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Direct oxidation of propane to isopropanol

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Abstract

Propane has been oxidised to a mixture of isopropanol and acetone at ambient conditions with high activity and selectivity using phthalocyanine complexes of Fe, Co and Cu encapsulated in zeolites as catalysts and O_2/tertiary butyl hydroperoxide as oxidants

Keywords: Propane; Isopropanol; Phthalocyanine; Oxidation; Zeolite catalyst

1. Introduction

The direct functionalisation of propane (instead of propylene) to oxygen and nitrogen containing intermediates (like propylene oxide, acetone, acrylonitrile, etc.) by reaction with oxygen is a research challenge with significant potential in the petrochemical industry. An additional impetus for the direct oxyfunctionalisation of propane is the present emphasis on the reduction of olefins and aromatics in fuels like gasoline. The latter requires the increasing use of oxygenates like MTBE, TAME, etc. Isopropanol and diisopropyl ether have been proposed as oxygenate additives for gasoline and diesel but present methods of their manufacture have limited their usefulness from a cost standpoint. Isopropanol is currently manufactured by either hydration of propylene or hydrogenation of acetone. In view of the large worldwide resources of propane, an economic process for its direct oxidation to isopropanol is desirable.

Two major routes have been reported in the literature for the oxyfunctionalisation of propane. In the first, an indirect process, propane is oxydehydrogenated to propylene at high temperatures over metal oxide catalysts [1] and the reactor effluent is passed to the second propylene oxidation or ammoxidation stages without separation of the intermediate propylene. Alternatively, paraffin activating catalysts may be combined with compatible olefin conversion catalysts to produce the corresponding oxygen or nitrogen-containing unsaturated products directly [2]. In contrast to these high temperature operations, the second route involves the low-temperature functionalisation of propane with O_2 using catalysts which mimic enzymes, like methane monoxygenase or cytochrome P450, in hydroxylating light alkanes. For example, Ellis and Lyons [3] have reported the oxidation of propane to isopropanol and acetone at 398 K under 1000 psi air over homogeneous, metalloporphyrin catalysts.

In the present paper, we report the direct aerobic oxidation of propane at ambient condition to a mixture of isopropanol and acetone in high yields over substituted phthalocyanines of Cu, Co and Fe encapsu-

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lated in zeolites X and Y. We had, earlier, reported that encapsulated copper phthalocyanines-containing electron-withdrawing groups on the aromatic ring are active catalysts in the direct conversion of methane to methanol [4], oxyhalogenation of aromatics [5], selective oxidation of phenols [6] and paraffinic [7], cycloparaffinic [8] as well as aromatic [9] hydrocarbons. The low temperature aerobic oxidation of propane over solid catalysts has not been reported in the open literature, so far.

2. Experimental

2.1. Materials

The preparation and physicochemical characterisation of all the catalysts utilised in the present work has already been reported [5].

2.2. Procedures

2.2.1. Catalytic reactions

In a typical oxidation reaction, the solid catalyst (0.2–0.75 g) was added to a suitable solvent (acetonitrile for example) and *tert*-butyl hydroperoxide in a 300 ml Parr reactor (USA). The temperature of the reaction vessel was maintained using a cryostat (Inlabo, FT 901). The Parr reactor was cooled to 273 K before propane was pressurised from a propane cylinder (Matheson). Periodically, samples were removed and centrifuged to remove the solid catalyst. The gas from the Parr reactor was collected in a gas bulb filled with a three-way valve. Copper, iron or cobalt were not detected (by atomic absorption spectroscopy, Hitachi Model Z-8000) in the colourless reaction product when using any of the solid catalysts used in the present study. In the case of oxidation using O_2 as the oxidant, *tert*-butyl hydroperoxide (TBHP, 70% aqueous solution (Aldrich) equivalent to 2% by weight of the substrate propane) was added to the reaction mixture before air was admitted to the Parr autoclave.

2.2.2. Product analysis

The products were analysed by a gas chromatograph (Hewlett-Packard, 5880A), employing an FID detector and equipped with a capillary column (50 m×0.25 mm crosslinked methyl silicone gum). At the end of the reaction, the gas was collected in a gas sampling vial. The analysis for CO_2 and H_2O was carried out using a Shimadzu GC-15-A equipped with a TCD detector and a poropak N column. The liquid products were extracted with ether and analysed. The identity of the products was further confirmed by GC–MS (Shimadzu QCMC-QP2000A).

3. Results and discussion

The physicochemical properties of the various substituted phthalocyanines encapsulated in zeolites X and Y have already been described [5–9] in detail. Briefly, the presence of the metal complex in the supercage of the faujasite is confirmed by (1) adsorption, and (2) scanning electron microscopy results [5,9]. IR and UV spectroscopies as well as modelling studies indicate that while the chemical stoichiometry of the complex remains intact upon encapsulation, the geometric environment around the metal atom is distorted from the square planar geometry (of the free complex). Experimental evidence that the oxidation of propane is indeed catalysed by the solid zeolite containing the encapsulated complex is presented in Fig. 1. In one set of two identical experiments, the solid catalyst was removed by centrifugation at a reaction time of 5 h. While the propane conversion continued in the presence of the catalyst (curve A),

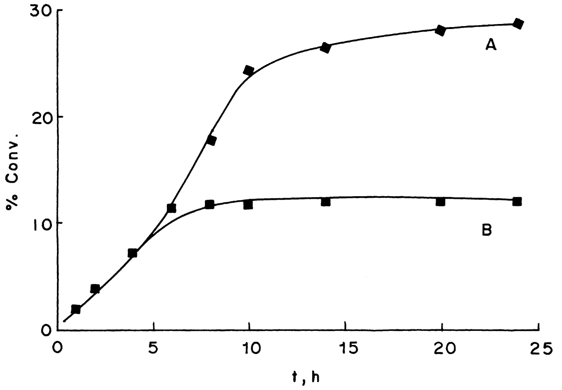

Fig. 1. Kinetics of propane oxidation in the presence of the solid catalyst $CoCl_{16}Pc$–Na–X(0.27) (A), and when the catalyst is removed from the reaction mixture at 5 h.

there was no further conversion of propane when the catalyst was removed from the reaction system (curve B). This indicates that:

1. The solid catalyst is essential for the oxidation reaction to occur.
2. Oxidation of propane by dissolved copper complexes leached out from the solid material is negligible. The latter conclusion was independently confirmed by the absence of copper in the filtrate (atomic absorption spectroscopy).
3. In the absence of the catalyst, O_2/TBHP are unable to oxidise propane to any significant extent.

In independent experiments carried out in the absence of the catalyst, the conversion of propane was less than 0.5 mol% under otherwise identical conditions of Fig. 1.

The results of the oxidation of propane using O_2/TBHP as the oxidants and acetonitrile as the solvent at 298 K over the various copper, iron, cobalt and nickel phthalocyanine complexes both in the neat and encapsulated states, are presented in Table 1. The following points may be noted:

1. The unsubstituted metal phthalocyanines have a low activity.
2. The intrinsic catalytic activity (turnover frequency, TOF=moles of propane converted per hour per mole of transition metal) of the neat chloro and nitro complexes of iron, copper and cobalt are of similar magnitude. Nickel chlorophthalocyanine has a low activity.
3. There is a dramatic increase in TOF (by two orders of magnitude) when the halogenated or nitrated complexes are encapsulated in the cavities of X, Y or L.
4. The central transition metal of the phthalocyanine complex is the seat of catalytic activity. $Cl_{16}Pc$ or phthalocyanines of non-transition metals (like Al) had negligible oxidation activity.
5. There is no apparent direct correlation between CO_2 formation and the extent of conversion of propane.

The identity of the catalyst (metal, zeolite type, nature of substituent on the phthalocyanine, etc.) is the predominant factor in the formation of CO_2.

The influence of catalyst weight on the reaction is illustrated in Fig. 2 for $CuCl_{16}Pc$–Na–X (0.28). The conversion levels off above 1 g of catalyst. This phenomenon is quite common in heterogeneous catalysis and may arise due to a variety of reasons

Table 1
Oxidation of propane with O_2 over phthalocyanines – comparison of catalysts

No.	Catalyst	Conversion (mol%)	TOF (h^{-1})	Products (mol%)			
				A	B	C	D
1	No catalyst	0.5	0	–	–	4.2	95.8
2	CuPc	0.6	0.02	–	–	–	100
3	CoPc	1.9	0.08	20	–	–	80
4	$Cu(NO_2)_4Pc$	3.1	0.17	10	70	–	20
5	$CuCl_{16}Pc$	5.0	0.42	63.2	30.5	–	6.3
6	$CoCl_{16}Pc$	7.7	0.65	48.5	50.0	–	1.5
7	$FeCl_{16}Pc$	4.8	0.41	42.5	39.7	–	17.8
8	$NiCl_{16}Pc$	0.2	0.02	10	–	–	90
9	$Cu(NO_2)_4Pc$–Na–X (0.$_{16}$)	0.75	2.25	15.9	65.6	–	18.5
10	$CuCl_{16}Pc$–Na–X (0.28)	17.6	31.6	48.2	37.6	9.2	5.0
11	$CuCl_{16}Pc$–Na–Y (0.11)	10.6	48.0	51.5	34.8	8.9	4.8
12	$CuCl_{16}Pc$–K–L (0.1)	7.8	39.0	42.5	36.8	17.2	3.5
13	$CoCl_{16}Pc$–Na–X (0.27)	36.1	62.0	42.2	40.0	16.3	1.5
14	$FeCl_{16}Pc$–Na–X (0.16)	13.5	37.1	39.9	37.8	9.0	13.3

Propane=50 psi, air=200 psi, TBHP=0.5 g, CH_3CN=99.5 g.
Temperature=298 K, reaction time=10 h.
Note: (1) (A) isopropanol, (B) acetone, (C) propylene, and (D) CO_2; (2) TOF is turnover frequency, moles of propane converted per mole of transition metal in the catalyst per hour; (3) the TOF and selectivity values are reproducible to about 10%.

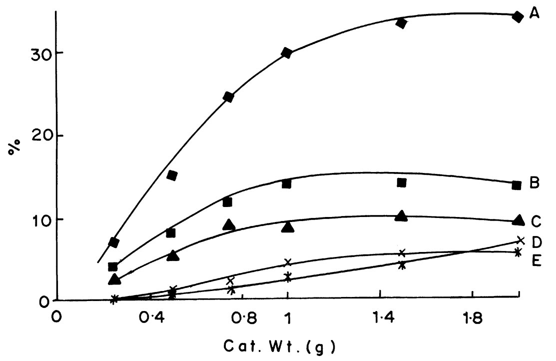

Fig. 2. Influence of the weight of catalyst ($CoCl_{16}Pc$–Na–X(0.27)): propane conversion (A); concentrations of isopropanol (B); acetone (C); CO_2 (D); and propylene (E).

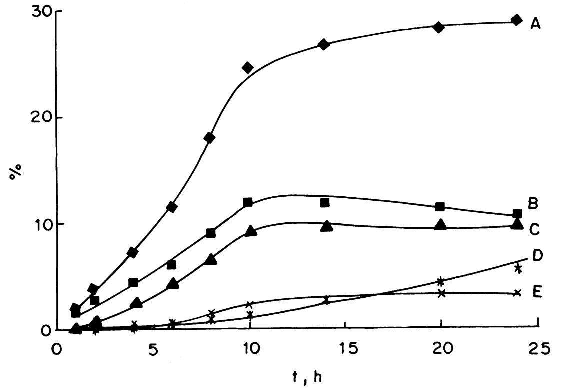

Fig. 3. Kinetic plots for the oxidation of propane over $CoCl_{16}Pc$–Na–X(0.27) (A); curves B–E indicate the formation of isopropanol, acetone, CO_2 and propylene, respectively.

Table 2
Effect of solvent in aerobic oxidation of propane over $CuCl_{16}Pc$–Na–X (0.28)

Solvent	TOF (h^{-1})	Products (mol%)			
		A	B	C	D
Acetonitrile	31.6	48.2	37.6	9.2	5.0
Acetic acid	36.0	38.6	45.0	8.9	7.5
Pyridine	41.2	12.8	60.2	11.5	15.5
t-Butanol	34.5	34.5	30.6	9.9	25.0
Methanol	22.0	40.0	50.9	5.1	4.0
Water	10.5	59.9	18.8	4.1	17.2

See Table 1 for reaction conditions and other details.

including thermodynamic limitations, poisoning of the catalyst by the secondary products formed, mass transfer limitations at high reaction rates, etc. CO_2 formation increases significantly at high catalyst concentrations. The yield of oxidation products of propane is shown in Fig. 3 as a function of reaction period. A notable feature in Fig. 3 is the presence of only isopropanol in the product at low levels (below 2 mol%) of propane conversion. Acetone is formed (probably from isopropanol) at higher conversion. Both isopropanol and acetone are further oxidised to CO_2 (Fig. 3). Both Figs. 2 and 3 suggest that the primary product of propane oxidation is isopropanol which undergoes further oxidation to acetone or dehydration to propylene. A surprising feature of the present catalytic system is the large variation in the formation of CO_2 with the solvent (Table 2). Over $CuCl_{16}Pc$–Na–X (0.28), and at similar conversion levels the formation of CO_2 was only 5% (mole) in acetonitrile, while it was 25% in *tert*-butanol. Even though propane could be oxidised over our catalysts using O_2 alone, the conversion levels were below 1% and only CO_2 was produced. On the other hand, sources of singlet oxygen like TBHP readily oxidised propane to acetone even in the complete absence of molecular oxygen (Table 3). At low concentrations of TBHP, isopropanol and acetone were the major products. The formation of CO_2 increased with increasing concentration of TBHP. At the end of the oxidation reaction, TBHP was converted into *tert*-butanol. There was a synergistic enhancement of conversion when both O_2 and TBHP are used as oxidants. The origin of the synergism of O_2 and TBHP is not clear. When propane was oxidised over $CuCl_{16}Pc$–Na–X (0.28) in

Table 3
Oxidation of propane – influence of propane:TBHP ratio

Propane:TBHP ratio (mole)	TOF (h^{-1})	Products (mol%)			
		A	B	C	D
5:1	32.0	42.5	35.8	9.2	12.5
3:1	38.1	38.3	37.0	9.7	15.0
2:1	47.0	36.5	35.6	9.9	18.0
1:1	49.0	35.0	32.3	10.5	22.2
1:3	50.0	30.0	29.5	11.0	29.5
1:5	51.5	28.8	23.3	11.2	36.7

Note. Catalyst – $CuCl_{16}Pc$–Na–X (0.28). See Table 1 for other details. The C_3H_8:TBHP ratio was varied by changing TBHP. The amount of CH_3CN (solvent)+TBHP was kept constant at 100 g.

the absence of O_2, substituting N_2 for air under otherwise identical conditions of Table 1, the TON was only 11.5 instead of 31.6 (Table 1, row 10).

4. Summary and conclusions

The salient features of our results can be summarised as follows: Phthalocyanines of Fe, Cu and CO, wherein all or most of the ring hydrogens have been substituted by electron withdrawing groups like the halogens or nitro groups, when encapsulated in zeolites X, Y or L, possess high catalytic activity in the oxidation of propane using sources of O_2/TBHP as the oxidants. A particularly advantageous feature is that even at these high conversion values, the selectivity for CO_2 was relatively low.

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