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Linoleic acid isomerization over mesoporous carbon supported gold catalysts

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ABSTRACT

Gold catalyst supported on mesoporous carbon and silica were synthesized, characterized by TEM, XRD, XPS and tested in linoleic acid isomerization. Nature of the support affects the selectivity towards isomerization in relation to unwanted hydrogenation. In particular carbon support allowed much higher selectivity in double bond migration compared to silica. Effect of carbon surface oxidative pre-treatment on selectivity of catalyst was investigated.

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1. Introduction

Linoleic acid $(C_{18,2})$, which has double bonds located on carbons 9 and 12, both in *cis* configuration, can be isomerized through double bond migration to conjugated linoleic acids (CLAs) (see Scheme 1). These acids are widely used as health promiting agents in food and pharmaceuticals due to their anticarcinogenic and antioxidative properties [1], which can be attributed to the presence of 9-cis,11-trans and the 10-trans,12-cis isomers [2-6]. The CLAs are produced industrially under alkaline conditions, implying alkali bases, solvents and neutralizing agents being a real shortcoming from an ecological and economic point of view. In addition, solvents are limited to the ones that are harmless to human body. These drawbacks could be circumvented using heterogeneous catalysis. However, in the isomerization reaction small quantity of hydrogen is needed to enhance the activity. Selective isomerization under hydrogen atmosphere is challenging due to hydrogenation of a C=C bond over typical metal catalysts (e.g. ruthenium) and subsequent formation of stearic acid instead of CLAs. In our previous work it was demonstrated that isomerization of linoleic acid is possible over heterogeneous catalysts [7]. The reaction was performed in two-steps; first the catalyst was pre-treated with hydrogen, and linoleic acid was subsequently converted into CLAs under nitrogen. However, it would be beneficial to carry out the selective isomerization in onestep under hydrogen atmosphere without C=C double bond

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hydrogenation. In fact, selective isomerization under hydrogen atmosphere has been carried out by using Ag/SiO₂ as a catalyst. The differences in the selectivity of ruthenium and silver catalysts are based on the differences in the hydrogen adsorption behavior on the metal catalysts. It is evident that the weakly bound hydrogen plays a key role in the selective isomerization of conjugated double bonds (to CLAs) [8]. From this point of view, gold is a potential catalyst for the selective isomerization reaction as it is reluctant to hydrogenate C=C double bond. Using mesoporous carbons as a support for preparing gold catalysts is attractive for several reasons, namely better mechanical stability is achieved as well as better accessibility of large organic compounds to the active sites compared to the microporous supports [9]. However, the formation of carbon supported gold catalysts is challenging due to reduction of the metal ions by free electrons of the carbon matrix taking place immediately after carbon is brought in contact with the solution. Gold is adsorbed on carbon surface only in the form of Au⁰, followed by aggregation of particles [10–14]. Therefore, surfactant-protected gold particles are formed to avoid the direct adsorption of gold complexes on carbon surface. Preparation of gold catalysts by immobilization of gold sols on carbon surfaces allows to support gold particles in a highly dispersed state. The size of supported gold particles can be varied in the range of 3–15 nm. The systematic study of the gold sols application as a catalyst precursor for preparation of Au/C catalysts is presented by the group of Prati and co-workers [14-18].

In this work we aimed to investigate selectivity of mesoporous carbon supported gold catalysts in comparison with silica supported gold catalyst in linoleic acid isomerization.





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Scheme 1. Isomerization of linoleic acid to biologically active conjugated linoleic acid isomers.

2. Experimental

2.1. Catalyst preparation and characterization

Hydrogen tetrachloroaurate (99.9% ABCR, Darmstadt) was diluted with deionized water up to concentration 60 µg/ml. Maintaining this solution under vigorous stirring, 2 wt.% solution of PVA was added at Au/PVA weight ratio equal to 1:5. Freshly prepared 0.1 M solution of NaBH₄ was added dropwise at Au/ NaBH₄ weight ratio equal to 1:100. Within a few minutes of sol generation, the sol was immobilized by adding mesoporous carbon material Sibunit ($S_{BET} = 450 \text{ m}^2/\text{g}$, micropore area 37.7 m²/g, average pore diameter 9 nm). The nominal metal loading was 1 wt.%. Carbon support was used as such or after an oxidative treatment. Gold sols were thus supported on non-oxidized and pre-oxidized by nitric acid carbon materials in order to study the influence of the support surface on physical-chemical properties of catalysts. Powdered carbon material Sibunit was mixed with 5 wt.% HNO₃ agua solution at 373 K for 3 h to introduce oxidic surface group as described in [19]. Due to the oxidative pretreatment of carbon the formation of functional groups (phenolic, aldehydic, carboxylic, etc.) on the surface was achieved [20]. Such groups presumably allow stabilization of highly dispersed gold. After 2 h the slurry was filtered and the catalysts were washed thoroughly with hot deionized water, followed by drying overnight at 60 °C in air.

The sample of 1 wt.% Au/SiO₂ was synthesized by deposition– precipitation method with urea (DPU) as described in [21] using SiO₂ (Merck, S_{BET} = 480–540 m²/g, 40–63 µm fraction), HAuCl₄ (99.9% ABCR, Darmstadt), and urea (Riedel-de-Häen, 99.5%).

2.2. Catalyst characterization

A Carlo Erba sorptometer 1900 was utilized in the measurements of the surface area and micropore volume by nitrogen physisorption. BET method was used to calculate the surface areas.

X-ray diffraction experiments were performed using Cu K α radiation (Siemens D5000 diffractometer equipped with a graphite monochromator to suppress fluorescent and Cu K β radiation). The average crystallite size of gold catalyst particles was estimated using Scherrer's equation from the peak half-widths of Au(1 1 1) reflection measured at $2\Theta \sim 38.3^{\circ}$. Instrumental broadening and unresolved Cu K α 1 and α 2 radiation are neglected (error less than 2%).

Electron microphotographs of the samples were taken by a LEO 912 OMEGA energy-filtered transmission electron microscope using 120 kV acceleration voltage. Histograms of particle size distribution were obtained by counting at least 100 particles on the micrographs for each sample.

The XPS measurements were carried out in a PHI Quantum 2000 Scanning ESCA Microprobe spectrometer with Al anode. The survey and multi-spectra were collected at 187.75 and 11.75 eV pass energy respectively. Spectra were processed by means of XPS Peak 4.1 software. The peak areas were computed by fitting the experimental spectra to Gaussian/Lorentzian curves after removing the background (using the Shirley function).

2.3. Catalytic linoleic acid isomerization

Linoleic acid (C₁₈H₃₂O₂) of 99% purity was supplied by Sigma-Aldrich (Germany). The solvent *n*-decane of 95.5% purity was purchased from Fluka (Switzerland). The trans-10, cis-12, cis-9,trans-11, cis-9,cis-11, and trans-9,trans-11 isomers of CLA $(C_{18}H_{32}O_2)$ were supplied by Matreya Inc. (USA). The isomerization experiments were carried out in a 200 ml stirred glass reactor, which was equipped with a reflux condenser and a heating jacket. The catalyst ($m_{cat} = 1$ g, fractions of Au/C and Au/SiO₂ catalysts below 70 and 40-63 µm respectively to suppress internal diffusion) was introduced into the reactor, preactivated under hydrogen flow (100 ml/min) at 150 °C for 1 h. An amount of 200 mg of linoleic acid was mixed with 70 ml of solvent in a glass drip funnel. The amounts of the catalyst and the substrate were chosen following the paper which reported the best results for linoleic acid isomerization performance over ruthenium on carbon catalysts [22]. Such conditions correspond to the substrate/metal molar ratio equal to 14 mol/mol. The air above the reaction mixture and dissolved in the liquid phase was purged out by a nitrogen flow of 100 ml/min. The isomerization reaction was conducted at 150 °C under stirring at 900 rpm to eliminate external mass transfer. Samples (5 µl) were withdrawn from the reactor at certain intervals through a sampling valve.

2.4. Analytical procedure

The samples from the batch reactor were analyzed by a temperature-programmed gas chromatograph (GC, Hewlett Packard 6890 Series) using 50 m HP-5 column (inner diameter: 0.20 mm, film layer: 0.11 μ m) and a flame ionization detector (FID) operating at 300 °C. Prior to GC method analysis the samples were silylated by using N,O-bis(trimethylsilyl)trifluoroacetamide (BSTFA) and trimethylchlorosilane (TMCS) at 60 °C, both supplied by Fluka (Switzerland).

3. Results and discussion

3.1. Gold particle size

Characterization data confirmed that gold can be successfully deposited on mesoporous carbon from gold sols. The metal particle size was measured by TEM and XRD techniques. It was shown that the dispersion of gold particles reached on silica and carbons is approximately the same (Figs. 1–4). The carbon support seems to be partially graphitized shown by the C(002) reflection at $2\Theta \sim 26^{\circ}$. In both samples, Au(111) reflection is missing indicating very small catalyst size. TEM micrographs show the support is having a weekly ordered structure consisting of



Fig. 1. TEM image and gold particle size distribution of 1 wt.% Au/SiO₂.



Fig. 2. X-ray diffraction patterns and particle size distribution of gold particles in 1 wt.% Au/SiO₂.



Fig. 3. TEM images and X-ray diffraction patterns of 1 wt.% Au/C (non-oxidized Sibunit).

connected ball-shaped carbonaceous features of ca. 100 nm diameter. The carbon content is (partly) graphitized as indicated by the strong $C(0\ 0\ 2)$ and $C(0\ 0\ 4)$ rings in the electron diffraction patterns. The particles size distribution of Au/C (not shown) is very narrow, with almost 100% of supported gold particles in the range of 1–2 nm (some of them are indicated by the arrows in the micrographs). The lack of diffraction patterns from Au is in agreement with the small particle size. Metal particles size distribution in 1 wt.% Au/SiO₂ can be considered to be monomodal with the particles predominantly below 3.5 nm, since besides a minor amount of particles in the range of 5–6 nm also a

few very large gold crystals about 20 nm were presented. This particle size distribution can be explained by the following mechanism of the active component formation. Point Zero Charge (PZC) of applied silica was found to be equal to 4. The value of the initial solution pH is 2.5. Since pH < PZC and the surface of silica is positively charged, adsorption of anionic complexes of gold can be performed. First gold is adsorbed as $[AuCl_3(OH)]^-$ complexes [23] followed by hydrolysis of Au–Cl bonds on the support surface. This species forms highly dispersed gold particles. Other $[AuCl_3(OH)]^-$ gold complexes are hydrolyzed in the solution and adsorbed on the surface as larger hydroxocomplexes of gold.



Fig. 4. TEM images and X-ray diffraction patterns of 1 wt.% Au/C (oxidized Sibunit).

3.2. XPS measurements

The XPS analysis of 1 wt.% Au/SiO₂ shows that Au 4f contains two contributions. The binding energy (BE) of the metallic gold is 84 eV. The doublet observed at lower BE is 0.9 eV shifted (Fig. 5). In gold catalysts this situation could be a consequence of two phenomena: electron transfer from the support towards the gold particles [24], or a dominant effect of the atoms at low coordinated sites as proposed by Radnik et al. [25]. The first possibility should be rejected due to the well known weak interactions of silica with noble metal clusters [26]. The second one should be possible if the gold particle size is lower than 2 nm. In XPS spectra of carbon supported gold catalysts the BE for metallic gold is 84 eV, for surface oxygen BE is taking 285 eV (for C(=O)-O-, C=O, C-OH, C-O-C, C-C, C-H surface groups) and 533 eV (for C-OH, C-O-C groups). The XPS shows that supported gold is in the zero valent state in the case of non-oxidized and oxidized carbons. Atomic ratio for Au/C and O/C was calculated from the peak areas ratio. The results are presented in Table 1. Comparison of the Au surface concentration in case of 1 wt.% Au/C and 1 wt.% Au/Cox shows lower concentration of gold on the carbon surface in the case of the oxidized support. The main difference between Au/C is observed in the O1s region. The pre-oxidized support has a new contribution at lower BE attributed to oxygen from the C=O group. The ability of carbon supports to stabilize dispersed metals is often attributed to



Fig. 5. Au (4f) region in XPS spectra of 1 wt.% Au/SiO₂.

the presence of the acidic oxygen-containing groups at the edges of graphene networks due to acid-base interactions [12]. Nevertheless the metal loading is lower in case of supporting gold on the oxidized carbon. Formed by PVA stabilization in the solution prior to immobilization gold sols are negatively charged and thus could be repulsed by surface oxygen groups due to electrostatic interactions.

3.3. Catalytic properties

Selectivity of synthesized catalysts towards hydrogenation and conjugation, especially towards desired products was investigated. 1 wt.% Au/C_{ox} provided the highest conversion of linoleic acid and the highest yield of hydrogenation products (Table 2), while the evaluated metal loading is the lowest among the tested catalysts. Although the conversion over 1 wt.% Au/C and 1 wt.% Au/SiO₂ was the same the yield of CLAs is higher in the case of linoleic acid isomerization over 1 wt.% Au/C. Moreover, in the latter case there are no hydrogenation products. Thus, the highest selectivity towards conjugation was observed over non-oxidized carbon supported gold catalyst. Despite the fact that three different samples of gold catalysts have approximately the same gold particle size, the behavior of these catalysts in linoleic isomerization is different. It can be thus concluded that chemical properties of support play an important role. Different catalytic behavior of gold catalysts can be most likely related to the difference of their surface chemistry. Presence of acidic groups on the supports surface in case of oxidized carbon and silica results in formation of hydrogenation products in linoleic acid isomerization due to higher acidity of the supports compared to non-oxidized carbon resulting in the protons donation. Although silica and non-oxidized carbon supported gold catalysts show the same activity, at the same time there are no hydrogenation products in the case of the carbon supported catalyst. That can be attributed to the mechan-

Table 1	
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Atomic ratio of the atoms on the surface of 1 wt.%Au/C and 1 wt.%Au/C_{ox}, calculated from XPS analysis.

1 wt.% Au/C	1 wt.% Au/C _{ox}
0.0009	0.0005
0.1328	0.1624
	1 wt.% Au/C 0.0009 0.1328

Table 2

Catalytic properties of gold catalysts in linoleic acid isomerization. Reaction time 4 h. X = conversion; S_i = selectivity; Hydr. = hydrogenation; \sum CLA = sum of CLAs.

Sample	X, %	S _{9-cis,11-trans} , %	S _{10-trans,12-cis} , %	S _{9-trans,11-trans} , %	S _{Hydr.} , %	∑CLA, %	Hydr./∑CLA
1 wt.% Au/C	4	32	23	45	0	100	0
1 wt.% Au/Cox	60 ^a	2	0	6	90	8	11
1 wt.% Au/SiO ₂	4	34	0	40	26	74	0.4

^a The same values of selectivity were observed at conversion of 4%.

ism of the reaction involving the proton transfer due to Brønsted and Lewis acidity (relatively weak in case of silica [27]) and the subsequent hydride transfer mechanism leading to hydrogenation [28,29]. This mechanism explaining the isomerization kinetics is most likely operative, while the conventional hydrogen addition (Horiuti–Polanyi mechanism [30]) is much less probable since Au does not adsorb readily H (H₂).

4. Conclusions

Gold catalysts supported on silica and mesoporous carbons were prepared by deposition–precipitation with urea and from gold sols respectively resulting in similar gold dispersion. However, when tested in linoleic acid isomerization, these catalysts exhibited different selectivity and activity. Different behavior of the catalysts can be attributed to the support acidity leading to different mechanism of isomerization reaction in the presence of hydrogen. Thus, oxidative treatment of the mesoporous carbon, although resulting in overall higher catalytic activity, promotes higher selectivity towards hydrogenation in comparison with linoleic acid isomerization. Selectivity towards isomerization is higher for the silica supported catalyst, that for Au/C_{ox} , however, hydrogenation is also taking place. The reaction over the non-oxidized carbon supported catalyst leads to formation of conjugated linoleic isomers only with high selectivity towards the desired isomers.

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