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Activated carbons containing TiO_2: Characterization and influence of a preparation method on the state of TiO_2 supported

J. PRZEPIÓRSKI*, N. YOSHIZAWA, Y. YAMADA‡
National Institute of Advanced Industrial Science and Technology, Onogawa 16-1, Tsukuba, Ibaraki 305-8569, Japan
E-mail: y-yamada@aist.go.jp

In this study preparation procedure and characterization of coal-based activated carbons supporting TiO_2 is presented. Decomposition of titanium organic complex introduced into three raw coals of a different composition is described and illustrated by XRD patterns taken at different stages of the preparations. Influence of a coal rank and titanium supported on coals on the development of a mesoporous structure is shown. Titanium revealed a positive influence on the formation of mesopores in activated carbons. Titanium contents were higher in those carbons activated for a longer time. Loss of some part of Ti supported was observed during preparation and the loss remained in a straight relation with the activation time. As confirmed by TEM, size of TiO_2 particles supported on the activated carbons increased with the activation time. Distribution of the particles was irregular. Rutile was the only crystalline form of TiO_2 found in Ti-loaded activated carbons.

1. Introduction

During preparation of city water, chlorine is often used as a disinfecting agent. However, in contact with large-moleculed humic acids (naturally present in waters), chlorine produces secondary contaminants commonly called as trihalomethanes (THMs). In order to make the water suitable for drinking, both, the humic acids and THMs have to be removed. As an alternative to conventional processes commonly used, we considered removal of the mentioned contaminants as possible to perform by use of a connection of both adsorption and photolysis. So, we believe that a carefully designed adsorbent containing mesopores and micropores, and additionally supporting a proper photocatalyst can be a proper material to get following targets:

- Adsorb small molecules of THMs in micropores
- Adsorb large molecules of humic acids in larger pores
- Decompose photocatalytically both kinds of the organic contaminants.

It is well known that finely dispersed TiO_2 suspended in water is often difficult to separate. This can be a serious drawback (overlooked in many studies) when a quick filtration of purified water from the photocatalyst is required. Hopefully, this problem can be overcome by use of Ti-loaded activated carbon instead of TiO_2 alone. Preparation of TiO_2-containing activated carbons was tried to be performed by several alternative methods: (i) by an impregnation of the activated carbon with a TiO_2 colloid [1], (ii) by the carbonization of a mixture of coal and TiO_2 [2], (iii) by the deposition of TiO_2 on the activated carbon by use of ionized cluster beam method [3, 4]. As we have already reported [5], titanium was found as a promoter for formation of mesopores in carbons.

It is common in catalytic processes (and also in the photolysis using crystalline TiO_2 [6]) that dispersion of catalyst remains in a straight relation with its catalytic efficiency. For that reason, finer particles of catalyst should exhibit a higher activity in catalytic processes. Hence, to obtain a proper dispersion of a catalyst, a great attention should be paid to the preparation conditions. In order to obtain the finely dispersed catalyst, in general, it is recommended to minimize duration of high temperature processes used during the manufacturing. Ti-loaded activated carbons described in our previous work [5] were prepared by one-step several minutes long carbonization and activation. Samples were quickly inserted to a high temperature zone of a furnace, kept there for a certain period of time, and then

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*Present Address: Technical University of Szczecin, Institute of Inorganic Chemical Technology and Environmental Engineering, ul. Pulaskiego 10, 70-322 Szczecin, Poland.

‡ Author to whom all correspondence should be addressed.

TABLE I Characteristics of raw coals

	Grodziec	Wirek	Uhli
Proximate analysis [wt%]			
Fixed C	52.5	61.5	69.7
Volatile matter (daf)	37.7	33.7	26.0
Moisture	3.2	1.9	1.3
Ash (db)	6.6	2.9	3.0
Elemental analysis [wt%]			
Carbon (daf)	83.1	85.2	89.2
Hydrogen (daf)	5.3	5.3	4.9
Nitrogen (daf)	1.7	1.4	1.4
Sulfur (db)	0.9	0.4	0.4
Oxygen (daf)	9.1	7.7	4.2

quickly removed to a low temperature zone. In this way we could avoid long heat-up and cool-down times required usually when conventional methods are used. By the decrease of the time of exposure to a high temperature we intended to minimize a possible catalytical graphitization that could occur because of a presence of inorganics in coals. Prepared in the described way Ti-loaded activated carbons showed presence of both anatase and brookite forms of TiO_2. Supported photocatalyst was only of several nm in size and was distributed uniformly over the activated carbon volumes. However, a main drawback of the method was that only very small amounts of carbon were possible to prepare in one lot. In order to increase the amount of activated carbon possible to obtain at once, we started to use an infrared image furnace. The furnace allowed reducing considerably residence time of samples at high temperatures, and increasing quantities of activated carbons possible to prepare in a single lot as wider described in the next section of this work.

2. Experimental section

2.1. Preparations

One Czech (Uhli) and Two Polish (Grodziec and Wirek) coals of different characteristics (see Table I) were used in this work. After grinding to a form of fine powder with particles below 100 mesh, 10 g of each raw coal was mixed with a solution of bis(2,4-pentanedionato)-titanium oxide (II) (hereinafter TiOAA), in THF (500 cm^3). Amount of TiOAA used was set as 1.37 g that correspond to 2.5 wt% of Ti in the raw coals. TiOAA was of 95% purity commercially available chemical, and THF was of a reagent grade (99.5%). Both chemicals were supplied by Wako, Co. Ltd., Japan, and were used directly without extra purification. Suspensions obtained in that way were stirred for 2 h at room temperature, followed by a distillation of the solvent under vacuum and at the temperature up to 100°C. In order to get dry powders, samples were kept in the same system at the temperature and under vacuum for 30 minutes. Subsequently, the impregnated powders were placed in a quartz boat and put into a quartz tube (40 mm in diameter) of a temperature-programmable horizontal infrared image furnace (Ulvac, Sinku-Riko, E410). To carbonize the impregnated coals, these were rapidly heated (heating rate: 400 $degmin^{-1}$) up to 900°C under N_2 flow (1.5 dm^3min^{-1}). After 10 min long residence at this high temperature, the system was quickly cooled down. Due to accumulate enough amounts of materials for further uses, the impregnated powders were subjected to the described processing repeatedly, in several lots (ca. 3 g of the impregnated powder per lot). Because of a partial fusion, cokes obtained during carbonization were ground again below 100 mesh of a grain size and then subjected to the activation process. An activation medium used in our study was a mixture of steam and nitrogen (relative humidity: 100% at 70°C, space velocity: 0.7 dm^3min^{-1}). In order to keep carbon during activation under continuous mixing, we designed and applied a rotating system, as illustrated in Fig. 1. The powdered coke (ca. 1.3 g per lot) was placed inside the rotating quartz chamber located in a central part of the tube of the infrared image furnace. The activating mixture could reach the rotating chamber through a quartz pipe, working also as a passage for a thermocouple used to control temperature of the process. The

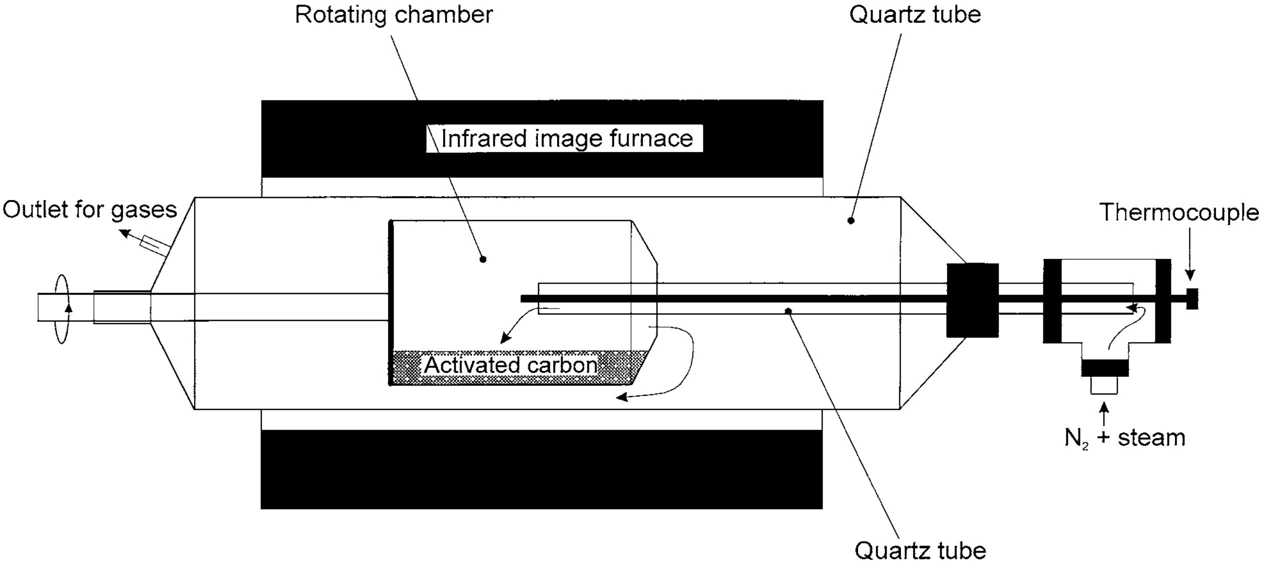

Figure 1 Drawing of the system used for activation.

TABLE II Duration of the activation process

Original coal	Activation time [min]	Burn-off [%]	
		Unloaded	Ti-loaded
Grodziec	60	52.5	43.6
	90	66.2	63.5
	120	76.7	73.4
Wirek	80	38.2	49.1
	110	51.0	59.3
	140	56.4	69.8
Uhli	100	40.3	44.6
	130	50.4	53.6
	160	61.3	67.9

temperature-time program used for the activation process was similar to that applied for the carbonization, however, samples were kept at 900°C in the stream of N_2/steam mixture for longer periods of time as shown in Table II. Steam for activation was introduced into the pre-washed with nitrogen rotating chamber at the initial phase of the process, when temperature was 100°C. After heating at 900°C, when temperature dropped down to 300°C, N_2/steam mixture flow was stopped and nitrogen alone was introduced to the system again. For a reference, non-loaded activated carbons were also prepared. Essentially, the preparation procedure employed in these cases was similar to that applied for the preparation of Ti-loaded activated carbons. Certainly, the impregnation of coals with TiOAA was omitted in these cases. For a simplification, each activated carbon used in this work has got some short name. For example: GTi90 is a Ti-loaded, Grodziec coal-based carbon, activated for 90 min.

2.2. Measurements

The elemental analyses of the coals were performed using Leco CHN-1000 apparatus (to analyze C, N, and H contents) and Leco S-132 (to analyze S contents). Proximate analyses of the coals, i.e. moisture, ash, and volatile matter contents were performed according to Polish standards: PN-80/G-04511, PN-80/G-04512, and PN-81/G-04516, respectively. Rigaku RU-300 diffractometer with Cu K_α radiation at 40 kV and 80 mA was used to obtain X-ray diffraction (XRD) patterns presented in a next section of this work. The Ti contents in activated carbons were measured using Geigerflex IKF (Rigaku) X-ray fluorescence equipment. Transmission electron microscopy (TEM) photographs shown later were taken with a transmission electron microscope (Philips CM30) using acceleration voltage of 100 kV. For each TEM observation, measured sample was dispersed on a grid. Finally, nitrogen adsorption isotherms for prepared activated carbons were taken using BELSORP 28SA (Bel Japan, Inc.) equipment.

3. Results

Fig. 2 includes XRD patterns taken for both Ti-doped carbon materials and for the source of titanium (TiOAA) used in this work. XRD measurements were performed after every step of the preparation process. In the case of TiOAA, XRD patterns were taken for a non-treated chemical, and also after treatments corresponding with those utilized during preparation of activated carbons.

All the raw coals used in this study revealed presence of some mineral matter (see Table I). Yet, the highest content of the mineral matter exhibited coal of the lowest rank, Grodziec (see also XRD patterns, Fig. 2a). XRD patterns of coals impregnated with TiOAA (Fig. 2b) did not contain peaks coming either from TiOAA introduced during impregnation or from any new phases. As confirmed by Fig. 2c, still it was rather difficult to analyze XRD patterns of carbonized samples. At this stage, only some peaks could be recognized as those of TiO_2 (rutile form). The situation changed substantially during the activation process. As shown in Fig. 2d, all the activated carbons prepared exhibited well defined, sharp peaks, easily recognized as derived from rutile. Rutile was the only crystalline form of TiO_2 observed in these carbons. For a comparison, XRD measurements were performed for TiOAA alone. Undoubtedly (see upper patterns in Figs. 2b–d), already conditions corresponding with the carbonization caused turning of TiOAA to TiO_2 (rutile). Subsequent activation process resulted in a very pronounced sharpening and increasing in an intensity of rutile peaks.

The Ti contents measured in the Ti-loaded activated carbons varied from ca. 5 wt% to ca. 11 wt% (Fig. 3). In comparison with the theoretical contents calculated from a total weight loss achieved during carbonization and activation, the measured titanium loadings were lower than expected. As illustrated by dotted lines in Fig. 3, the loss occurred in activated carbons was of few weight percents and increased with the activation time (burn-off).

Fig. 4 contains TEM photographs of Ti-loaded Wirek coal-based both coke and activated carbon. The photographs presented, however, shown for Wirek coal-originated materials only, illustrate a common situation observed also in other coals-based samples investigated in this work. Hence, during TEM observations of the cokes (Fig. 4a), only some very small (up to few nm in diameter) particles could be sporadically looked. Figs. 4b and c show the situation in Wirek coal-based activated carbons activated for 80 and 140 min, respectively. Here, presence of grown up TiO_2 particles is evident. Additionally, mean size of the particles was bigger in WTi140 than in WTi80. After observation of other samples it came out that generally typical size of TiO_2 particles supported in Ti-loaded activated carbons increased with the activation time. More detailed data concerning the size of TiO_2 crystallites in relation with the activation time and with the carbon origin is presented in Table III. In addition, it has to

TABLE III Typical TiO_2 particle size observed in prepared Ti-loaded activated carbons

Carbon	Typical TiO_2 particle size, [nm]
GTi60	15-30
GTi120	40-60
WTi80	17-35
WTi140	75-90
UTi100	25-40
UTi160	80-100

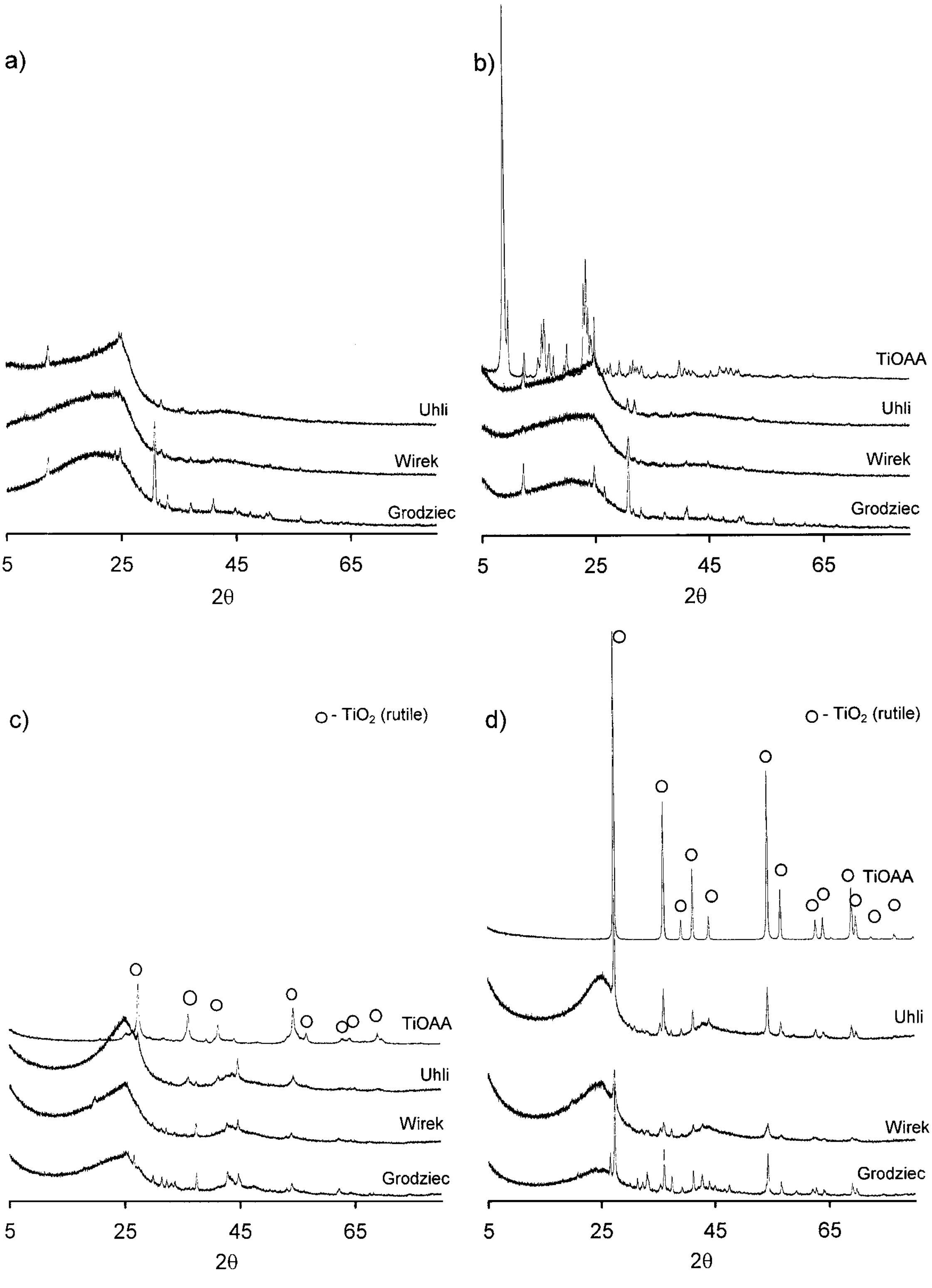

Figure 2 XRD patterns of coals and TiOAA at raw stages and after different treatments: a) raw coals, b) pure TiOAA and coals after impregnation, c) TiOAA and coals after carbonization at 900°C for 10 min, d) TiOAA and coals after activation at 900°C for 20 min.

be emphasized that all the prepared Ti-loaded activated carbons showed an irregular distribution of TiO_2 agglomerates. Sparsely, larger TiO_2 crystallites (in some cases even up to ca. 300–400 nm, Fig. 4d) could be also observed. Typically, the number and mean of these large agglomerates were higher for the carbons activated for a more extended period of time.

Fig. 5 contains N_2 adsorption isotherms taken at 77 K for all (with and without Ti loading) the prepared activated carbons. Each sample exhibited presence of both micropores and mesopores in various ratios. As can be easily observed from the shape of the isotherms, mesoporosity of Grodziec coal-based activated carbons is particularly pronounced and higher than for the other activated carbons. Fig. 6 illustrates changes in values of N_2-BET and D-H specific surface areas for the studied carbons, calculated from the isotherms presented in the Fig. 5. Thus, our activated carbons showed N_2-BET specific surface area of ca. 500–1000 m^2g^{-1} (Fig. 6a), and D-H specific surface area (for mesopores, Fig. 6b) of ca. 100–500 m^2g^{-1}. These values remained dependent on the activation time and the composition of

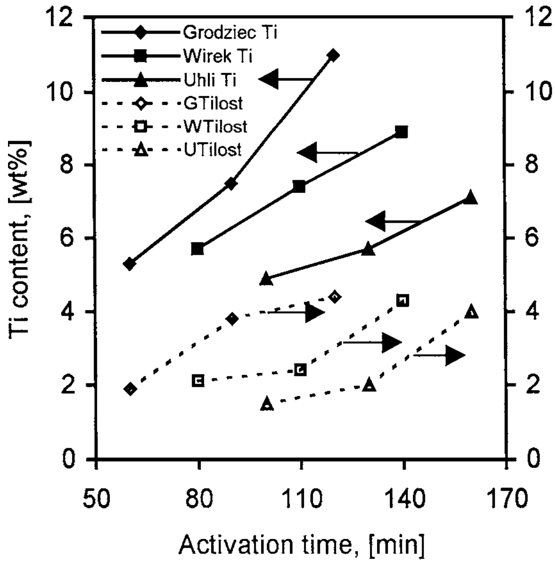

Figure 3 Ti contents and Ti losses versus activation time for different carbons.

the starting coal. Some influence of Ti loading on the porous structure, and consequently on the shape of isotherms can be observed for each activated carbon. Enhancing influence of TiO_2 on formation of mesopores in Wirek coal-originated activated carbons was observed as significant and this was independent on the activation time. However, the impact of titania on the porous structure of Grodziec coal-based activated carbons was noticeable only for carbons activated for 60 and 90 min. Regardless of activation time, D-H specific surface areas of Uhli coal-based activated carbons were little influenced by supported titanium. Since values of both absolute D-H specific surface area (Fig. 6b) and relative mesoporosity (obtained by division of D-H SSA by N_2-BET SSA, Fig. 6c) increased with the activation time for each prepared carbon, the progress of the activation process was concluded to be closely associated with a continuous developing of mesopores. As illustrated by Fig. 6, Grodziec coal-based cokes underwent activation easily, and the

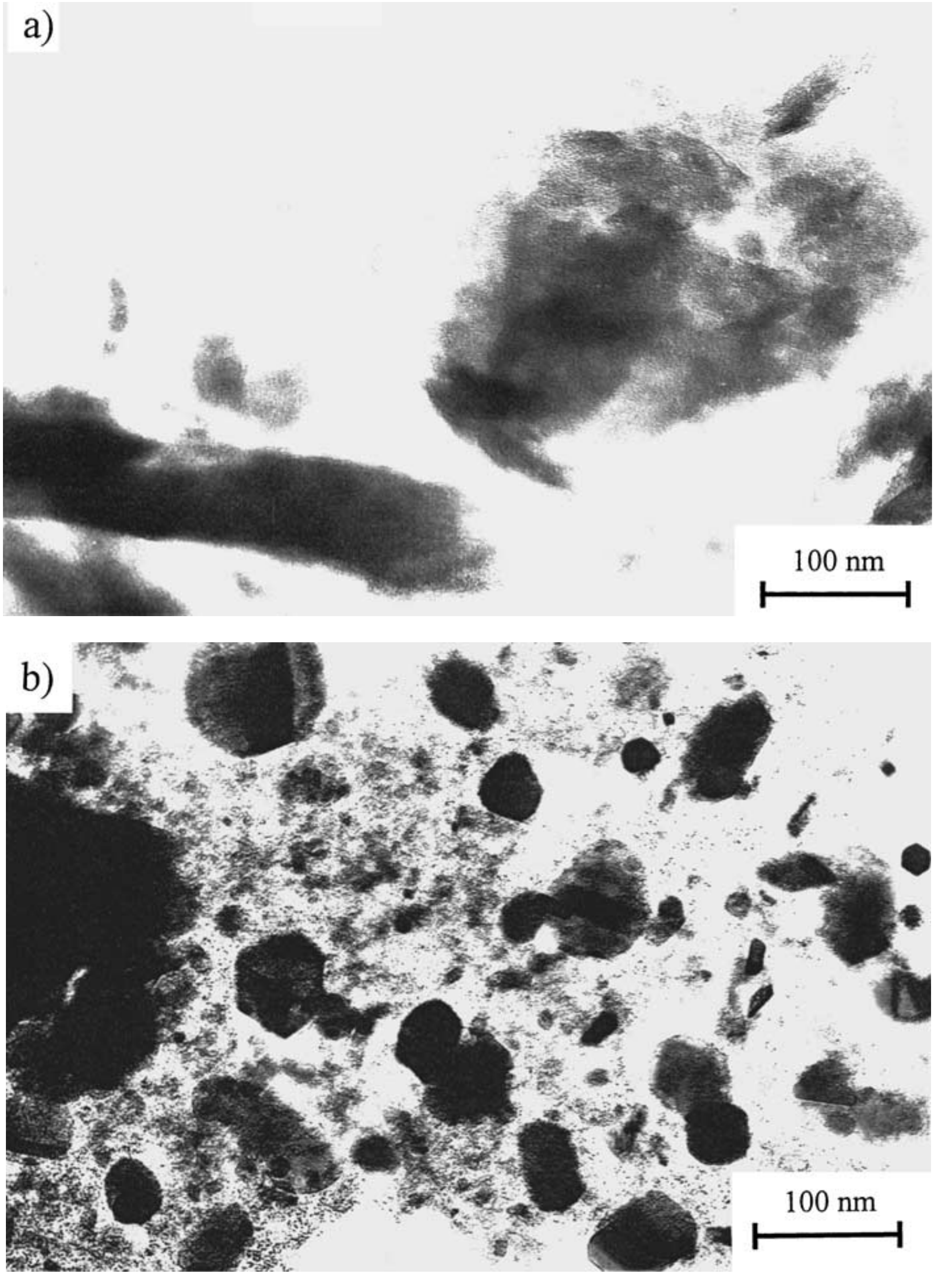

Figure 4 TEM photographs of Ti-loaded Wirek coal-based carbons after carbonization (a), and after activation for 80 min (b), and 140 min (c, d). (*Continued.*)

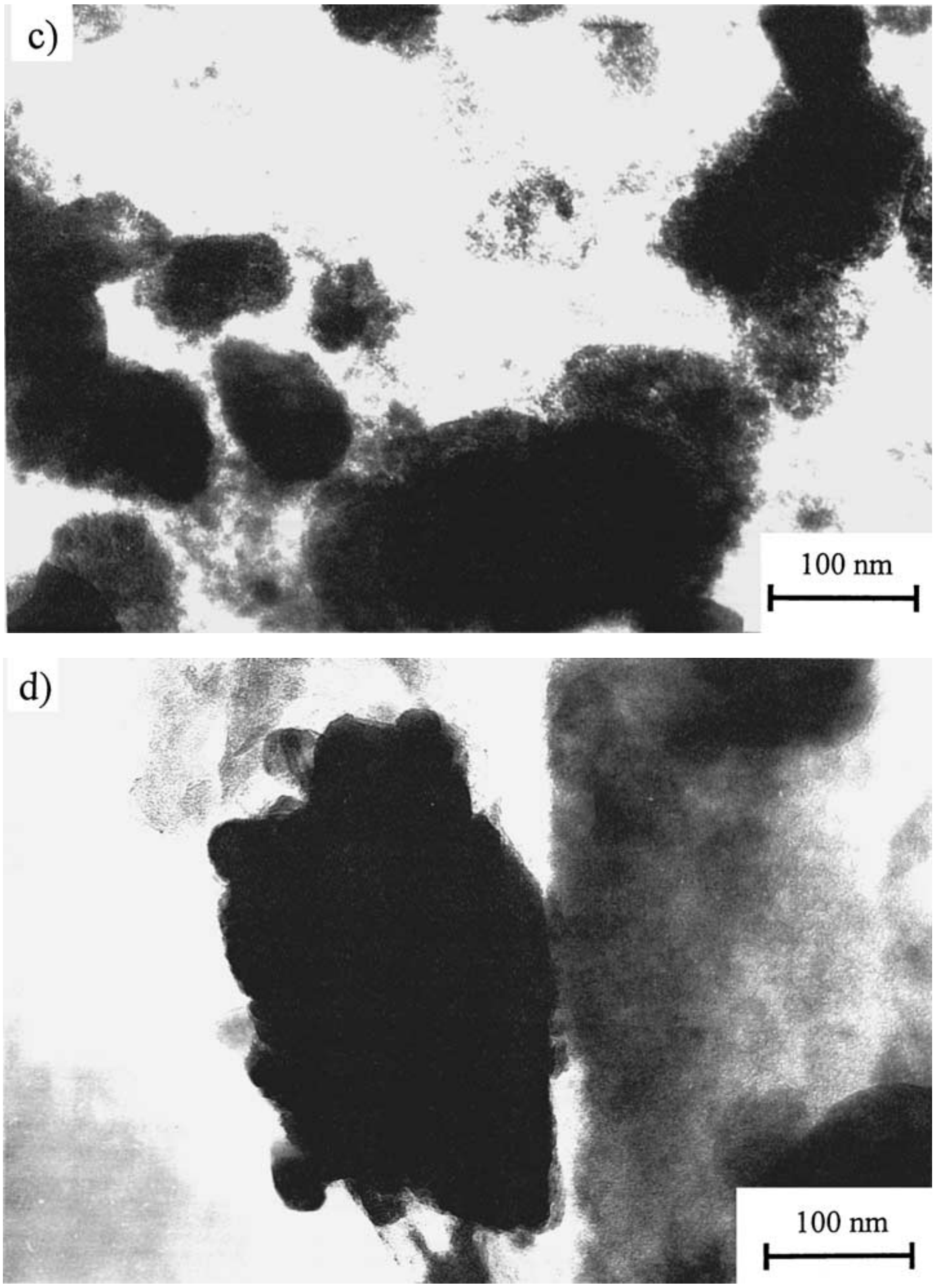

Figure 4 (*Continued.*)

activated carbons obtained showed the highest values of both N_2-BET SSA and D-H SSA. Cokes prepared from Wirek and Uhli coals required longer activation time and produced activated carbons of lower both meso- and microporosity.

4. Discussion

Presented changes in the chemical state of titanium supported in carbons (Fig. 2) appear to be directly related with the thermal decomposition of TiOAA introduced into the raw coals at the initial step of preparation. XRD patterns of the pure compound exposed to the adequate treatments as Ti-loaded coals and cokes prove this assumption. Certainly, TiOAA turned to TiO_2 (rutile) already during the same treatment as used for the carbonization of coals (see upper pattern in Fig. 2c). The activation process caused further strong increase in an intensity and sharpness of rutile peaks (upper pattern in Fig. 2d). TiOAA supported in carbons behaved similarly, however, as a general rule, intensity of observed peaks was lower than of those obtained when the pure chemical was measured. We assumed, that this difference occurred because of a low total Ti loading in coals.

As mentioned before carbonization and activation processes applied in our earlier work [5] continued for a relatively short time. Distinct from the present results, activated carbons prepared before commonly showed also presence of another crystal form of TiO_2 (brookite). This difference can be simply explained by a well-known higher stability of rutile than of brookite. In fact, it is well recognized that at temperatures above 700°C the only stable crystalline form of TiO_2 is rutile. Apparently, this long time of exposure to the high temperature used in our present study (see Table II) caused the change of brookite (if any was formed) to rutile.

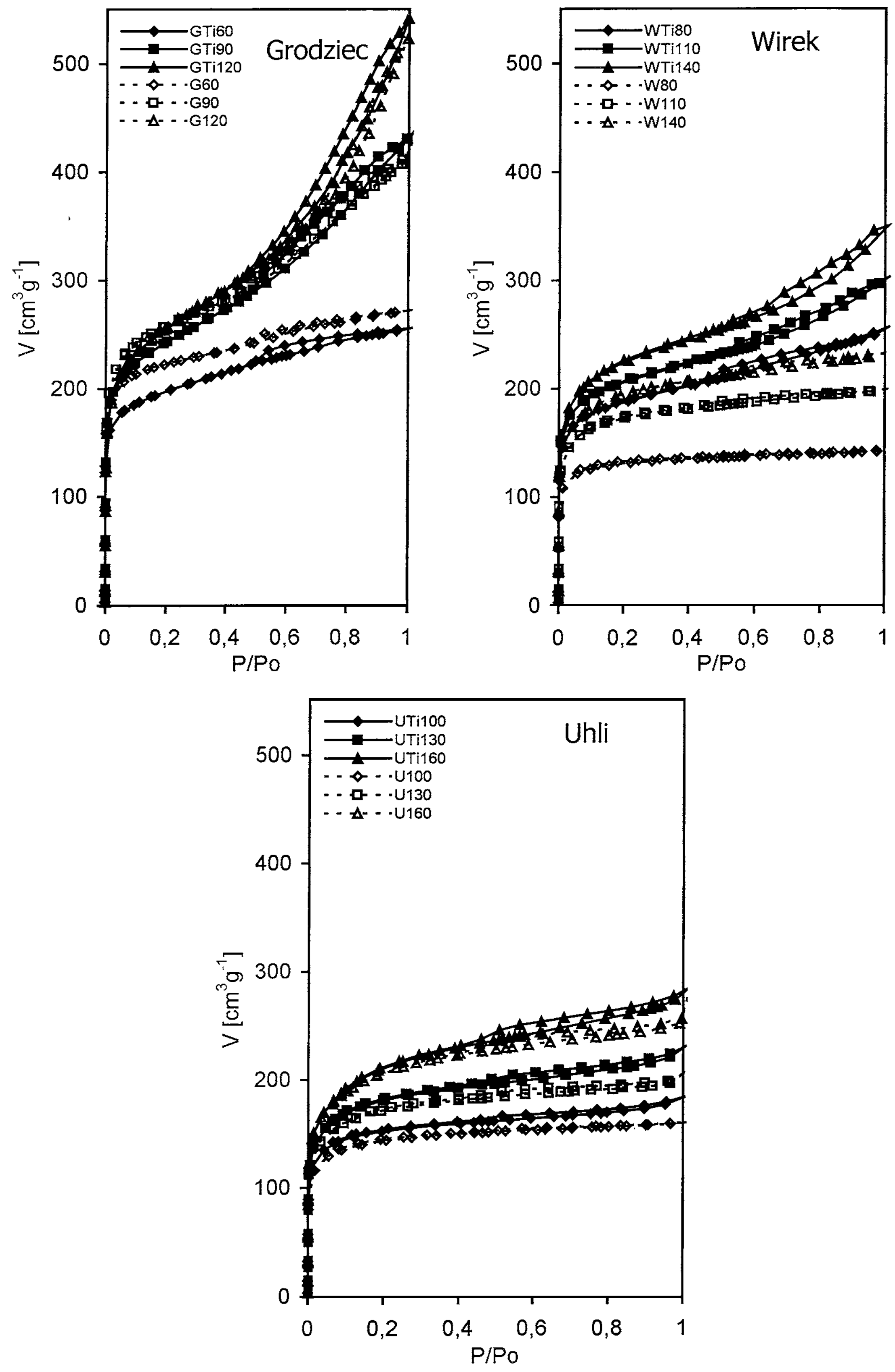

Figure 5 Changes in the shape of N_2 adsorption isotherms at 77 K with the activation time for studied carbons.

The content of Ti supported on the investigated activated carbons is straightly related with a total yield achieved during the preparations. Hence, coals containing more volatile matter and activated for a longer time showed higher Ti content as a result of a higher carbon loss attained. The loss of titanium described a previous section of this work appears to be related with a dropping off of TiO_2 from the surface of activated carbons during manufacturing and handling. However, at present we have no doubtless explanation for that. The size of TiO_2 particles deposited on carbons was also found as dependent on the activation time. As proved by TEM observation results (Table III, Figs. 4b, c, and d), carbons of the same origin activated for a longer time commonly showed presence of larger TiO_2 agglomerates. As shown in Table III, bigger TiO_2 particle size

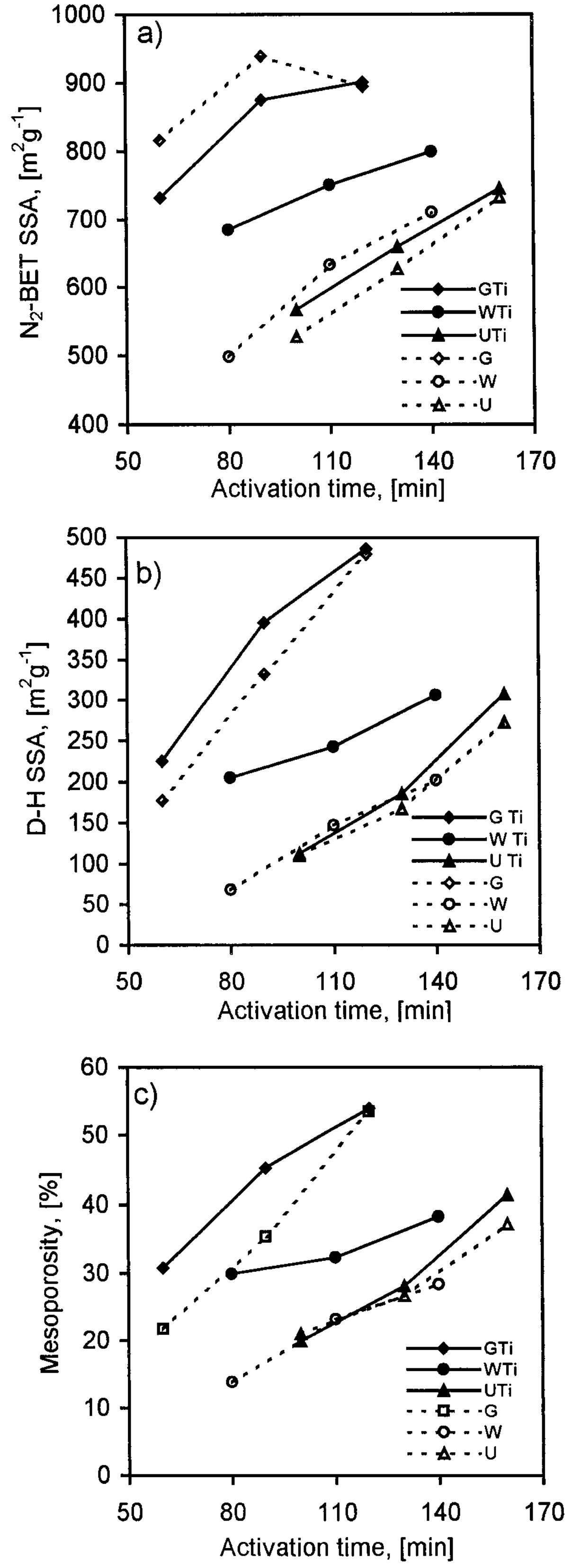

Figure 6 Changes in N_2-BET specific surface area and D-H specific surface area as a function of activation time.

is only related with the longer activation time and does not depend of the origin of carbons. Phenomena of such a growth during exposing to high temperatures have been widely known for a number of other oxides or metals, and it appears to be a common problem occurring during preparation of additive-supporting activated carbons. In comparison with the preparation method utilized by us before [5], the present technique results in both much wider range of TiO_2 particles size and much more irregular distribution of them. Moreover, the typical size of TiO_2 particles is higher. As proved (see Table III and TEM photographs, Fig. 4), this drawback must be a result of the relatively long time of treatments at high temperatures.

Both N_2-BET and D-H specific surface area values were different for all the studied activated carbons. From the Figs. 6b and c it is evident that within the range applied in this work, the longer activation time is associated with higher both relative and absolute mesoporosity of activated carbons studied. As noticed, activated carbons produced from lower rank coals were more mesoporous. Taking into account data from Table I, we assumed that formation of mesopores is more pronounced in carbons prepared from coals containing more volatile matter, or in other words containing less fixed carbon. Grodziec coal-based activated carbons exhibited particularly high mesoporosity while the content of volatile matter was not much higher than in other coals. Considering especially high content of ash in Grodziec coal, the high D-H SSA values suggest also much more pronounced catalytic action (by mean of carbon gasification) of the mineral matter on the formation of mesopores. As a rule, Ti-loaded activated carbons showed higher mesoporosity than these unloaded, and this remains in agreement with our former observation as described elsewhere [5]. The influence of titanium on the formation of mesopores in individual carbons varied and was relatively low in the case of the highest rank coal-based ones. However, this problem remains out of scope of this work.

To sum up, it can be said that coals of a higher rank gave activated carbons containing less mesopores and the mesoporosity was more developed in the Ti-loaded carbons. From the data obtained and presented above it comes out that the decomposition of organic complex of Ti (TiOAA) on carbonaceous material can be an easy way to produce activated materials supporting TiO_2. During work on the three coals-based activated carbons we have concluded followings:

- It is very probable that only rutile form of TiO_2 will be present in the Ti-loaded activated carbons.
- Both TiO_2 crystallites size and distribution are supposed to be irregular.
- Longer activation time will results in a bigger TiO_2 particles deposited on activated carbons.
- Longer activation time is expected to be associated with a higher loss of titanium introduced.
- In general, introduced titanium should accelerate formation of mesopores.
- Those coals with a higher both volatile and mineral matter contents tend to produce activated carbons with a more developed mesoporosity.

As it comes out from the literature review, better results in TiO_2-photocatalysed mineralization can be obtained when more (to some extent) TiO_2 is used, and when crystals of the catalyst are finer. On the contrary, the size of TiO_2 crystallites observed in our carbons was relatively big. By these reasons it is recommended to make further improvements to the preparation method described above. Reducing duration of a high temperature processes (carbonization and activation) and decreasing the highest temperature to the necessary minimum are expected to result in both smaller size of the catalyst and also in a lower loss of TiO_2 supported. But, to find out the optimal conditions for the preparation, more experimental data are necessary to be collected. Worth emphasizing is that mesoporosity of Grodziec coal-based activated carbon can be relatively high even without titanium introduced at the beginning of preparation. Therefore, alternative ways (e.g. impregnation with proper chemicals) to prepare TiO_2-loaded containing mesopores activated carbons from the coal should be also considered.

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