

CATALYTIC PROPERTIES OF ACTIVATED CARBONS IN LIQUID PHASE OXIDATION OF ORGANIC COMPOUNDS

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Introduction

Liquid phase oxidation of organic compounds by molecular oxygen catalysed by heterogeneous catalysts such as metals, their oxides and salts has been studied in details [1]. In many cases, the oxidation proceeds via a free radical chain mechanism with degenerated branching. The latter occurs in homolytic decomposition of the intermediate hydroperoxide interacting with the catalyst surface. In this paper kinetics and a mechanism of liquid phase oxidation of hydrocarbons catalysed by activated carbons has been investigated.

Experimental

Activated carbon SCN was produced by step pyrolysis of a mesoporous vinylpyridine-divinylbenzene copolymer at 350-900° C in an inert atmosphere (argon), and further steam activation at 850° C. The carbon particles are spheres of 0.2-1.0 mm in diameter. A distinctive feature of SCN carbon is nitrogen atoms incorporated into its lattice [2]. Oxidised SCN sample was obtained by treatment of SCN with a diluted (25%) nitric acid at 95-98°C for 4.0 h, carbon/acid v/v ratio being 1:4. The distribution of functional groups on the surface of oxidised SCN determined by acid-base titration was as follows: total exchange capacity - 1.9 mg-equiv/g; phenolic - 0.5 mg-equiv/g; carboxylic - 0.5 mg-equiv/g.

Oxidation rate was measured by oxygen uptake using an in-house made volumetric apparatus similar to that described in [3]. The total pressure in course of the reaction was kept constant at 1 atm. Catalytic activity of carbons in the decomposition of peroxides was determined by oxygen evolution. The products of cumene hydroperoxide decomposition were analysed by glc. Cumene hydroperoxide purchased from Aldrich was additionally purified to remove phenol traces as determined by glc.

Results and Discussion

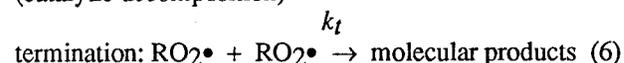
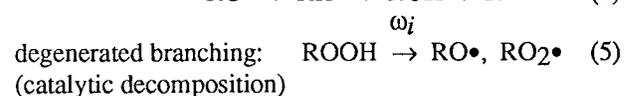
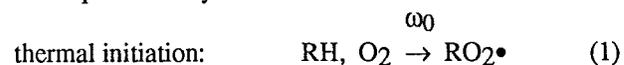
Catalytic activity of carbons in H₂O₂ decomposition is well known. SCN and oxidised SCN carbons effectively decompose cumene hydroperoxide and oxidise cumene and styrene (Figs. 1 and 2, Table 1). The main products of these reactions are dimethylphenylcarbinol ROH and acetophenone R'C(O)CH₃ which indicates that

the hydroperoxide undergoes homolytic cleavage of the O-O bond generating RO• and RO₂• free radicals [1,3].

Table 1. Oxidation of hydrocarbons, mL O₂/min, in the presence of carbon catalysts. Experimental conditions: 343 K, 10 mL hydrocarbon, 200 mg catalyst.

Catalyst	Cumene	Styrene
None	0.024	0.045
SCN	0.73	> 1.0
SCN oxidised	0.25	0.37

Here R is C₆H₅-C(CH₃)₂ and R' is C₆H₅. The product distribution gives a strong evidence in favour of a free radical chain mechanism of cumene oxidation. Catalytic decomposition of intermediate cumene hydroperoxide, ROOH by activated carbons accelerates the degenerated branching step of this process accounting for the overall catalytic effect of carbon samples. An abridged scheme of the process may be written as follows:



The main product dimethylphenylcarbinol, ROH is formed in the reaction (4), the other main product acetophenone is formed via β-scission of RO• (not shown in this scheme).

It is a general tendency that oxidised carbons are less catalytically active in the peroxide decomposition, and N-containing carbons are more active catalysts than ordinary carbons [4]. The promoting role of N atoms can be explained in terms of increased electron donor ability of the surface due to the additional electron on N compared to C atom. Excessive electron density in N-carbons decreases the energetic gap between the Highest Occupied Molecular Orbit (HOMO) and Lowest Unoccupied Molecular Orbit (LUMO) making the electron transfer

peroxide easier. Contrary to nitrogen, oxygen atoms in the oxidised carbon play the opposite role of electron acceptors being located in the -OH and -C(O)OH groups.

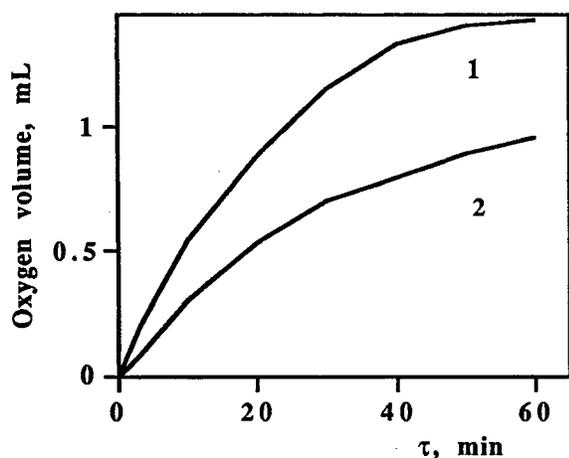


Fig. 1. Kinetics of cumene hydroperoxide decomposition catalysed by SCN (1) and oxidised SCN (2). 293 K, 1.5 mL 3% aqueous solution, 0.5 g carbon.

A variety of oxygen-containing groups on carbon surface makes its role in free radical reactions more complex. For example, phenolic compounds and quinones are known as strong inhibitors of such processes reacting with free radicals and converting them in less reactive species [3]. As phenolic groups and quinones are present on the surface of oxidised carbons, one may expect that these groups would be the sites for radical termination. It was shown earlier that oxidised wood charcoal inhibited oxidation of cumene and styrene, the more oxidised surface having stronger inhibiting properties [5]. We discovered a phenomenon of the critical catalyst amount in the liquid phase oxidation of cumene in the presence of high amount of a non-oxidised activated carbon SCN (Fig. 3). "Critical" phenomena, in other words, a dramatic change of one reaction parameter (reaction rate in this case) vs. a small change of another (catalyst amount) is characteristic of free radical branched chain processes [3]. Activated SCN has also a small number of surface O-functional groups which can terminate free radical chains according to the scheme:



At low amount of carbon and $\omega_i \gg \omega_0$, rate of chain propagation, $W_p = k_p (k_t)^{-1/2} [RH] \omega_i^{1/2}$.

At high amount of catalyst, termination of free radicals by the surface (7) dominates over the termination in the volume (6) and $W_p = k_p (k_7)^{-1} [RH] \omega_i \cdot q^{-1}$. In the initial stage of the process free radicals formed in the reaction (5) are caught by the surface inhibiting sites and the reaction course depends on the ratio between the

initial concentration of hydroperoxide and amount of inhibiting sites, $[ROOH]/[InH]$. If this ratio is high, all the inhibiting sites will eventually expire and the oxidation proceeds. If the ratio is low, all free radicals will decay and the reaction stops.

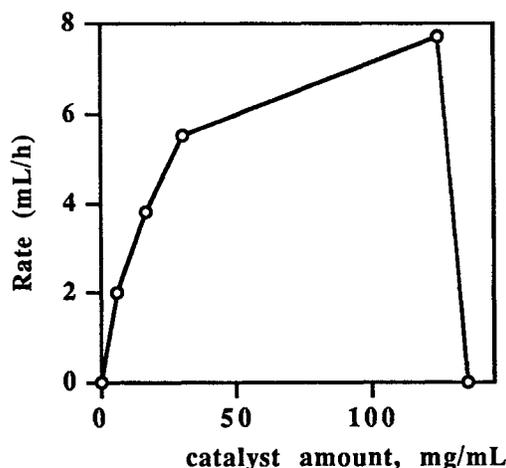


Figure 2. Rate of oxygen uptake in the cumene oxidation catalysed by SCN carbon. 323 K, 3 mL cumene, $[ROOH]_0 = 0.01$ M.

Conclusions

In the liquid phase oxidation of hydrocarbons activated carbons have a dual function. They catalyse the reaction of intermediate hydroperoxide decomposition accelerating the degenerated branching step and their surface O-functional groups suppress free radical steps acting as an inhibitor.

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