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MICROWAVE ASSISTED CARBONIZATION OF GLYCEROL ON SILICA SURFACE

A.V. Korobeinyk *, R.B. Kozakevych, Yu.M. Bolbukh, V.A. Tertykh

Chuiko Institute of Surface Chemistry of National Academy of Sciences of Ukraine
17 General Naumov Str., Kyiv, 03164, Ukraine

Microwave assisted carbonization of glycerol chemically and physically adsorbed on fumed silicas surface (initial and methylated) has been studied. It has been found that physically adsorbed glycerol cannot undergo carbonization under used conditions whereas an assumption about such transformation for chemically adsorbed glycerol has been confirmed with FTIR analysis.

INTRODUCTION

Carbonization of different organic compounds over silica nanoparticles has called a great attention [1]. Modifiers, such as different organics and polymers, were used to obtain silica/carbon hybrid nanocomposites with new interesting functionalities [2–4] through the carbonization [5]. Hybrid organo-inorganic nanocomposites (carbosils and silicacarbons [6, 7]; silicas containing surface carbonaceous structures of different architecture SiO_2–C) have attracted interest of researchers. Pyrolytic carbonization of different organics [8–11] is a popular pathway to obtain carbonaceous materials and silica-carbon hybrids [12]. Utilization of the microwave technique is a new way of the development in functionalized nanomaterials [13–15]. Microwave carbonization as a low-cost technique [16] has advantages compared with conventional techniques, which are mainly attributed to a selective, fast, and homogenous heat [17–19] that significantly reduce processing time and costs [20].

Glycerol-modified silicas are novel, very stable, inexpensive and easily prepared solid precursors for the carbonaceous nanostructures preparation [15, 21]. The glycerol-bonded silica could be obtained by adding glycerol into a suspension of silica chloride in acetonitrile [22] or by polycondensation of glycerol with hydroxyl groups at silica surface in the presence of amine.

Herein we are reporting a novel pathway for low cost microwave assisted carbonization of the silica nanoparticles (pristine and methylated) modified with glycerol in order to obtain carbon nanostructures on the silica surface. Properties of the obtained modified silica materials were tested using a variety of methods of physical and chemical analysis. Thermal stability and quantity of the grafted organics were determined using thermogravimetry. Chemical composition of the grafted surface layer was analyzed with IR-spectroscopy. Functionality of samples was evaluated through dye adsorption.

MATERIALS AND METHODS

Fumed silica, abbreviated in the following text A300, where 300 is the specific surface area given by the manufacturer, purchased from Pilot plant of the Chuiko Institute of Surface Chemistry (Kalush). A300 was heated at 150 °C for 2 h before the use to remove the adsorbed water [23]. Methylated silica (AM300, Pilot plant, Kalush) was heated at 120 °C to remove possible contaminants. Glycerol (Gly, Fluka) and methylene blue (MB, Aldrich) were used without previous purification. Ethylenediamine (ED) purchased from Fluka was refined before the use.

Thermal analysis was performed using a MOM Derivatograph (Hungary) with simultaneous record of TG-DTG/DTA curves, in air with the heating rate of 10°/min within the 20–800 °C range. Fourier transmission infrared (FTIR) spectra were recorded for samples stirred with dried KBr using a Thermo Nicolet FTIR spectrometer. UV-spectra were obtained using a SF-46 LOMO spectrophotometer (Russia). Silica dispersions were prepared using a UZDN-2D (Ultrasonic Ltd) submersible sonicatior. Before analysis samples were heated at 110 °C for 1 h in vacuum.

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* corresponding author *akorobeinyk@gmail.com*

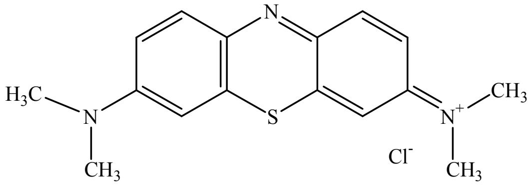
EXPERIMENTAL

Glycerol attachment. Impregnation of hydrophilic (A300) and hydrophobic (AM300) silicas by glycerol was performed via mechanical mixing at glycerol/silica mass ratio 5:1. Chemisorption of glycerol on hydrophilic silica was performed from a benzene solution. In brief, 1 g silica and 5 g glycerol were dispersed in 10 ml of benzene via ultrasonication. The mixture was heated at 80 °C for 4 h under reflux. Then an initiator of polycondensation (ED) was added and reaction was continued at 110 °C for 2 h. Samples were centrifuged at 3000 rpm and dried at ambient temperature in vacuum.

Microwave carbonization. Silica samples with attached glycerol were exposed to preliminary carbonization tests employing a household microwave operating at 800 W (Hundai, H-MW1317). Several tests were conducted at varying power level in order to identify the carbonization optimum conditions. The conditions that provide homogeneous carbonization are described as follows: the silica/glycerol samples (1 g each) were placed in a quartz beaker (100 ml), which then were placed, individually, inside the microwave oven. Samples were irradiated for 20 and 40 min at 700 W and then taken out and sequentially cooled down to room temperature.

METHYLENE BLUE ABSORPTION

Methylene blue (Scheme 1) is a water soluble non-toxic dye which is blue in colour (but λ_{max} = 664 nm in a red part of the spectrum). Stock solution was prepared by dissolving an appropriate quantity of methylene blue in a volume of ethanol. Working solutions were prepared by diluting the stock one.

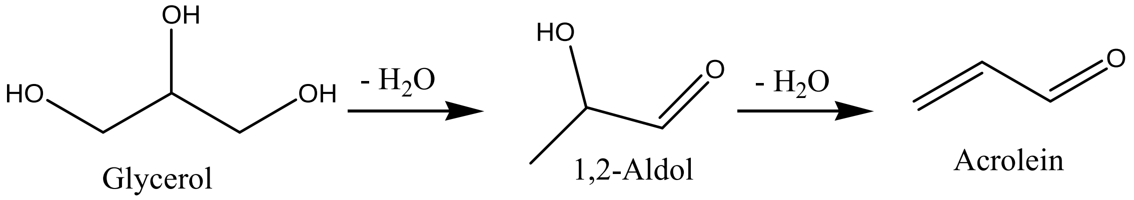


Scheme 1. Methylene blue structure

The initial and final concentrations of MB solutions were determined by measuring the absorbance at 664 nm using an UV-visible absorption spectrophotometer. 25 ml of MB solution were mixed with 0.1 g of silica-based composite and stirred in dark at 25 °C, then a suspension of the composite and dye solution was separated by centrifugation.

RESULTS AND DISCUSSION

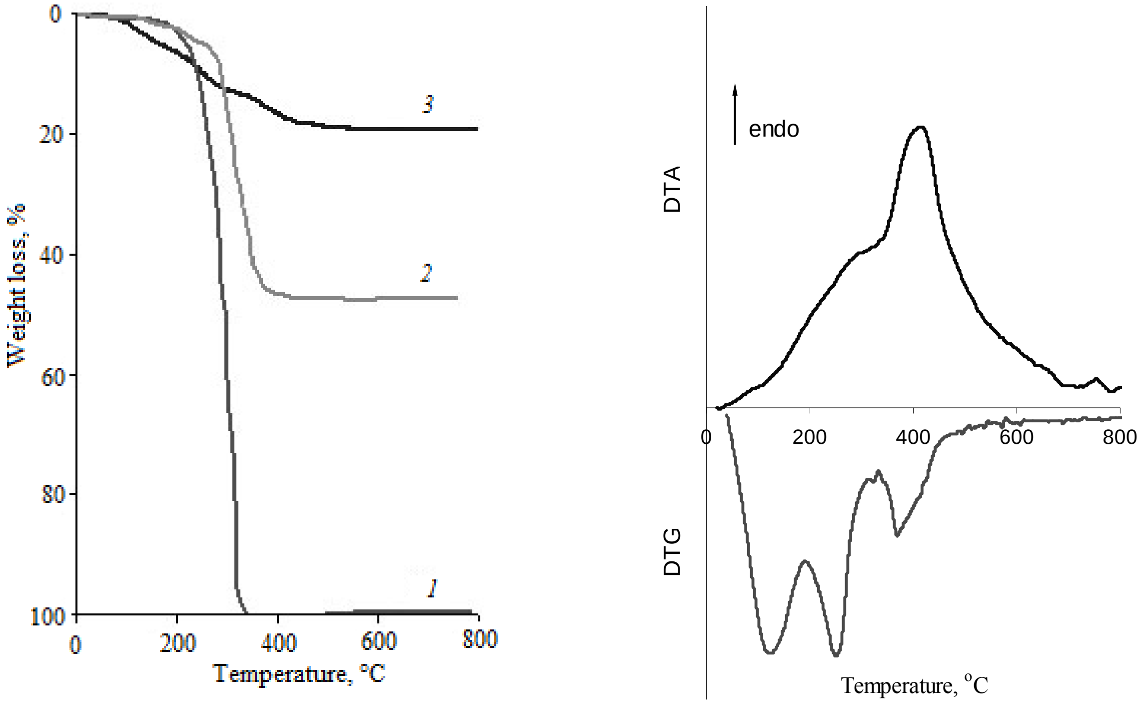
Properties of glycerol are determined by the presence of three hydroxyl groups, two primaries and one secondary. In the reactions of chemical modification glycerol can form mono-, di- and three-substitutes (due to presence of the OH groups). Fig. 1 shows the thermograms of glycerol (Fig. 1 *a, 1*) and of silica samples after glycerol impregnation (Fig. 1 *a, 2*) and chemisorption (Fig. 1 *a, 3*). Thermo-oxidative degradation of glycerol occurs in the range of 185–350 °C with a maximum of the destruction rate at 300 °C. Detaching of water molecules during thermal degradation of glycerol leads to aldol and acrolein formation (Scheme 2) [24].



Scheme 2. Transformation of glycerol into 1,2-aldol and acrolein via dehydratation [25]

In spite of the complexity of thermal degradation of glycerol, the "one-step" curve profile indicates that all the reactions occur in the narrow temperature interval with complete glycerol destruction. The activation energy of destruction calculated using the DTG-curve [26] is 95 kJ/mol and order of reaction is 2.5. The presence of water in glycerol reduces the initial degradation temperature, i.e. 5 wt. % of water reduces the glycerol decomposition temperature from 290 (in N_2 flow) to 160 °C, as reported elsewhere [27].

The modified layer obtained via mechanical mixing of glycerol with hydrophilic silica cannot transform into a carbonaceous product under selected conditions. Thermooxidative destruction of the sample obtained via physical sorption of glycerol is a two stage process which begins at 161 °C (Fig. 1 *a, 2*); the mass loss in the first temperature range (161–235 °C) is 5 %, attributed to the water content in glycerol. The second step of thermal degradation ends at 439 °C and the mass loss during this step is ca. 42 %. Shifting of the initial temperature of glycerol decomposition toward the high temperature region (from 185 to 253 °C) is associated with the stabilizing effect of the silica surface. The total mass loss for the sample is 47 wt. % which is much lower than expected. However, complete decomposition of glycerol impregnated on the hydrated silica surface was confirmed by the IR spectra (not shown here).



a *b*

Fig 1. Thermogravimetric analysis. (*a*) TG curves of glycerol (*1*) and of silica with adsorbed (*2*) or chemisorbed glycerol (*3*); (*b*) DTA and DTG curves of silica with chemisorbed glycerol

Chemisorbed glycerol undergoes carbonization at the stage of aldol formation. Mass loss for silica with chemically adsorbed glycerol (Fig. 1 *a, 3*) is a three stage decomposition process terminating at 464 °C. The total mass loss of 19 wt. % corresponds to completeness of the silica-glycerol interactions, where one hydroxyl group on the silica surface coordinates one glycerol molecule. Three extremes on the DTG curve at 130, 258, and 374 °C (Fig. 1 *b*) correspond to the formation of aldol, acrolein, and carbonizate. Carbonizate formation is followed by its total decomposition at 425 °C. Demerging in the temperature intervals of the glycerol decomposition stages is conditioned by formation of bridge structures via interaction of two adjacent aldehydes at 150–200 °C. Migration of coordinated water molecules from inner volume towards the sample surface in this temperature region leads to hydrolyzation of the unstable Si-O-C bonds on the sample surface. Hydrolysis of Si-O-C links ensures formation of aldol oligomers, which inhibits the rate of degradation and results in an intensive endothermal effect in DTA curve in region of 200–350 °C (Fig. 1 *b*).

FTIR spectra of the sample with physically absorbed glycerol, recorded after heating at 130 °C, shows bands at 2946, 2888 cm^{-1} and 1460, 1427 cm^{-1} assigned to vibration of the CH/CH_2 and alcohol respectively, so indicating presence of glycerol. Chemical attachment of glycerol is confirmed indirectly by the absence of the adsorption band of free hydroxyls. A shoulder at 933 cm^{-1} indicates formation of Si–O–C bonds in the sample. Absence of adsorption band at 1630 cm^{-1} characteristic of silica in the spectra of chemically modified sample allows us to assign the bands at 1658 cm^{-1} to the vibration in C=O fragment, which in turn corresponding to the oxidation products of glycerol (glyceraldehyde, dihydroxyacetone) and/or free fatty acids. Presence of the C=O groups is also confirmed by absorbance band at 1730 cm^{-1}. Microwave treatment leads to reduction of the bands at 1658 and 3350 cm^{-1} related to reduction in number of carboxyl groups and in amount of water in the sample and to origin of an intensive band exceeded by siloxane groups vibrations at 1126 cm^{-1}. Bands broadening in the range of 1700–1600 cm^{-1} indicates the presence of various oxygen-containing groups, aldehydes (aldol and acrolein), and carboxyl. Determination of oxygen-containing groups was conducted through the reaction with enthylene diamine (ED) followed by identification of the products. Interaction of amines with carboxyls leads to formation of amides whereas ketone and/or aldehyde with amines undergo a complex reaction of nucleophilic addition resulting in substituted imines. In the spectra of chemically modified silica after reaction with ED, the band at 1716 cm^{-1} (C=O in ketone) was changed insignificantly; though the ethanol group bands at 1460 and 1419 cm^{-1} are reduced significantly, and new bands appear at 1643, 1654 cm^{-1} and 1456, 1565, 1547 cm^{-1} assigned to bonds C=O Amid I and to N–H Amid II respectively. Absorption bands related to the vibrations of imides were not observed in the spectrum, thus ED reacts with carboxyl groups. Presumably, the microwave oxidation of chemically attached glycerol undergo through origination of an acidic group followed by acrolein formation (confirmed by the band of C=C vibration at 3070 cm^{-1}). Repeated microwave treatment leads to total destruction of the modified layer, resulting in restoration of the native silica surface.

Considering the fact that the hydration shell of silica particles prevents carbonization of glycerol on silica surface, glycerol impregnated the methylated silica, which doesn't contain water in bulk and at the surface, should transform into carbonized product under selected conditions.

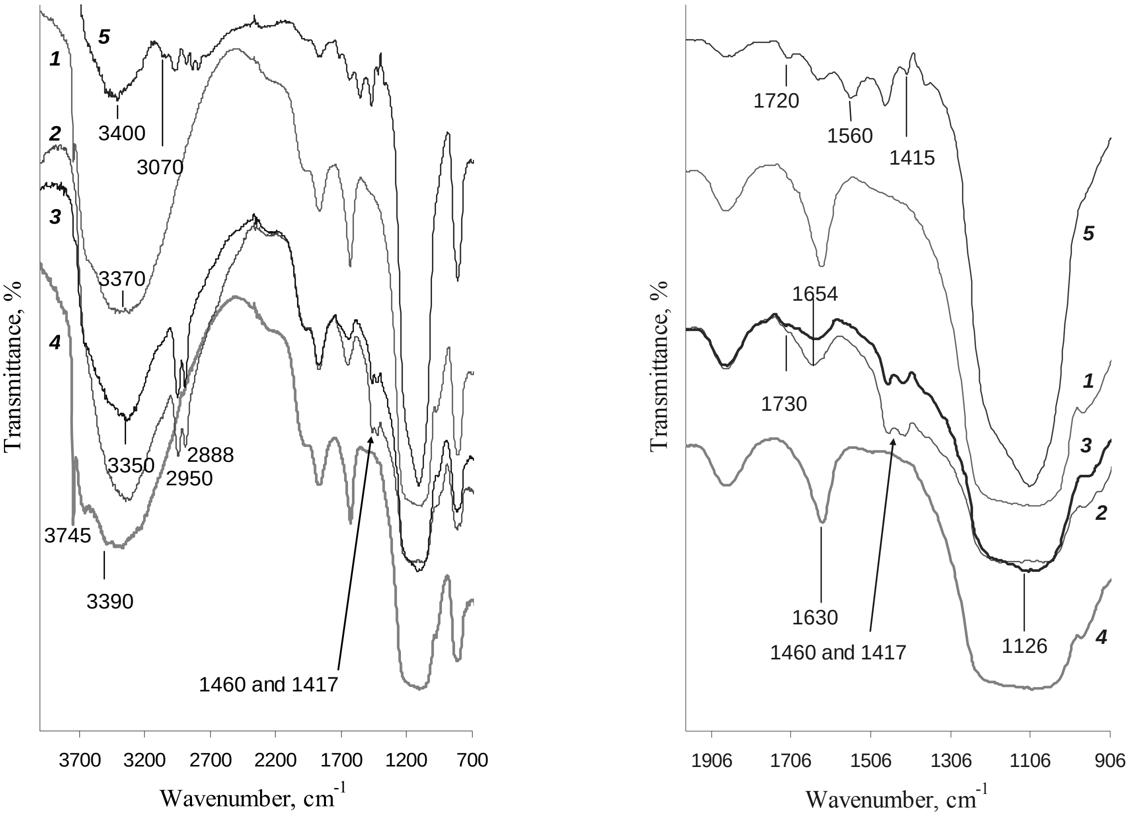


Fig. 2. FTIR-spectra of A300 (*1*); silica with chemisorbed glycerol initial (*2*), after microwave for 20 min (*3*) and 40 min (*4*); silica with chemisorbed glycerol after microwave treatment for 20 min and modified with ethylenediamine (*5*)

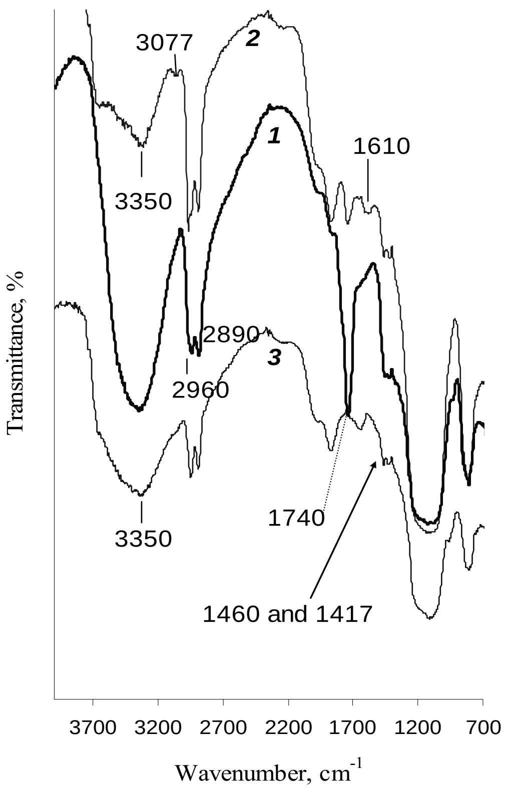


Fig. 3. FTIR-spectra of methylated silica impregnated with glycerol after 20 min (*1*) and 40 min microwave treatment (*2*) and of silica with chemisorbed glycerol after microwave treatment for 20 min (*3*)

Figure 3 shows IR spectra of the samples after microwave treatment. After the first microwave treatment in spectra of silica impregnated with glycerol (Fig. 3, *1*) an intensive band appears at 1740 cm^{-1} which corresponds to the C=O vibration in saturated aldehydes. Characteristic band of silica at 1630 cm^{-1} does not appear whereas a wide band of adsorbed water and hydroxyl groups (3360 cm^{-1}) ascribing silica and glycerol is presented. In spectra of silica with chemisorbed glycerol, after analogous microwave treatment (Fig. 3, *3*), the CH in HC=CH– band (at 3070 cm^{-1}) is not perceived. Repeated treatment with microwave irradiation leads to significant reduction in intensity of the vibration band at 3350 and 1740 cm^{-1} (Fig. 3, *2*) whereas the intensity of CH and CH_2 bands doesn't change. Disappearance of the band of silicon-nonbridging oxygen vibrations (950 cm^{-1}) and emerge of the band of non-saturated carbon-carbon bond indicates a formation of the aldol resin on the silica surface due to the condensation reaction. Therefore, on the surface of hydrophobic silica a layer of polymerized compounds of glycerol with minimum content of oxidative products is formed after second microwave treatment.

Methylene blue is adsorbed by the hydroxylated surface of silica or carboxylated surface of various carbons. On the surface of carbons, subject to concentration of working solution, MB can be adsorbed in a monolayer or agglomerates of different structure. In regards to [28], quantity of the dye adsorbed is predetermined by the sorbent capacity rather than the nature of the functional groups. The values of adsorptions of methylene blue from solution with concentration 25 10^{-6} mol l^{-1} are listed in Table.

Table. Values of the methylene blue adsorption

	A300	**AM300**	**A300_Glyc (chem)**	**A300_Glyc (chem) therm 1**	**A300_Glyc (chem) therm 2**
C, x10^{-6}, mol/g	8.54	5.72	3.23	6.49	6.59
mg/g	2.72	1.83	1.05	2.11	2.07

CONCLUSIONS

A300 or AM300 undergoes modification with glycerol through the mechanical mixing and chemically promoted interaction. Obtained silica/glycerol hybrids were carbonized using a household microwave oven. It has been found that adsorbed glycerol cannot transform into carbonaceous product under used conditions whereas evidences of such transformation are presented in the IR spectra of silica containing chemisorbed glycerol.

The values of dye adsorption for samples with glycerol impregnated in the surface are independent on the mode and structure of modified layer (samples after first and second microwave treatment). Samples with chemisorbed glycerol shows the lowest values of MB adsorption, presumably the complicated architecture of the surface impedes the dye adsorption.

The degree of glycerol modification and the structure of the grafted layer on silica surface during the chemical attachment, using ethylenediamine as a catalyst, are in direct dependence on the degree of silica surface hydration. Migration of coordinated water from the bulk towards the sample surface, under heat treatment, ensures formation of aldol oligomers.

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Мікрохвильова карбонізація гліцерину на поверхні кремнезему

А.В. Коробейник, Р.Б. Козакевич, Ю.М. Больбух, В.А. Тьортих

Інститут хімії поверхні ім. О.О. Чуйка Національної академії наук України
вул. Генерала Наумова, 17, Київ, 03164, Україна, korobeynyk@mail.ru

Досліджено процеси термічного та мікрохвильового розкладання композитів, одержаних шляхом фіз- та хемосорбції гліцерину на поверхні кремнезему. Аеросили А300 та АМ300 були використані як субстрати для прищеплення і подальшої карбонізації гліцерину. Деструкція композитів проводилася в побутовій мікрохвильовій печі, де радіація забезпечувала необхідну температуру для карбонізації гліцерину. Встановлено, що ефективність карбонізації гліцерину залежить від ступеня гідратованості поверхні носія і типу взаємодії гліцерин–носій.

Микроволновая карбонизация глицерина на поверхности кремнезема

А.В. Коробейник, Р.Б. Козакевич, Ю.Н. Больбух, В.А. Тертых

Институт химии поверхности им. А.А. Чуйко Национальной академии наук Украины
ул. Генерала Наумова, 17, Киев, 03164, Украина, korobeynyk@mail.ru

Исследованы процессы термического и микроволнового разложения композитов, полученных путем физ- и хемосорбции глицерина на поверхности кремнезема. Аэросилы А300 и АМ300 были использованы в качестве субстрата для прививки и последующей карбонизации глицерина. Деструкция композитов проводилась в бытовой микроволновой печи, где радиация обеспечивала необходимую температуру для карбонизации глицерина. Установлено что эффективность карбонизации глицерина зависит от степени гидратированности поверхности носителя и типа взаимодействия глицерин–носитель.