the reaction works better in nitrogen atmosphere as presence of oxygen (air) hinders the reduction of V^{5+} species back to V^{4+}. The redox mechanism was also indicative from the color changes of the reaction mixture where the initial color of the reaction mixture was green (V^{4+}) that slowly changed to greenish yellow and then to brown (V^{5+}) which further changed to green (V^{4+}). In other words, it appears that dispersed V^{5+} species in combination with $(VO)_2P_2O_7$ (V^{4+}) is important for the oxidation of cyclohexane wherein the V^{5+} act as a dynamic oxidizing center.



Scheme 1

In summary, a calcined VPO catalyst with a P/V ratio of 1.1 is found to be a very efficient catalyst for the quantitative oxidation of cyclohexane using hydrogen peroxide, especially in a nitrogen atmosphere.

U. R. P. is a postgraduate research participant at the National Risk Management Research Laboratory administered by the Oak Ridge Institute for Science and Education through an interagency agreement between the US Department of Energy and the US Environmental Protection Agency.

Notes and references

† In a typical reaction procedure, cyclohexane (14.3 mmol) was mixed with calcined VPO catalyst (10 mg), solvent (10 mL) and 30% hydrogen peroxide (~ 57 mmol) and heated to 65 °C with a heating mantle under vigorous stirring in a nitrogen atmosphere. The reaction mixture was sampled out at regular intervals and extracted with ether and the organic layer was analyzed by GC-MS and the aqueous layer by HPLC (for carboxylic acids). Quantification of the oxygenated products was obtained using a multi-point calibration curve for each product.

1 (*a*) J. M. Thomas, *Nature*, 1985, **314**, 669; (*b*) T. Ito and J. H. Lunsford, *Nature*, 1985, **314**, 721.
2 U. Schuchardt, W. A. Carvalho and E. V. Spinacé, *Synlett*, 1993, **10**, 713.
3 K. U. Ingold, *Aldrichim. Acta*, 1989, **22**, 69.
4 R. A. Sheldon and J. K. Kochi, *Metal-catalyzed oxidation of organic compounds*, Academic Press, New York, 1981.
5 V. I. Pârvulescu, D. Dumitriu and G. Poncelet, *J. Mol. Catal. A: Chem.*, 1999, **140**, 91.
6 (*a*) E. V. Spinacé, H. O. Pastore and U. Schuchardt, *J. Catal.*, 1995, **157**, 631; (*b*) M. H. Zahedi-Niaki, M. P. Kapoor and S. Kaliaguine, *J. Catal.*, 1998, **177**, 231.
7 W. A. Carvalho, P. B. Varaldo, M. Wallau and U. Schuchardt, *Zeolites*, 1997, **18**, 408.
8 R. Raja, G. Sankar and J. M. Thomas, *J. Am. Chem. Soc.*, 1999, **121**, 11926.
9 U. Schuchardt, D. Cardoso, R. Sercheli, R. Pereira, R. S. da Cruz, M. C. Guerreiro, D. Mandelli, E. V. Spinacé and E. L. Pires, *Appl. Catal. A: Gen.*, 2001, **211**, 1.
10 *Vanadyl Pyrophosphate Catalysts, Catal. Today*, ed. G. Centi, 1993, **16**, (1)).
11 F. Trifiro, *Catal. Today*, 1998, **41**, 21.
12 W. P. A. Jansen, M. Ruitenbeck, A. W. D. von der Gon, J. W. Geus and H. H. Brongersma, *J. Catal.*, 2000, **196**, 379.
13 A. Brückner, B. Kubias and B. Lücke, *Catal. Today*, 1996, **32**, 215.
14 J. Haber, V. A. Zazhigalov, J. Stoch, L. V. Bogutskaya and I. V. Batcherikova, *Catal. Today*, 1997, **33**, 39.
15 M. Abon, J. M. Herrmann and J. C. Volta, *Catal. Today*, 2001, **71**, 121.
16 D. Wang, H. H. Kung and M. A. Barteau, *Appl. Catal. A: Gen.*, 2000, **201**, 203.