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OXYDEHYDROGENATION OF CYCLOHEXANOL OVER CARBON CATALYSTS

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Abstract—The reaction of cyclohexanol over carbon catalysts with surfaces of different chemical nature was studied. The catalyst samples were prepared by treating a parent activated carbon with HNO_3, H_2O_2, O_2 and N_2O. The catalytic tests were performed in a packed-bed reactor at 350°C. Dehydration as well as dehydrogenation of the substrate occur under the reaction conditions. The main products obtained are cyclohexene, cyclohexanone, benzene and phenol. Dehydration occurs preferentially over the carbon treated with HNO_3, while the best selectivity to cyclohexanone is achieved with the carbon treated with H_2O_2. The catalyst sample treated with N_2O is highly selective to phenol. A mechanism involving nitro groups on the carbon's surface is proposed. © 1998 Elsevier Science Ltd. All rights reserved.

Key Words—A. Activated carbon, B. chemical treatment, D. catalytic properties.

1. INTRODUCTION

The dehydrogenation of cyclohexanol to cyclohexanone is an industrially important reaction in the manufacture of Nylon [1,2]. This is so because the two major raw materials for the production of polyamide fibre are caprolactam and adipic acid, and both of which can be obtained from cyclohexanone. Cyclohexanone has traditionally been obtained by the direct non-oxidative dehydrogenation of cyclohexanol. Copper based catalysts have been used extensively in this reaction [3,4]. Since direct dehydrogenation is an endothermic reaction and is limited by the equilibrium, high reaction temperatures are required and typical conversions are low [2]. These conditions also lead to catalyst sintering and deactivation [1,5]. For these reasons, there has been a great deal of interest in developing oxidative dehydrogenation schemes [6–8].

Cyclohexene is usually the main side product of the dehydrogenation reaction of cyclohexanol. The selectivity of this reaction is known to be related to catalyst acidity. Indeed, the selectivity to cyclohexanone increases with decreasing acidity of the catalysts [1–4].

Attempts to develop highly active and thermostable dehydrogenation catalysts have been carried out [3,5]. Uemichi *et al.* [5] have shown that the use of carbon as a support is essential for increasing the reactivity of cyclohexanol dehydrogenation due to its role in increasing the catalyst dispersion.

Apart from their use as catalysts supports, carbons are known to catalyse many reactions, such as the decomposition of primary alcohols to produce acetals [9–11]. Due to the presence of acidic and/or basic surface oxides, carbons can be used as catalysts [9–12]. They participate in a number of reactions, including oxydehydrogenation, dehydration, chlorination, gas phase oxidation and reductive NO removal [12].

Functionalized activated carbons have been proved to be efficient catalysts for the non-oxidative dehydrogenation of light alcohols [9–11]. Carbon catalysts have also been successfully used in the oxydehydrogenation of ethylbenzene to styrene [13,14]. This paper presents the results of the catalytic oxidative dehydrogenation of cyclohexanol to cyclohexanone over activated carbons with different surface chemical natures. The objective is to compare the activities and selectivities obtained using the functionalized carbons as catalysts. Complementary characterization studies to determine the pore structure and surface area and also characterization of the surface groups was carried out.

2. EXPERIMENTAL

2.1 *Catalyst preparation*

Catalyst samples were prepared using a commercial granular carbon (NORIT, GAC 1240, 0.5 wt% ash content and particle size > 12 mesh) as the starting material. The chemical nature of the carbon surface was changed by the following treatments: pure (99.9%) N_2O flow at 500°C for 1 hour. The sample was prepared by ramping the temperature in flowing nitrogen and switching to N_2O when the temperature was reached. Cooling to room temperature was car-

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ried out in flowing nitrogen (sample C1): 5M HNO_3 at room temperature for 1 hour, followed by washing until a constant eluant pH was attained (sample C2): 5M H_2O_2 at 100°C, for 1 hour, followed by washing until no peroxide was detected (sample C3): dry air flow at 750°C for 1 hour, followed by cooling in flowing nitrogen (sample C4): He flow at 800°C for 1 hour, followed by O_2 flow at 300°C for 1 hour and cooling in flowing nitrogen (sample C5). The sample denoted as C6 is the as-received carbon.

2.2 *Catalyst characterization*

X-ray photon spectroscopy (XPS) analysis was performed on a XSAM800 (KRATOS, Manchester, UK) X-ray spectrometer. Temperature programmed desorption (TPD) analysis were carried out using a Micromeritics TPD/TPR 2900 instrument, with the evolution of CO, NO and CO_2 being monitored by mass spectrometry using a FISONS MD800 (Leicestershire, UK) gas chromatography mass spectrometry (GCMS) instrument. The procedure employed consisted of initially drying *ca* 0.3 g of the sample at 383 K for at least 12 hours in flowing helium. The temperature was then increased at 10 K min^{-1} to 1273 K, under helium flow (60 cm^3 min^{-1}, 0.1 MPa). Temperature programmed reduction (TPR) analysis was carried out on a Micromeritics TPD/TPR 2900 instrument (Norcross, USA), with the evolution of H_2 being monitored by a thermal coupled detector (TCD). In TPR experiments a mixture of argon and 10% H_2 (30 cm^3 min^{-1} at 298 K and 0.1 MPa) was used. Textural characterization was performed by nitrogen adsorption at 77 K on a Micromeritics ASAP 2010 V1.01 B instrument. The contents of oxygenated surface groups were determined, according to the method of Boehm [15], by performing titrations with bases of increasing strength. The point of zero charge (PZC) was determined by mass titration [16].

2.3 *Catalyst activity*

The reaction of cyclohexanol in the gas phase was conducted in a fixed-bed, plug flow type reactor working at atmospheric pressure, using nitrogen as the carrier gas. The catalytic tests were carried out at 300°C, using 0.6 g of catalyst, a cyclohexanol partial pressure of 400 hPa and an oxygen partial pressure of 300 hPa. Cyclohexanol was fed at a contact time of 41 g h mol^{-1}.

3. RESULTS AND DISCUSSION

3.1 *Catalyst characterization*

The results of XPS (Table 1) suggest that all treatments aimed at achieving chemical functionalization of the carbon surface lead to the formation of carboxylic, and alcoholic and ketonic functional groups. Treatment with HNO_3 (sample C2) lead to the highest content of carboxylic groups (3.2% C 1s), while treatments with N_2O (sample C1), H_2O_2 (sample C3), air (sample C4) and O_2 (sample C5), form mainly alcoholic (probably phenolic) and ketonic groups.

On the other hand, sample C1 does not show any XPS peak assignable to sp_2 carbon. Since the XPS technique only provides information about the external surface of solid particles, that observation implies that on the outer surface of the carbon particles most of the aromatic structure was destroyed.

Surface areas and pore volumes (Table 2) measured from the nitrogen adsorption data at 77 K show clearly that, with the exception of sample C1, all the carbon samples are essentially microporous. On the contrary, for sample C1 the external area (macro and mesoporous area) is much higher than the microporous area. This observation suggests that this carbon sample was subjected to strong oxidation conditions leading to a partial gasification of the carbon, which is in complete agreement with the XPS results (Table 1).

Figure 1 shows the TPD profiles of the carbon samples. The samples treated with HNO_3 and H_2O_2 (C2 and C3, respectively) show strong CO_2 desorption signals in a relatively low temperature range (180–400 °C, Fig. 1(A)). Such low temperature CO_2 desorption peaks have been assigned to the decomposition of carboxylic acid groups [17,18]. On the other hand samples C1, C4 and C5, subjected to high temperature treatments, do not show those low temperature CO_2 desorption peaks. Instead, they exhibit relatively strong CO desorption signals at high temperatures (Fig. 1(B)), corresponding to the decomposition of alcoholic and ketonic functional groups [17,18].

From all the samples tested only samples C1 and C2 exhibited NO desorption signals (Fig. 1(C)).

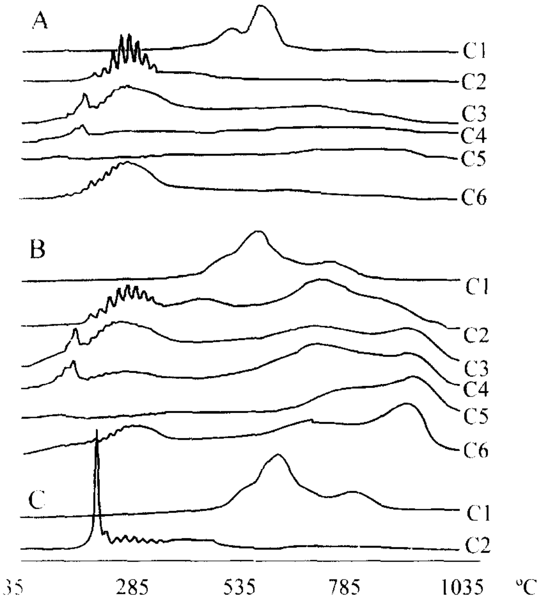

Fig. 1 TPD profiles of the catalyst samples. (A) CO_2; (B) CO; (C) NO.

Table 1. Area (%) of the relevant XPS peaks of the activated carbon studied

A. C 1s-associated peaks relative to 100% C 1s

Sample	Csp$_2$	Csp$_3$	COR	C=O	COOR
C1	—	61.1	24.1	2.5	1.0
C2	44.1	23.6	12.0	6.1	3.2
C3	46.8	23.9	14.4	2.8	1.2
C4	46.6	24.4	12.8	3.3	1.6
C5	46.7	24.0	13.3	3.5	1.5
C6	45.3	24.8	13.3	3.1	1.7

B. O 1s-associated peaks relative to 100% C 1s

Sample	Aromatic C=O	COC, COH, COOR, C=O	Phenol, COOR
C1	30.8	31.9	26.6
C2	24.5	45.9	16.1
C3	23.2	46.1	15.9
C4	16.2	38.5	18.3
C5	23.0	36.9	28.0
C6	19.2	38.3	25.0

C. Relative percentages of carbon, oxygen and nitrogen

Sample	% C	% O	% N
C1	90.06	9.76	0.19
C2	85.45	13.52	1.03
C3	92.99	6.63	0.37
C4	92.68	6.9	0.42
C5	94.97	4.67	0.35
C6	93.69	5.83	0.48

Table 2. Textural characterization of the carbon samples studied; external and micropore areas are expressed as percentages of the total surface area

Sample	Surface area* (m^2 g^{-1})	External area† (%)	Micropore area† (%)	Pore volume (cm^3 g^{-1})
C1	1446	64	36	1.178
C2	1242	28	72	0.598
C3	1205	26	74	0.580
C4	1314	25	75	0.622
C5	1292	25	75	0.613
C6	1235	24	76	0.580
C2‡	22	—	—	0.011

*Langmuir.

†*t*-Method.

‡After 250 minutes on stream.

However, sample C2 (HNO_3 treated) shows a narrow peak at *ca* 170°C, probably due to the decomposition of HNO_3 residues adsorbed on the carbon's surface. In contrast, sample C1 exhibits a high temperature broad NO desorption band (470–890°C), thereby revealing the presence of functional groups containing nitrogen strongly bound to the carbon structure. Since XPS analysis reveals a low surface nitrogen content (Table 2), possibly those functional groups are located deeply inside the pores.

The acid–base neutralization capacities of the carbon samples (Table 3) are in good agreement with the results already discussed. Sample C2 exhibits the highest uptake of each of the bases tested, thus revealing itself to be the most acidic sample. The high acidity of sample C2 is also confirmed by its low pzc value (2.88). According to Boehm [19] the high uptake of $NaHCO_3$ corresponds to a high content of free carboxylic acid groups. However, this sample shows a much higher uptake of Na_2CO_3 and

Table 3. Neutralization behaviour of the carbon samples (Boehm titration). Uptake of bases expressed in m-equiv/100 g of carbon

Sample	NaOH	Na_2CO_3	$NaHCO_3$	PZC
C1	69	30	15	1.64
C2	100	100	15	2.88
C3	55	20	10	6.14
C4	53	10	10	6.47
C5	49	12.5	12.5	7.41
C6	36	10	0	6.86
C1*	–	–		2.3

*After TPR experiment.

NaOH. According to Boehm, this result suggest a high content in carboxylic groups in the form of lactone rings. The similar value obtained for the uptake of those two bases by sample C2 indicates a very low content of phenols.

Samples C1 and C3 to C6 exhibit relatively large differences between the uptakes of NaOH and Na_2CO_3 (20–40 m-equiv/100 g), indicating that their phenolic group contents are high. With the exception of C1 and C2, all these samples show relatively high pzc values (between 6 and 8), indicating that the samples treated with air, O_2 and H_2O_2 also exhibit basic surfaces, probably due to the presence of carbonyl groups in them.

Sample C1 in particular shows a somewhat peculiar acid–base behaviour. It bears not only a high content of acid sites, as its high base uptakes reveals, but also shows the highest acid strength, as revealed by its very low pzc value. In spite of this high acidity, the absence of a low temperature CO_2 desorption band in the TPD profile suggests the absence of weakly thermostable carboxylic acid groups, in agreement with the XPS results (Table 1) which indicate a relatively low content in carboxylic acid groups.

Although XPS results suggest that most of the carbon aromatic structure on the outer layers of C1 particles has disappeared, that structure remains possibly intact inside the particles, in regions accessible through their pore system. As mentioned above, the NO TPD profile of sample C1 reveals the presence of nitrogen containing groups strongly bound to the carbon. Therefore, a possible explanation for the acid–base behaviour of this sample consists in assuming that those nitrogen containing groups are nitro groups bound to the aromatic rings of the carbon. As a consequence, the neighbouring phenolic groups would have their acid strength enhanced by an inductive effect.

The above hypothesis is also supported by the results of TPR experiments. Figure 2 shows the profile of the hydrogen uptake during a TPR of sample C1, in the temperature range 50–350°C, compared to that of a sample oxidized with oxygen (C5). The TPR profile of sample C1 not only shows a higher hydrogen uptake than that of sample C5 but also exhibits a maximum at a lower temperature. It is known that the hydrogen consumption during the TPR of an activated carbon is due to either chemisorption on the nascent sites formed by decomposition of oxygenated functional groups, or to the direct hydrogenation of those groups [17,18]. However, Calo *et al.* [18] reported a low temperature water evolution peak during the TPR of a carbon sample previously treated with HNO_3. That peak was attributed to the decomposition of carboxylic acid groups. However, that water evolution peak was not coincident with any noticeable hydrogen consumption [18]. Therefore, the TPR profile of sample C1 exhibiting a strong hydrogen uptake in the low temperature range, suggests the presence of functional groups other than carboxylic acid groups in C1 but not in C5. On the other hand, sample C1 shows a higher pzc value after reduction (2.3) than before reduction (1.64). In the absence of nitro or carboxyl groups the pzc value could be expected to decrease upon reduction, due to the transformation of carbonyl groups into phenolic groups. The increase of the pzc value could be interpreted as being due to the reduction of nitro groups to nitroso or amine groups, which exhibit basic properties.

3.2 *Reaction studies*

The reaction of cyclohexanol catalyzed by metals and metal ions on a variety of supports, including carbon, has been widely studied [1–3,5,20]. It is well known that cyclohexanol undergoes dehydrogenation not only on the C–O bond to give cyclohexanone, but also in the cyclohexane ring to yield phenol. Simultaneously, the carbon acid sites can catalyze the dehydration to cyclohexene which, in turn, can undergo dehydrogenation to yield benzene (Fig. 3).

Over all the carbon catalyst samples tested in this work cyclohexene, benzene, cyclohexanone and phenol were found to be the main products of the gas phase reaction of cyclohexanol. Figures 4 and 5 show the dependence on the reaction temperature of conversion and selectivity, respectively, for the catalyst sample C3. In agreement with what was

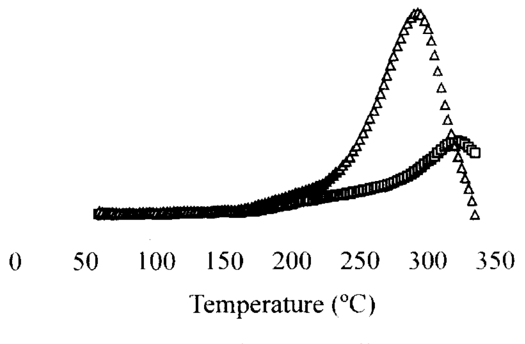

Fig. 2. Hydrogen consumption TPR profiles. △, C1; □, C5. The curves are plotted on the same relative scale.

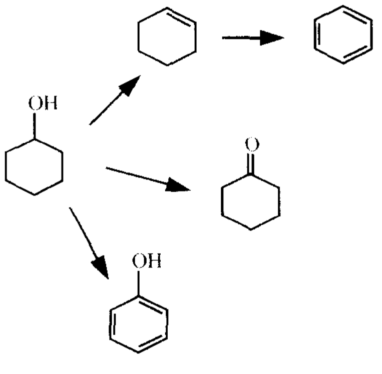

Fig. 3. Reaction scheme for the gas phase conversion of cyclohexane over carbon catalysts.

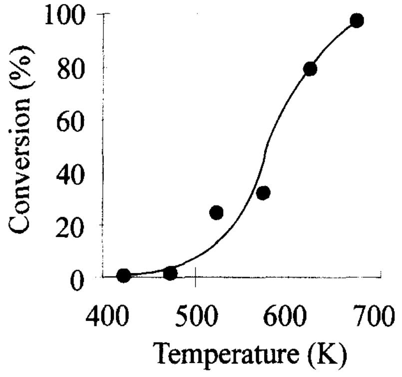

Fig. 4. Dependence of cyclohexane conversion on reaction temperature.

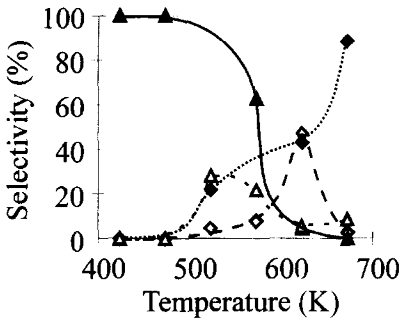

Fig. 5. Dependence of selectivity on reaction temperature. ♦, Cyclohexane; ◇, benzene; ▲, cyclohexane; △, phenol.

previously observed for the non-oxidative dehydrogenation of aliphatic alcohols over carbon catalysts [9–11] it was found that while the selectivity to cyclohexanone decreases with temperature, the selectivity towards cyclohexene increases. This result shows clearly that the dehydration reaction is favoured by an increase in reaction temperature.

The dependence of conversion on time-on-stream is shown in Fig. 6. The highest activity and stability are reached with the catalyst sample C1 (treated with N_2O). This stability is probably due to the mesoporous character of this sample (Table 2).

With the exception of sample C2 (treated with HNO_3), for all the other catalyst samples an increase in activity is observed during the first 10–20 minutes of time-on-stream. Assuming the concerted mechanism for the dehydrogenation reaction (Fig. 7), as proposed by several authors for the oxydehydrogenation of ethylbenzene [8,21–23], that initial increase in activity could correspond to the initial oxidation of phenolic groups to quinone groups. On the other hand, sample C2 exhibits initially a high activity (~98% conversion) which remains constant during the first 40 minutes on stream. After that period of time, the sample undergoes strong deactivation. After 180 minutes on stream, conversion is <20%.

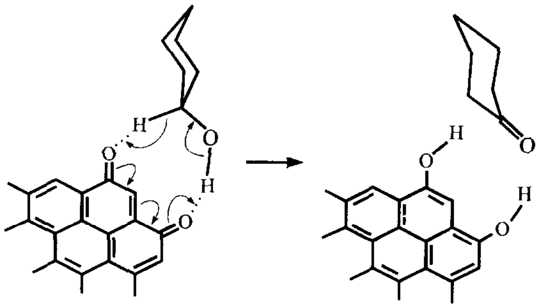

Fig. 7. Mechanism of the oxidative dehydrogenation of cyclohexanol over an oxidized carbon.

That loss of activity can be explained, at least partially, by coke accumulation. It was observed that the sample's surface area decreases from *ca* 1200 m^2 g^{-1} before use to 22 m^2 g^{-1} after 250 min on stream. In addition, deactivation can also be caused by decarboxylation. As discussed above, sample C2 seems to bear a high content of carboxylic acid groups exhibiting strong TPD CO_2 desorption peaks in the temperature range 180–400°C. Since the reaction is carried out at 350°C, catalyst decarboxylation can be expected to occur simultaneously. This expectation is also supported by the trends in selectivity towards cyclohexanone (Fig. 8) and towards cyclohexene (Fig. 9). The initial part of the curve illustrating the selectivity towards cyclohexanone for the catalyst sample C2 (Fig. 8), more or less parallels the overall conversion curve for the same sample. Since alcohol dehydration takes place preferentially

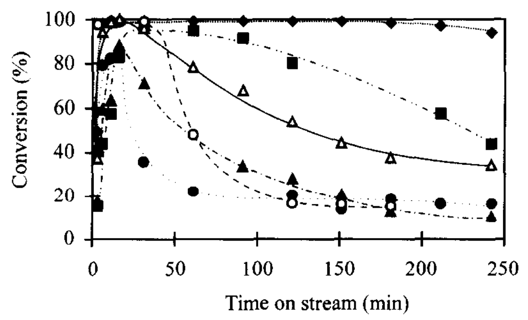

Fig. 6. Cyclohexanol conversion as a function of time on stream for the different carbon catalysts. ♦, C1; ○, C2; △, C3; ●, C4; ▲, C5; ■, C6.

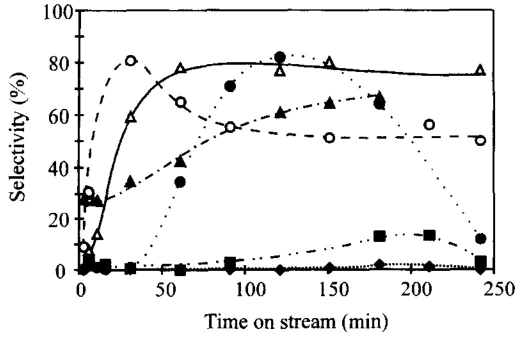

Fig. 8. Selectivity to cyclohexanone as a function of time on stream for the different carbon catalysts. ♦, C1; ●, C2; △, C3; ○, C4; ▲, C5; ■, C6.

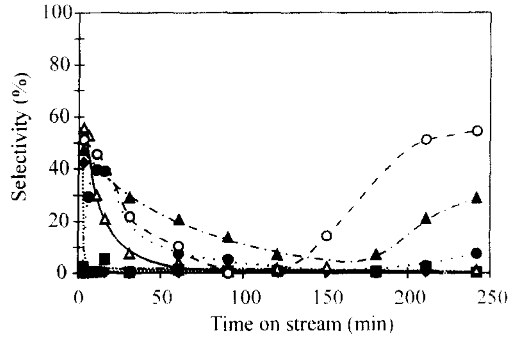

Fig. 9. Selectivity to cyclohexene as a function of time on stream for the different carbon catalysts. ◆, C1; ○, C2; △, C3; ●, C4; ▲, C5; ■, C6.

on the strongest acid sites [9–11], which are the free carboxylic groups, selectivity to cyclohexene is initially high and it decreases with time-on-stream as decarboxylation occurs (Fig. 9). Correspondingly, selectivity to cyclohexanone (Fig. 8) remains <3% during the first 30 minutes on stream, increasing to *ca* 80% after extensive decarboxylation. The further decrease in selectivity observed for higher time-on-stream is possibly due to coking. According to Szymanski and Rychlicki [10] dehydration takes place preferentially on acid sites located on the outer surface of carbon particles. As the pore system of the catalyst particles becomes increasingly blocked due to coke accumulation, the reaction takes place more and more on the outer surface. The remaining carboxylic acid groups or phenols located on this outer surface are thus able to promote the dehydrogenation to cyclohexene.

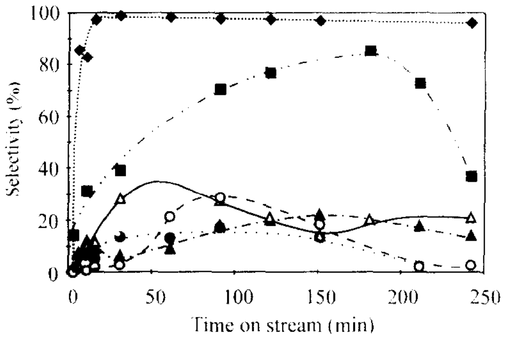

Fig. 10. Selectivity to phenol as a function of time on stream for the different carbon catalysts. ◆, C1; ○, C2; △, C3; ●, C4; ▲, C5; ■, C6.

The previous explanation can also account for the trends in selectivity towards cyclohexene (Fig. 9). With the exception of samples C1 and C5, all the other catalyst samples show, more or less, a high initial selectivity which decreases with time-on-stream to very low values, possibly due to decarboxylation. At high values of time-on-stream the selectivity towards cyclohexene increases again because now the reaction takes place predominantly on the outer surface of the catalyst particles.

As expected, because benzene is a product of the dehydrogenation of cyclohexene, the selectivity towards benzene (not shown) exhibits a behaviour similar to that of the selectivity to cyclohexene for all the catalyst samples tested.

The best selectivities towards cyclohexanone are obtained with the catalyst samples oxidized with hydrogen peroxide or oxygen (samples C3–C5, Fig. 8). As already shown, these catalyst samples bear the highest content in phenol groups. With the catalyst sample obtained by treatment with H_2O_2 selectivity remains more or less constant even at high

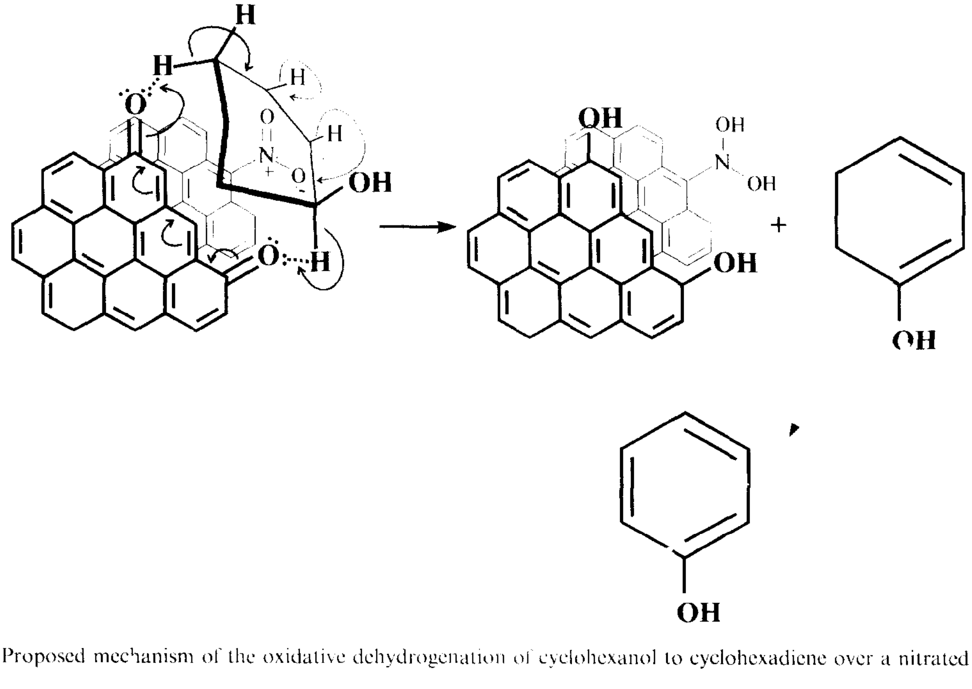

Fig. 11. Proposed mechanism of the oxidative dehydrogenation of cyclohexanol to cyclohexadiene over a nitrated carbon.

contact times. After 250 minutes on stream, selectivity towards cyclohexanone is still *ca* 75% at a conversion of *ca* 30%. Assuming the mechanism of Fig. 7 the initial increase of selectivity with time-on-stream can be explained by the initial oxidation of phenols to quinones.

On the other hand, samples C1 and C6 (the untreated activated carbon) show the worst selectivities to cyclohexanone. The behaviour of sample C6, however, can be justified by the results of Boehm titration (Table 2): the smallest uptakes of the tested bases indicates the lowest content in oxygenated functional groups.

The catalytic behaviour of sample C1 seems to be very peculiar. As pointed out above, it exhibits the highest stability: after 250 minutes on stream conversion remains practically unchanged *ca* 95%. But this sample also exhibits the highest selectivity to phenol (Fig. 10), which also remains unchanged with time-on-stream: *ca* 97%.

Although sample C1 shows the lowest pzc value indicating a high acidity, it does not promote the dehydration reaction. Therefore, for alcohol dehydration the presence of carboxylic groups on the carbon surface seems to be necessary.

Instead of alcohol dehydration, sample C1 promotes dehydrogenation. However, this dehydrogenation takes place on the cyclohexane ring yielding phenol, and not on the C–O bond. Assuming the presence of nitro groups in this catalyst sample, an explanation for this peculiar behaviour could be provided by the mechanism shown in Fig. 11: dehydrogenation would take place in a concerted mechanism involving two quinone groups and a nitro group located in two different basal planes. This reaction would lead to cyclohexadienol which, by further dehydrogenation would give phenol.

4. CONCLUSIONS

The main products of the gas phase reaction of cyclohexanol over carbon catalysts are cyclohexene, cyclohexanone, phenol and benzene. The surface functional groups play an important role in cyclohexanol conversion and selectivity.

The catalytic activity is determined by the presence and the character of oxygen surface groups. Dehydration to cyclohexene takes place preferentially on the carboxylic acid groups and is improved by an increase in temperature. The catalyst deactivation seems to be due not only to coke formation but also to decarboxylation.

The best selectivities to cyclohexanone are obtained with the catalyst samples treated with hydrogen peroxide or oxygen, with high contents in phenolic groups. With the catalyst sample treated with H_2O_2 selectivity to cyclohexanone still 75% at 30% conversion.

The catalyst sample treated with N_2O not only shows the highest stability but is also highly selective to phenol. This high selectivity to phenol can be explained by assuming the participation of nitro groups in the oxydehydration mechanism.

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