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Catalysis Today 137 (2008) 460–465

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Catalytic destruction of methyl tertiary butyl ether (MTBE) using oxidized carbon

Grzegorz S. Szymański *

Faculty of Chemistry, Nicholas Copernicus University, Gagarina 7, 87-100 Toruń, Poland

Abstract

Decomposition of methyl *tert*-butyl ether (MTBE) in the gas phase was studied using carbon catalysts with chemically modified surface. Carbon samples with different surface chemical properties were obtained from commercial activated carbon D43/1 (CarboTech, Essen, Germany) by oxidation in liquid phase with various oxidants as well as in air. The catalytic tests were performed in a flow reactor at a temperature range of 353–473 K. Isobutene and methanol are the only products of the MTBE decomposition. The generation of surface acidic oxides considerably enhances the catalytic activity of the carbons. However, the activity is controlled not only by the number and strength of acidic groups, but also by their accessibility. The most active carbon is that oxidized with air at 673 K, which contains pores wider than the pores of other oxidized carbons.
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Keywords: Activated carbon; MTBE; Decomposition; Acid–base catalysis

1. Introduction

There is an urgent need to find technically and economically feasible solutions to prevent contamination with MTBE in general and to refine water from MTBE in particular. Several technologies have been proposed, some of which proven to be practical, such as air stripping, sorption with granular activated carbon, biofiltration, chemical oxidation (with ozone, ozone/hydrogen peroxide or ultraviolet/hydrogen peroxide), and separation using hydrophobic hollow fiber membranes [1]. Air stripping and the hydrophobic hollow fiber membranes are the most cost-effective options, but it is necessary to consider the additional treatment of the MTBE vapors in the gas phase, using either adsorption or catalytic destruction. One alternative is to use the gas-phase catalytic decomposition with or without oxygen. To increase the reaction rate, the gas phase is usually heated before the decomposition, which requires the use of an external fuel source since the MTBE vapors are usually too dilute to sustain a high temperature in the catalytic reactor. Lower treatment costs can be achieved if the catalytic decomposition can be conducted at relatively low temperatures. However, only heteropolyacids and ion-exchange resins are catalytically active at such temperatures but they have some drawbacks. They strongly adsorb polar substances, like water and alcohols, the presence of which strongly retards the reaction [2].

The granular activated carbon can be used not only as an adsorbent or catalyst support but also as a true catalyst. Carbon surface chemistry is mainly determined by the presence of various oxygen surface complexes. The surface groups most often suggested are carboxyl, phenolic hydroxyl, and quinone carbonyl groups [3,4]. Slightly fewer in number are the reports on ether, peroxide, ester groups, lactones, carboxylic acid anhydrides and cyclic peroxides. Because of the presence of such surface oxides, carbons can be used for acid–base reactions. It was reported earlier that suitably oxidized activated carbon effectively promotes dehydration of aliphatic alcohols (C_2–C_4) at relatively low temperatures due to the presence of acidic sites of moderate strength [5,6]. In addition, MTBE demonstrates low affinity towards the granular activated carbon. Preliminary studies have shown that activated carbon catalyzes also the decomposition of MTBE [7]. Thus, it seems reasonable to study the catalytic behavior of modified activated carbons in this process in more detail.

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* Fax: +48 56 6542477.
E-mail address: gszym@chem.uni.torun.pl.

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doi:10.1016/j.cattod.2008.01.003

2. Experimental

2.1. Carbon modification and characterization

Commercial granulated activated carbon D43/1 (D), obtained from CarboTech GmbH (Essen, Germany), was used. Portions of this carbon were oxidized in liquid phase using (i) 65% HNO_3 (353 K, 3 h) (DONA), (ii) Hummer's reagent (mixture of H_2SO_4, $KMnO_4$, and $NaNO_3$) [8] (338 K, 1 or 3 h) (DOHR1, DOHR3), (iii) 10% $(NH_4)_2S_2O_8$ in 1 M H_2SO_4 (353 K, 12 h) (DOAPS) and (iv) 30% hydrogen peroxide (368 K, 5 h) (DOHP). All oxidized samples were washed with redistilled water until the rest of oxidant and low molecular products of oxidation were removed. After drying at 383 K overnight, portions of the oxidized carbons were additionally heated at 498 K and 573 K for 3 h, respectively. In addition, a portion of the virgin carbon D43/1 was deashed with HF and HCl by the Korver's method [9] (DD) and subsequently oxidized with air (25 dm^3/h, 623 K, 4 h or 673 K, 3 h) (DDOA6234, DDOA6733). All the prepared samples were then stored in ambient atmosphere.

The porous texture of the carbons was determined from the nitrogen adsorption isotherm at 77 K using the Dubinin–Astakhov model [10]:

$$W_{DA} = W_0 \exp\left\{ -\left(\frac{A}{\beta E_0} \right)^n \right\}$$

where W_0 is the total micropore volume, E_0 is the characteristic energy of adsorption, A is the adsorption potential, β and n are the affinity coefficient and parameter of D-A equation, respectively. In addition, the mean micropore width (L_{mic}) was calculated by means of the model of slit shaped pores [10]:

$$L_{mic} = \frac{10.8}{E_0 - 11.4}$$

The adsorption measurements were conducted volumetrically with an automatic ASAP 2010 instrument (Micromeritics, Atlanta, USA) at 77 K.

Elemental composition was determined using a Vario El III CHN analyzer (Elementar Analysensysteme GmbH, Hanau, Germany).

The acidic group content was determined according to the Boehm's [3,4] method by neutralization with bases of increasing strength (sodium bicarbonate, $pK_a = 6.37$; sodium carbonate, $pK_a = 10.25$; sodium hydroxide, $pK_a = 15.74$; sodium ethoxide, $pK_a = 20.58$), while the number of basic groups was estimated by neutralization with 0.05 M hydrochloric acid. Additionally, the acidities (pHs) of carbon slurries in 0.1 M NaCl were determined.

Surface chemistry of the modified carbons was studied by the FTIR spectroscopy. The transmission FTIR spectra of the carbon samples were obtained with a PerkinElmer FHR Spectrum 2000 spectrometer using the KBr pellet technique [9]. In addition, the surface chemistry of the investigated carbons was characterized by temperature-programmed desorption (TPD-QMS) of decomposition products. The TPD-QMS experiments were carried out using a Netzsch STA409C apparatus equipped with a quadrupole mass spectrometer. The experiments were carried out for 50 mg of sample with 50 mg of Al_2O_3 as reference. At the beginning of each experiment the sample was evacuated to 1 mbar in order to remove air and physically adsorbed gases. Then it was linearly heated at 10 K min^{-1} up to 1273 K in a stream of pure helium. The weight loss and the intensities of mass numbers 18 (H_2O), 28 (CO), and 44 (CO_2) were recorded as a function of temperature.

2.2. Catalytic tests

The decomposition of MTBE was investigated in a fixed-bed flow-type microreactor, made of glass (length 10 cm, inner diameter 5 mm), operating under atmospheric pressure. The catalytic tests were conducted in the temperature range of 353–473 K. The product analysis was performed by on-line gas chromatography (column: Carbowax 20M on Chromosorb WAW (10%), length 3 m, i.d. 3 mm; detector: FID). The GC–MS identification of gaseous products was carried out using a Varian 3300 gas chromatograph (column: DB 17, length 30 m, i.d. 0.249 mm) coupled with an ITD 800 mass spectrometer (Thermo Finngan MAT, San Jose, USA). Prior to the catalytic tests, the samples placed in the microreactor were conditioned in a helium stream at 383 K for 2 h.

3. Results and discussion

3.1. Characterization of carbon catalysts

It was already demonstrated that both the commercial activated carbon D43/1 and its deashed form reveal a well-developed porous structure with a high micro- and macroporosity [5,9] (Table 1). However, as for other carbon materials, some decrease in the pore volume and mean micropore width (L_{mic}) after oxidation in the liquid phase was observed (Table 1). This is a consequence of the fixation of a part of surface oxygen complexes at the pore entrances [11,12] which increases their constriction. Such functionalities narrows pore entrances or even may block them [12]. The decreasing value of the parameter n (Table 1) indicates that the microporosity has become less uniform [10]. After annealing in a stream of helium at 498 K, the restitution of the lost porosity occurs due to the removal of the mentioned groups. This suggests that heating under mild conditions removes mainly surface groups located at the entrances of the pores. In contrast to oxidation in the liquid phase, the oxidation with air at 673 K increases the micropore volume as well as pore diameter due to partial burning.

The application of several oxidants with different reactivity leads to generation of various amounts of oxygen surface oxides with different acid–base properties. The higher the oxygen content, the higher the acidity (Table 1). Among the used oxidants nitric acid is the most efficient in oxidation of activated carbon.

According to Boehm [3,4], $NaHCO_3$ ($pK_a = 6.37$) neutralizes the carboxylic groups (–COOH), Na_2CO_3 ($pK_a = 10.25$)

Table 1
Surface characteristics of the oxidized carbons

Carbon	Apparent surface area, S_{BET} (m^2/g)	Micropore volume, W_0 (cm^3/g)	n	Characteristic energy, E_0 (kJ/mol)	Micropore width, L_{mic} (nm)	Oxygen content (%)	pH of carbon suspension	Concentration of surface acidic and basic groups (mequiv./g)				
								$NaHCO_3$, pK_a 6.37	Na_2CO_3, pK_a 10.25	NaOH, pK_a 15.74	EtONa, pK_a 20.58	HCl
D	920	0.46	1.8	19.6	1.32	6.0	9.44	–	–	–	–	0.545
DD	875	0.43	2.7	20.3	1.21	4.7	8.90	0.006	0.078	0.199	0.439	0.457
DONA	827	0.33	2.7	21.5	1.07	14.2	3.27	0.942	1.308	1.891	2.143	0.207
DOHR3	870	0.35	3.1	21.5	1.07	10.6	3.92	0.451	0.653	1.122	1.441	0.274
DOHR1	825	0.34	3.1	22.1	1.02	10.2	3.88	0.378	0.690	1.084	1.376	0.321
DOAPS	864	0.35	2.9	21.6	1.06	9.9	3.92	0.426	0.769	1.146	1.354	0.284
DOHP	920	0.39	2.4	21.3	1.09	6.5	7.60	0.098	0.268	0.414	0.513	0.405
DONA498	856	0.42	1.8	19.7	1.30	13.8	3.38	0.720	1.029	1.790	1.932	0.179
DOHR3498	877	0.43	1.9	20.2	1.23	10.2	4.71	0.370	0.540	1.105	1.350	0.232
DOHR1498	878	0.41	2.1	20.7	1.16	9.9	4.93	0.360	0.537	1.061	1.411	0.257
DOAPS498	881	0.44	1.8	20.0	1.25	9.6	4.65	0.411	0.645	1.063	1.361	0.278
DOHP498	919	0.48	1.6	20.0	1.26	6.2	7.51	0.016	0.108	0.323	0.437	0.379
DONA573	897	0.43	1.7	19.3	1.37	12.4	3.83	0.613	0.995	1.624	1.752	0.206
DOHR3573	–	–	–	–	–	9.7	4.57	0.312	0.558	0.958	1.226	0.299
DOAPS573	–	–	–	–	–	9.0	4.72	0.281	0.516	0.989	1.219	0.264
DOHP573	–	–	–	–	–	5.9	8.40	0	0.082	0.250	0.455	0.349
DDO6234	931	0.44	2.0	20.0	1.26	6.9	7.14	0.049	0.224	0.543	0.755	0.446
DDO6733	1060	0.50	1.8	18.8	1.47	10.6	4.77	0.393	0.577	1.152	1.260	0.317
DONA498C	865	0.42	1.8	19.3	1.36	–	–	–	–	–	–	–

neutralizes the carboxylic (–COOH), and lactonic groups (–COO–), NaOH (pK_a = 15.74) neutralizes the carboxylic (–COOH), lactonic (–COO–), and phenolic (–OH) structures whereas C_2H_5ONa (pK_a = 20.58) neutralizes all the groups mentioned above and reacts with carbonyls (>C=O). However, other authors [13] indicated that the validity of this technique to determine different acidic groups is open to question, because the same acidic functional group, depending upon its location, may have different strength; thus the different acidities obtained by neutralizing alkalies of different relative strengths might be to the neutralization of the same acid group to different extents. As the virgin activated carbon (D) contains considerable amounts of inorganic contaminants of the basic character, it was impossible to determine the content of surface acidic groups. However, after removing the impurities in the process of deashing, their contents could be established. The deashed carbon DD becomes amphoteric, with a slight excess of basic properties (Table 1). The oxidation enhances the formation of acidic (carboxyls, lactones and phenolic groups)

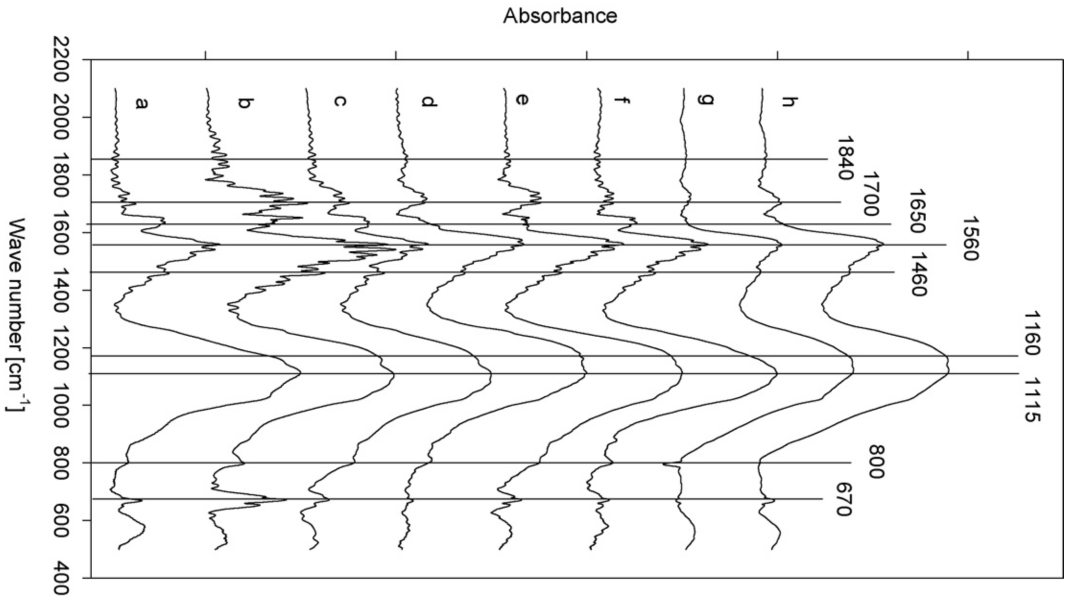

Fig. 1. FTIR spectra of the oxidized carbons: (a) D; (b) DONA498; (c) DOHR3498; (d) DOHR1498; (e) DOAPS498; (f) DOHP498; (g) DO6234; (h) DO6733.

as well as neutral (carbonyls) surface structures. The acidic groups with $pK_a < 10.25$ (carboxylic and lactonic structures) are partially removed after gradual desorption under mild conditions (498–573 K) with simultaneous formation of additional weak acidic groups (hydroxyls) (Table 1).

The obtained FTIR spectra confirm the above-mentioned statements about the presence of carboxylic, phenolic and carbonyl structures in different chemical environments. Below 2000 cm^{-1}, the FTIR spectra for all the investigated carbons (Fig. 1) exhibit absorptions typical of oxygen species. The bands at (i) 1710 cm^{-1}, (ii) 1645 cm^{-1}, and (iii) 1560 cm^{-1} can be attributed to the stretching vibrations of C=O moieties in, respectively, (i) carboxylic, ester, lactone [13–17], (ii) quinone and/or ion-radical structures [13,15,16], and (iii) conjugated systems such as diketone, keto-ester, and keto-enol structures [14,17]. The overlapping peaks, which form an absorption band in the 1300–1000 cm^{-1} region, can be assigned to ether (symmetrical stretching vibrations), epi-oxide and phenolic structures existing in different structural environments [13–17]. Absorption below 800 cm^{-1} can be assigned to out-of-plane deformation vibrations of the C–H groups located at the edges of aromatic planes [14,17].

As for other carbon materials [13,15–17], after oxidation of the virgin carbon D43/1 (D), a new band characteristic of the carbonyl moieties in carboxylic anhydrides appears in the 1850–1800 cm^{-1} region [13,14,17] and simultaneously increases the intensity of the band assigned to the carbonyl functional group included in the carboxyl (*ca* 1710 cm^{-1}), diketone, keto-ester, and keto-enol (*ca* 1572 cm^{-1}) structures.

The TPD results for the virgin carbon D43/1 (D) as well as for its deashed form (DD) showed decomposition products (e.g. CO, CO_2, and H_2O) in considerable amounts. The treatment with oxidizing agents, especially with nitric acid, enhances the yield of these products (Figs. 2 and 3).

During thermal decomposition of surface oxygen containing groups CO_2 is produced from carboxylic acid at low temperatures, and from anhydrides, lactones or lactols at higher temperatures; CO results from phenols, ethers and carbonyls (and quinones). Carboxylic anhydrides give rise to both a CO and a CO_2 peak [5,18–24]. The CO_2 desorption profiles of the investigated carbons (with the exception of the DONA498 sample) show two broad peaks located at about 550 and 1050 K (Fig. 2). The former peak is tentatively assigned to carboxyl groups, whereas, the latter to anhydrides, lactones or lactols

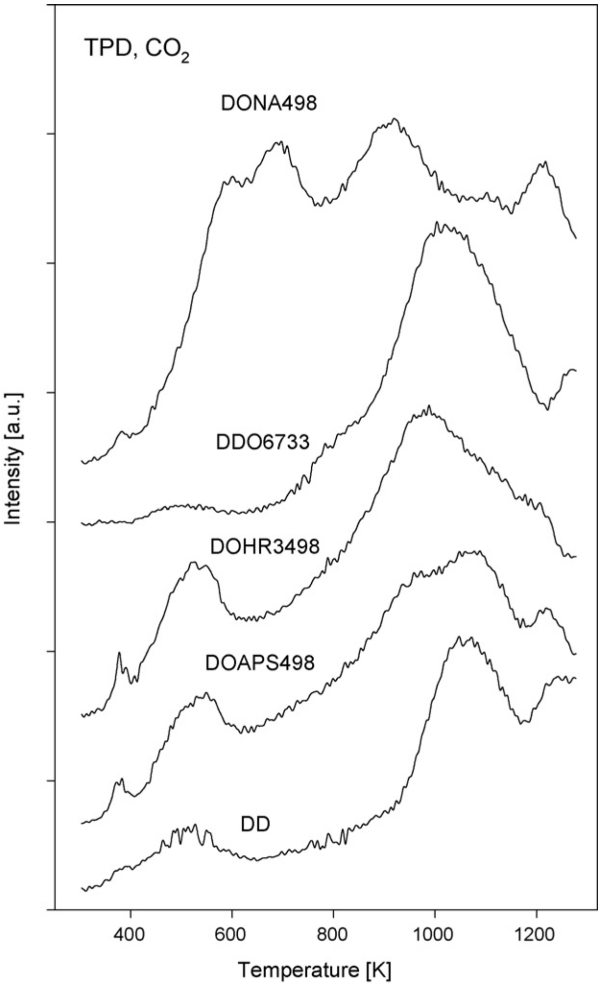

Fig. 2. CO_2 profiles for carbons DD, DONA498, DOHR3498, DOAPS498 and DDO6733.

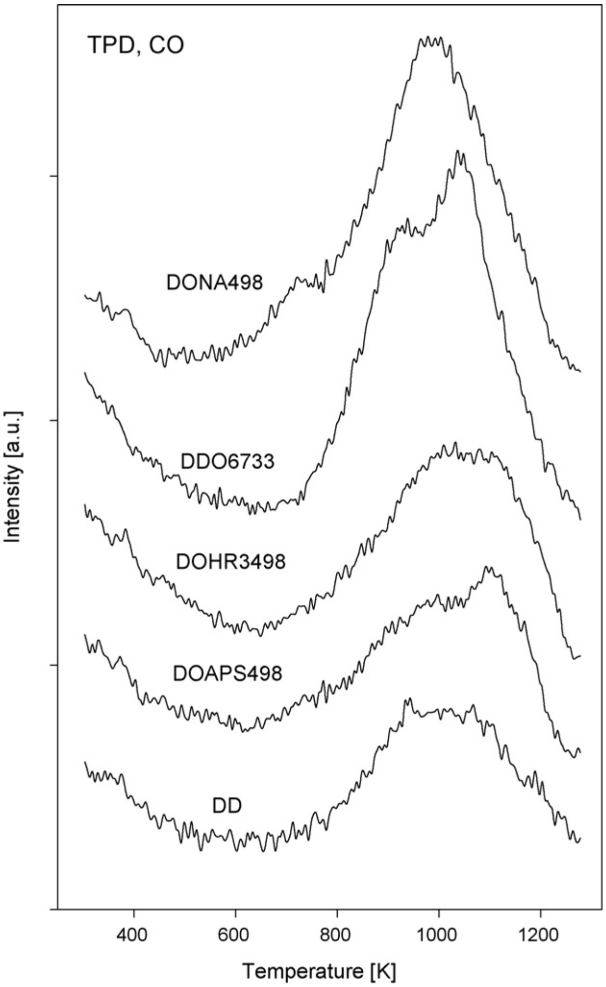

Fig. 3. CO profiles for carbons DD, DONA498, DOHR3498, DOAPS498 and DDO6733.

[5,18]. The cyclic structures are the dominating groups present on the surface of the carbon oxidized with air (DDO6733).

The CO_2 profile of DONA498 shows several broad overlapping peaks located at about 590, 680, 900, and 1200 K (Fig. 2). As carboxyl groups are thermally less stable than anhydrides or lactones, the peak that appears at 545–590 K is tentatively assigned to carboxyl groups, the second peak to anhydrides, lactones or lactols [5,18]. The peaks at 900 and 1200 K may suggest the presence of further chemically different lactones and/or the same oxygen complex existing in different environments [5,18].

The CO desorption profiles of all the investigated carbons show at higher temperatures a very broad peak which consists of at least two overlapping peaks located at about 950 and 1050 K, respectively (Fig. 3). The peak at 950 K can be assigned to phenol or hydroquinone groups [18,19,22–24], while the peak at 1050 K, to thermally more stable oxides, like semiquinones or quinones [5,19,21,22,24]. The highest intensity of the CO profile was observed for the DO6733 and DONA498 samples.

3.2. Catalytic activity

The preliminary GC–MS product analysis has shown that isobutene and methanol are the only products of the methyl *tert*-butyl ether decomposition. All the catalysts are active in this process in the investigated range of temperatures. Even the carbon sample with the lowest surface acidity (D) demonstrates a reasonable catalytic activity (Table 2). This indicates that weak acidic groups play also a role of active sites in the MTBE decomposition. The lack of changes in the porous structure after the catalytic run, e.g. for the DONA498 carbon (DONA498C in Table 2), indicates that there is no formation of deposits from reagents.

The carbon oxidized in air at 673 K (DDOA6733) exhibits the highest catalytic activity in spite of the fact that the carbon oxidized with nitric acid (DONA) is the most acidic. However, the increase in the feed rate diminishes drastically the MTBE conversion over the DDOA673 carbon, the activity of which becomes similar to that of other carbons (Table 2). The more developed porosity of the DDOA673 carbon, with wider pores (Table 1) than for other samples, indicates that steric effects play also an important role in this process as in the case of 2-methylpropan-2-ol dehydration over oxidized carbon [5]. According to the results of kinetic studies of the gas-phase decomposition of MTBE over porous solid acids [25–28], the MTBE molecule decomposition requires three acid sites. The surface reaction of the MTBE molecule bridged to two acidic groups of the catalyst with a third active site is the rate-

Table 2
Catalytic activity of the oxidized carbons

Carbon	MTBE conversion (%)							
	353 K	363 K	373 K	383 K	393 K	403 K	413 K	423 K
W/F = 51.8 kg s/mol								
D	0	0	0	1.1	3.3	6.8	14.9	27.4
DONA	1.2	3.5	7.4	15.2	27.4	43.1	62.2	81.6
DOHR3	1.56	1.9	7.3	12.8	29.4	43.6	71.7	86.0
DOHR1	0.90	2.8	5.7	12.4	25.0	51.8	63.2	79.3
DOAPS	1.1	2.7	6.3	13.4	23.4	33.7	59.1	79.8
DOHP	0.0	0.3	0.5	1.9	3.9	8.2	16.0	27.8
DONA498	1.3	3.7	7.5	15.2	29.0	46.7	67.2	90.1
DOHR3498	0.5	1.0	3.4	7.9	16.5	30.9	51.0	69.2
DOHR1498	0.4	2.2	5.1	9.7	16.6	30.0	42.8	61.6
DOAPS498	0.8	2.1	5.3	11.1	20.3	35.8	53.2	67.6
DOHP498	0.0	0.0	0.3	0.8	3.0	7.2	13.6	28.2
DONA573	0.7	2.4	6.1	13.9	26.0	44.5	60.6	84.9
DOHR3573	0.6	2.0	4.8	11.0	23.0	40.5	60.6	85.1
DOAPS573	0.6	1.4	3.9	8.5	17.0	28.8	46.1	63.5
DOHP573	0.0	0.2	0.6	1.5	3.6	8.8	15.5	27.7
DDOA6234	0.0	0.6	1.1	3.2	7.7	15.6	32.9	60.9
DDOA6733	7.7	17.2	32.9	52.4	80.2	100.0	100.0	100.0
W/F = 7.3 kg s/mol								
D	0.0	0.0	0.0	0.7	1.2	1.8	4.3	7.6
DONA	0.6	1.2	2.6	5.8	10.9	16.3	26.0	34.8
DOHR3	0.7	1.0	2.4	4.3	8.7	15.6	22.2	31.4
DOHR1	0.3	0.8	2.1	4.2	7.2	12.7	21.9	29.5
DOAPS	0.5	0.8	1.8	3.6	6.3	10.7	17.4	26.5
DOHP	0.0	0.0	0.0	0.8	1.8	2.1	4.1	7.6
DONA498	0. 6	1.1	2.3	4.6	8.1	13. 9	21.6	31.0
DDOA6234	0.0	0.5	0.8	1.5	2.8	6.0	12.4	22.5
DDOA6733	1.1	2.2	4.4	8.0	12.3	19.6	28.6	38.9

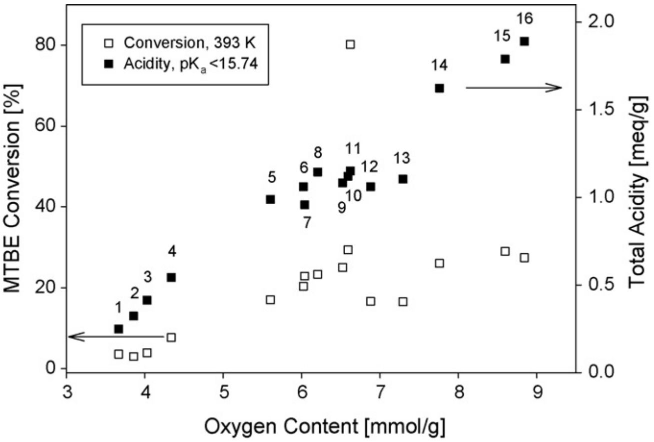

Fig. 4. The effect of oxygen content on the carbon acidity and the catalytic activity: (1) DOHP573; (2) DOHP498; (3) DOHP; (4) DDO6234; (5) DOAPS573; (6) DOAPS498; (7) DOHR3573; (8) DOHR1498; (9) DOAPS; (10) DOHR1; (11) DOHR3498; (12) DOHR3; (13) DDO6733; (14) DONA573; (15) DONA498; (16) DONA.

determining step. Thus, the extraordinarily high activity of DDOA673 is caused by more easier access of reagent molecules to active sites due the presence of wider pores. In case of narrower pores, when the concentration of surface groups is too high, the activity does not increase due to steric restrictions. Relation between the oxygen content and the catalytic activity (Fig. 4) indicates that there is some optimum concentration of surface oxides above which the activity does not change. For example, the acidic group content in the DONA carbon is so high that even the loss of reasonable amounts (20–30%) of most acidic groups ($pK_a < 6.37$) (Table 1) during heating does not affect its activity. On the other hand, for the other, less oxidized carbons, the partial desorption of acidic groups diminishes their activity.

4. Conclusions

The activated carbon D43/1 (D) promotes effectively the catalytic decomposition of MTBE at a temperature range of 353–473 K. Isobutene and methanol are the only products in this process. Generation of additional surface acidic oxides by oxidation with various oxidants enhances the catalytic activity. It seems that even weak acidic surface oxygen species with $pK_a < 15.74$ are catalytically active in the decomposition of MTBE into isobutene and methanol. However, the activity is controlled not only by the number and strength of acidic groups, but also by their accessibility. Thus, the carbon sample oxidized with air at 673 K is the most efficient one, which reveals the presence of pores with suitable diameter.

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