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Gold Catalysts for Selective Aerobic Oxidation of the Lignan Hydroxymatairesinol to Oxomatairesinol: Catalyst Deactivation and Regeneration

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Abstract The lignan oxomatairesinol was synthesized from the biomass-derived lignan hydroxymatairesinol via selective aerobic oxidation over a heterogeneous gold catalyst. The catalyst was prepared by direct ion-exchange and characterized by XRD, TEM and ICP-OES methods. The reaction was carried out at 70 °C and atmospheric pressure in a semi-batch reactor. To reveal the origin of catalyst deactivation, spent catalysts were studied by TEM, XRD, nitrogen physisorption, ICP-OES, TPO, and DSC-TGA techniques. Several regeneration procedures were applied—extraction by several solvents and calcinations in the oxidizing atmosphere. The former one was found to be the most effective way for the catalyst regeneration.

Keywords Gold catalysts · Selective oxidation · Biomass · Lignans · Oxomatairesinol · Hydroxymatairesinol · Catalyst deactivation

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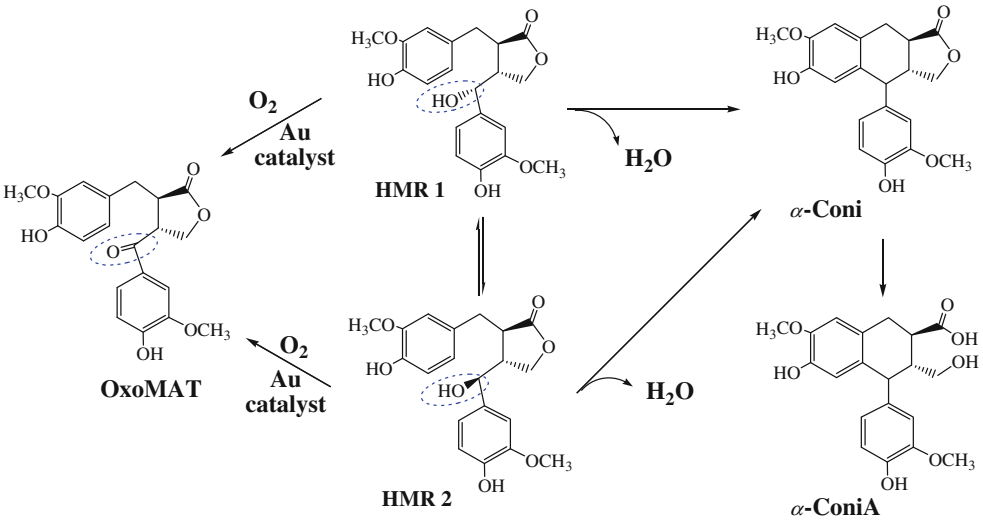
1 Introduction

Oxomatairesinol (oxoMAT) is a naturally occurring lignan, which has demonstrated a number of valuable properties for the cosmetic, textile and pharmaceutical industries. Recent studies have shown that lignans are active as human health-promoting agents by decreasing the risk for various cancers and cardiovascular diseases [1]. Studies of lignan radical and superoxide scavenging activities have shown that oxoMAT exhibits the highest superoxide scavenging activity [2]. Lignans or lignan derivatives, having antioxidative activity [3] and UV-protection properties [4], can be applied for cosmetic and pharmaceutical uses (skin- and hair-care products), as well as color-keeping agents for textile industry.

However, oxoMAT cannot be obtained in large quantities from wood or any other biomass, while it can be synthesized by using hydroxymatairesinol (HMR) as a starting material [5, 6]. The former one is a naturally occurring lignan, which can be extracted in considerable amounts from Norway spruce (*Picea abies*) knotwood, constituting 65–85 wt% of the total lignans and occurring in an unconjugated free form [7].

The formation of oxoMAT from HMR by light-irridation was reported in [8], while in [9] 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) was used as an oxidizing agent. As a first attempt to perform the reaction via heterogeneous catalysis, more attractive for industrial process, Pd/C catalyst has been studied for the synthesis of oxoMAT in anaerobic conditions and by using organic solvents [10]. However, oxoMAT was not the only product in this reaction.

Gold catalysts are well known for their high activity and selectivity in the alcohols aerobic oxidation reactions, mainly in oxidation of primary alcohols [11]. In general, the main advantage of gold based catalysts is environmentally-friendly manufacturing of organic chemicals employing molecular oxygen or air as oxidizing agents and relatively mild reaction



Scheme 1 The reaction pathway of HMR transformation over gold catalysts in aerobic conditions

conditions. Moreover, compared to typically utilized platinum and palladium catalysts gold is more stable at oxidative atmosphere [11, 12]. Since oxidation of secondary alcohols into ketones is an important synthetic procedure it was worth exploring a possibility to use gold catalysts also for synthesis of oxoMAT. The first reported study in [13] has demonstrated excellent activity and selectivity of heterogeneous gold catalysts, where the selectivity towards oxoMAT was 100 %. The reaction pathway is presented in Scheme 1.

The HMR oxidation reaction is in fact a reaction of secondary alcohol oxidation into the corresponding ketone (oxoMAT). The main by-products of the reaction are the lignans α-conidendrin (Coni) and its derivative—α-conidendric acid (ConiA). The lignan Coni is formed due to dehydration of HMR followed by a ring-closing reaction, while ConiA is a product of further Coni transformation, namely opening of the lactone ring.

Activity and selectivity were the main focuses of [13]. However, equally important is catalyst stability. Since in [13] a batch mode of operation was applied, catalyst deactivation could be obscured. A separate deactivation study should therefore reveal the reasons for deactivation if there are any, and the most suitable catalyst recycling to avoid additional catalyst deactivation or catalyst losses [14].

In this paper the aim was to study the catalyst deactivation during the oxoMAT synthesis and establish efficient catalyst regeneration procedures.

2 Experimental Section

2.1 Oxomatairesinol Synthesis over Au Catalysts

2.1.1 Catalyst Preparation and Characterization

Catalyst Au/Al_2O_3 was prepared by direct ion-exchange (DIE) method according to the procedure described in [15]. Gold precursor $HAuCl_4$, supplied by ABCR, Darmstadt (99.9 % of purity, 49.9 % Au), was dissolved in dionized water to reach the concentration 5×10^{-4} M. The solution was heated to 70 °C and kept under stirring for 1 h. After that the alumina support (UOP, A-201, $S_{BET} = 200\ m^2/g$) was introduced in an amount corresponding to a metal loading of 2 wt% Au on alumina. The slurry was mixed for 1 h at 70 °C. For the further hydrolysis and stabilization of the supported gold, 4 M ammonium hydroxide aqueous solution was added and the slurry was kept under the stirring for 1 h at 70 °C. The obtained slurry was filtered and washed with water, followed by drying at 70 °C over night and calcination at 300 °C for 4 h.

The prepared catalyst was characterized by transmission electron microscopy (TEM) and X-ray diffraction (XRD), inductively coupled plasma-optical emission spectrometry (ICP-OES), and nitrogen adsorption techniques. The applied procedures are described in more details below.

2.1.2 Synthesis of oxoMAT

2.1.2.1 Starting Material The lignan HMR was extracted from ground Norway spruce knots by acetone–water mixture as described in [16]. The extract was concentrated in a rotary evaporator and then purified by flash chromatography. HMR was obtained as a mixture of two diastereomers: (7R,8R,8′R)-(-)-7-allo-hydroxymatairesinol (HMR1) and (7S,8R,8′R)-(-)-7-allo-hydroxymatairesinol (HMR2), where the molar ratio between them HMR2:HMR1 was 2:1 mol/mol. The purity of HMR was determined by GC to be 95 %, the major contaminants being the lignans Coni and ConiA, which structures are presented in Scheme 1.

As was reported before [13], both isomers, HMR1 and HMR2, could be oxidized, and the isomerization between them also occured.

2.1.2.2 Reaction Performance The HMR oxidation reaction was performed under atmospheric pressure in a stirred 200 ml glass reactor, equipped with a heating jacket (using silicon oil as the heat transfer medium), a re-flux condenser (cooling medium set at −20 °C), an oil lock, a pitched-blade turbine and stirring baffles. The desired amount of catalyst was placed into the reactor. The catalyst grain size was 45–63 μm to suppress the internal mass transfer limitations. The catalyst was pre-activated in situ by heating under hydrogen (AGA, 99.999 %) flow (100 ml/min) until the temperature reached 150 °C, thereafter the reactor was cooled down to the reaction temperature 70 °C under the nitrogen (AGA, 99.999 %) flow (100 ml/min). Gold catalysts were studied using 2 vol% propan-2-ol (Sigma-Aldrich, 99.8 %) in water as a solvent, which earlier was shown to be the most effective solvent [13]. The reactant solution (100 ml) with an HMR concentration of 1 mg/ml was poured into the reactor. The gas flow was changed to synthetic air. The stirring (1,000 rpm to avoid external mass transfer limitations) was started at reaction time set to zero and the first sample was withdrawn. Typically the reaction was carried out for 4 h.

2.1.2.3 Products Analysis Samples were withdrawn from the reactor at different time intervals and analyzed by gas chromatography (GC) using an HP-1 column (length 25 m, inner diameter 0.20 mm, film thickness 0.11 μm) and a flame ionization detector (FID) operating at 300 °C. For the analysis, 100 μl (concentration of 1 mg/ml) of the sample was taken. Prior to analysis, samples were mixed with an internal standard, dried and silylated as described in [13]. 1 μl of the silylated sample was injected with an autosampler. The injection temperature was 260 °C and the split ratio was 1:20. Hydrogen served as a carrier gas. The initial temperature of the column was 120 °C (for 1 min), and the temperature was increased at a rate 6 °C/min to 300 °C (for 10 min). The peaks were identified by analysis with a gas chromatograph-mass spectrometer operating at the same GC conditions.

2.2 Catalyst Regeneration Procedures

The spent catalysts were filtered and washed with either water, acetone or propan-2-ol at their boiling temperatures: 100, 56 and 83 °C correspondingly, followed by drying overnight at 70 °C.

In situ catalyst washing was performed after the reaction. The reaction mixture was withdrawn from the reactor, and then 100 ml of propan-2-ol was added to the catalyst in the reactor. The slurry was mixed for 1 h at 83 °C. Thereafter alcohol was withdrawn from the reactor and analyzed by GC, as described in Sect. 2.1.2. The washed catalyst was applied in the next experiment.

The catalyst after the reaction was filtered, washed with water, dried overnight at 70 °C and calcined in air either at 300, 400 or 500 °C with temperature ramp 2 °C/min.

2.3 Catalyst Deactivation Study

2.3.1 Substrate Analysis

In order to determine inorganic impurities in the substrate HMR, as well as gold loading in the catalyst before and after the reaction, analysis by ICP-OES in a PerkinElmer Optima 5300 DV spectrometer was performed. The following procedures were applied. HMR sample of 300 mg was placed in a Teflon bomb, 5 ml HNO_3 and 1 ml H_2O_2 were added, digested in a microwave oven, diluted to 100 ml, and analyzed in the spectrometer.

Applied HMR contains up to 5 % of another lignan Coni. The former one can be transformed to ConiA (see Scheme 1). Both of these lignans could be adsorbed on the gold surface and thus decrease the catalyst activity. In order to distinguish the influence of impurity on the catalyst activity the lignan Coni was added to the reaction mixture with HMR. The reaction was carried out according to a typical procedure described in the Sect. 2.1.2.

2.3.2 Characterization of the Spent Catalyst

In order to study catalyst surface changes after the reaction, spent gold catalyst was analyzed by TEM, XRD, nitrogen physisorption, ICP-OES, temperature-programmed oxidation (TPO), and thermogravimetric analysis with differential scanning calorimetry (DSC-TGA) techniques in the following way.

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

XRD experiments were performed by using CuKα radiation (Siemens D5000 diffractometer equipped with a graphite monochromator to suppress fluorescent and CuKβ radiation). The average crystallite size of the gold particles was estimated using Scherrer's equation from the peak half-widths of Au(111) reflection measured at $2\Theta \sim 38.3°$. Instrumental broadening and unresolved CuKα1 and α2 radiation were neglected (error less than 2 %).

The metal loading was determined by ICP-OES in a PerkinElmer Optima 5300 DV. For analysis, 60 mg of sample was weighed into Teflon bombs, 5 ml of aqua regia was added, digested in a microwave oven, diluted to 100 ml, further diluted to a 1:1 ratio and analyzed by ICP-OES.

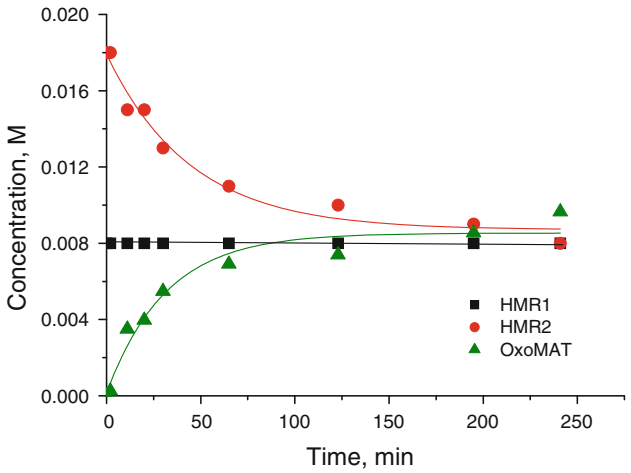


Fig. 1 Selective oxidation of HMR to oxoMAT over 250 mg of 2 wt% Au/Al_2O_3 under a synthetic air flow at 70 °C

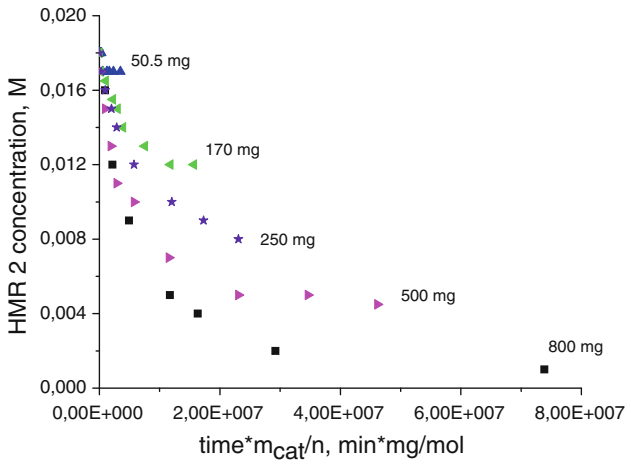


Fig. 2 Concentration profile of HMR2 during the reaction of selective oxidation over 2 wt% Au/Al_2O_3 at different catalyst mass (50.5–800 mg) under synthetic air flow at 70 °C

Specific surface area of the spent catalysts was measured by nitrogen adsorption by using Carlo Erba Sorptomatic 1900 and applying BET method. For the experiment, 200 mg of sample was used.

Spent catalysts were also analyzed by the TPO method. For that 200 mg of the sample was placed in the quartz tube reactor and heated in the oxidizing atmosphere (2.5 % O_2 in He gas mixture, supplied by AGA) in the range of the temperature 30–650 °C. The organic compounds from the outlet were analyzed by mass-spectrometry (Quadrupole mass spectrometer QMS 200). Predominantly, CO_2 and CO were analyzed to perform the gas calibration.

Thermogravimetric analysis was performed with DSC-TGA (Q Series instrument) by subjecting ca. 9 mg of spent catalyst to 400 and 500 °C at 2 °C min^{-1} under a steady stream of 20 % oxygen in nitrogen gas mixture at 100 ml/min.

3 Results and Discussion

3.1 Catalytic Results

HMR isomers have demonstrated different reactivity, with HMR2 being more reactive than HMR1. The difference in HMR diastereomers reactivity was earlier investigated and attributed to the different energy of formed intermediates as well as steric hindrance of the functional OH-group [10, 13]. The experiment with prolonged time resulted in zero conversion of HMR1 and 70 % conversion of HMR2. The reaction profile of HMR selective oxidation presented in Fig. 1 demonstrates the loss of the catalyst activity with time; furthermore, the reaction was stopped at 70 % of HMR2 conversion. In the studied case, HMR1 was not reacting, although it was already mentioned before, that both isomers could be oxidized to oxoMAT.

In order to study the catalyst deactivation phenomena, HMR oxidation was performed over different amounts of the Au on alumina catalyst (2 wt% Au/Al_2O_3), while the substrate amount was the same in all experiments. The activity of the catalysts was shown to decrease with the reaction time. The obtained kinetic curves depicted in Fig. 2 using the normalized reaction time. As could be seen from Fig. 1, curves at different catalysts amounts do not coincide. Smaller amounts of catalyst deactivated faster, which could be associated with the presence of impurities in the feedstock. Since the substrate is wood biomass derived substance, it could contain small amount of inorganics, similar to β-sitosterol. Moreover, catalyst deactivation during hydrogenation of naturally occurring β-sitosterol over palladium catalysts was studied and attributed in particular to the presence of inorganic impurities in the substrate poisoning the catalyst [17].

In a series of experiments where the reaction stops at HMR conversion lower than 100 %; fresh catalyst was added to the reaction mixture, while the spent one was removed. Three consequent experiments for 4 h each with the same substrate were carried out. Performing the reaction over fresh catalysts demonstrated an increasing HMR conversion after each experiment (Fig. 3). Thus, the conversion of HMR was 22, 36, and 44 %, respectively. Moreover, catalyst deactivation was faster in case of the first experiment, starting at 2 h of reaction time, while the next experiments resulted in the catalyst deactivation in 3 h after the reaction was started even in the presence of oxoMAT.

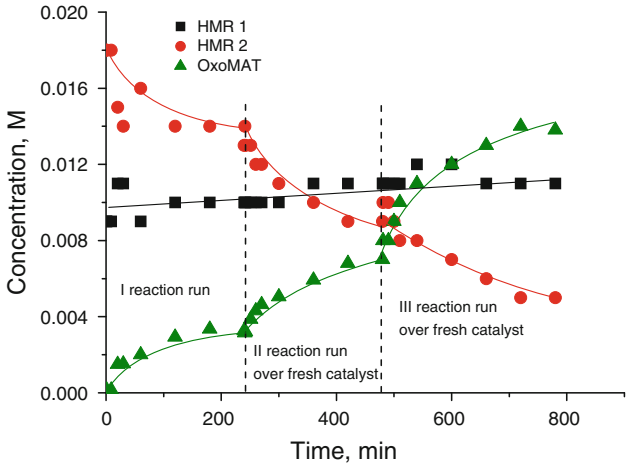


Fig. 3 Consequent experiments with fresh catalyst 2 wt% Au/Al_2O_3, 70 °C, under synthetic air flow

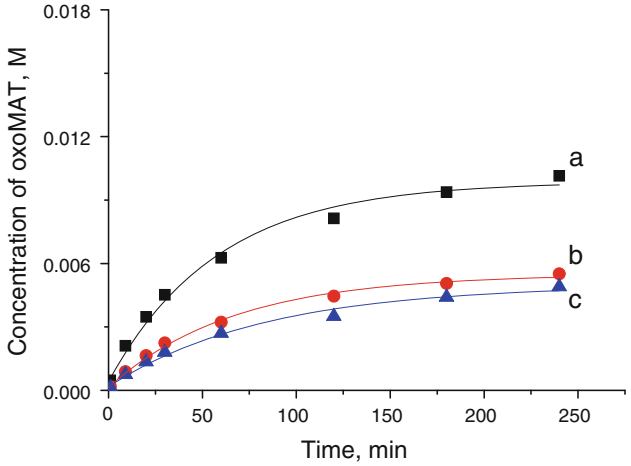


Fig. 4 HMR oxidation over 2 wt% Au/Al_2O_3 catalyst under synthetic air in the presence of Coni in the amounts of: (*a*) 0.0001 mol; (*b*) 0.0002 mol; (*c*) 0.0003 mol

3.2 Catalyst Deactivation

The reasons of the catalyst deactivation could be: poisoning by reagents and solvent impurities, catalyst leaching, gold particles sintering and catalyst surface reconstruction, or strong adsorption of the reaction and side-reaction products, which can form oligomeric or polymeric structures.

3.2.1 Poisoning by the Substrate

Element analysis of HMR was performed by ICP-OES. Since lignan HMR is extracted from wood biomass, some amounts of inorganic impurities were expected. However, the results revealed very low content of inorganic elements present in the lignan sample. Only six elements were detected. The content of metals in mg/kg of HMR was Ca ~2, Fe <10, Mg <5, Na <50, Si <10 and Ti <5.

Furthermore, there were no typical biomass related catalyst poisons as chlorine, sulphur or phosphorous. Thus, poisoning by these elements as a reason for catalyst deactivation was excluded.

Lignan Coni was added in the reaction mixture in order to understand the influence of this lignan on the catalyst activity during the HMR oxidation reaction. Obtained reaction profiles at different Coni concentrations are presented in Fig. 4. Increasing the Coni amount from 10^{-4} to 3×10^{-4} mol% significantly decreased catalyst activity. In the later case the reaction did not proceed after 130 min and resulted in 27 % of HMR conversion, while the catalyst was still active even after 175 min in case of 4 % of Coni content with HMR conversion being 56 %. These results suggest that the presence of the lignan Coni in the substrate was one of the reasons for catalyst deactivation. The lignan Coni can form another lignan ConiA on the catalyst surface, which can be strongly adsorbed on the catalyst surface by carboxylic group. Since lignan Coni has lower solubility than HMR in the same solutions, catalyst deactivation due to Coni sedimentation could also occur.

3.2.2 Leaching of the Active Phase

To study the metal leaching, samples of the gold catalyst before and after the reaction were analyzed by ICP-OES. Gold content in the spent catalyst was lower than in the fresh one by 10 % (decreasing from 2.1 ± 0.15 to 1.9 ± 0.13 wt%), which is within experimental error of ICP-OES measurements. In order to exclude the influence of homogeneous catalysis, HMR oxidation reaction was performed in two consequent experiments. First reaction run was carried out over Au/Al_2O_3, then the catalyst was removed and the second reaction run was performed at the same conditions. The results are presented in Fig. 5. Reaction over gold catalyst resulted in 40 % conversion of HMR at 100 % selectivity to oxoMAT, while in the absence of catalyst no oxidation of HMR was observed and the only product was ConiA, which can be formed via a base catalyzed reaction.

3.2.3 Sintering of Au Particles

Gold particle size of fresh and spent catalysts was studied by TEM and XRD measurements. It was noted, that both, fresh and spent, catalysts had an average gold particle size about 2 nm, although some slight changes in gold particle size were noticed (Fig. 6a, b). Due to the small size of gold in the catalyst no reflections were seen in XRD. Thus, catalyst deactivation cannot be attributed to sintering of Au particles.

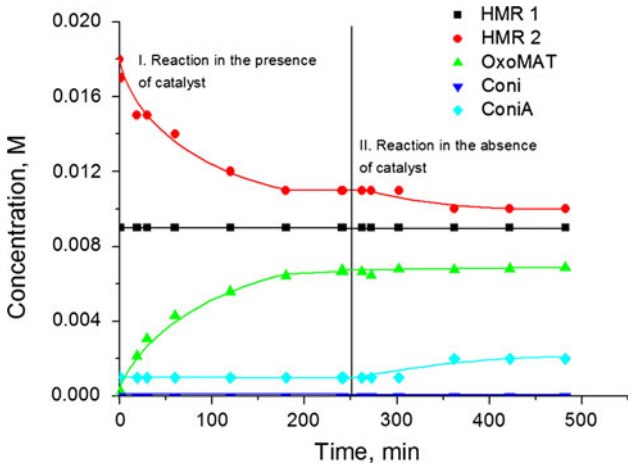


Fig. 5 Selective oxidation of HMR over 250 mg of Au/Al_2O_3 catalyst and in the absence of catalyst at 70 °C, under synthetic air flow

3.2.4 Strong Adsorption of Organic Molecules

The specific surface area of fresh and spent catalysts was measured. The BET specific surface area of the fresh catalyst was 245 m^2/g, while the spent catalyst had a BET specific surface area 4 % less than the fresh one, which was 235 m^2/g being within the adsorption measurements error, while it could also suggest the formation of organic deposits on the catalyst surface and hence decreases of catalyst activity.

More information was provided by analysis of the spent catalyst by TPO using MS, which revealed the presence of organic compounds on the catalyst surface. In the temperature interval 90–180 °C water was desorbed. Afterwards, in the interval of 250–450 °C the introduced oxygen was consumed, while CO_2, CO and water were desorbed. Desorption of these three compounds was attributed to the combustion of the adsorbed hydrocarbons.

In order to determine the amount of organic compounds adsorbed on the surface DSC-TGA was applied. The samples were treated at the same temperature and atmosphere as in the calcinations procedures for regeneration of the spent catalyst. The results of the measurements are presented in Fig. 7. Catalyst calcination at 400 and 500 °C resulted in ca. 16 and 17 % weight loss. Calcination at higher temperature was more efficient in the decomposition of organic residues on the catalyst surface. However, increasing of the calcination temperature led to gold particles sintering. Already after the calcination at 400 °C, average gold particle size increased from 1.8 nm (Fig. 6a) to 2.6 nm (Fig. 6c).

The reaction of HMR oxidation to oxoMAT was performed in the propan-2-ol mixtures in the presence of water. Due to limited solubility of HMR in water the reaction cannot be carried out with only water as a solvent. Application of other solvents was discussed previously in [13], where propan-2-ol/water mixture was chosen as the most effective solvent. However, propan-2-ol could be oxidized over gold catalyst followed by acetone formation [18] and adsorption on the gold active sites. Furthermore, there was no oxoMAT detected, when the reaction was carried out in the neat propan-2-ol, indicating competitive oxidation of propan-2-ol. The reaction of Meerwein–Ponndorf–Verley reduction catalyzed by aluminium isopropoxide could also be the reason for preferable formation of acetone [19], while oxoMAT was not produced. It was shown in [13] that increasing of the alcohol amount in water results in the dramatic decrease of the catalyst activity in oxoMAT synthesis. For that reason, to minimize acetone formation the reaction was performed using diluted alcohol solution, namely 2 vol% propan-2-ol in water.

Strong adsorption of the product during the HMR oxidation could be another reason of the catalyst activity decrease. Since oxoMAT being a ketone is formed during the reaction, its carboxylic group can be adsorbed stronger on the gold active sites, than hydroxyl-group of the reagent. Adsorbed molecules could also form polymeric compounds on the catalyst surface.

Nevertheless, the experiments with adding the fresh catalyst (Fig. 3) pointed out the acceleration of the reaction rate even in the presence of the product. This fact indicated that poisoning by substrate impurities decreases catalyst activity more than the product adsorption. Thus, the effect of adsorbed organic molecules (e.g. from the feedstock and formed during the reaction) was considered as the main reason of the catalyst deactivation in the studied case.

3.3 Catalyst Regeneration

3.3.1 Washing Treatment

Weakly adsorbed organic compounds in general could be extracted by organic solvents or hot water. Several solvents were applied in the present work: water, acetone and propan-2-ol. The results are presented in Table 1. During the reaction, HMR 2 can be oxidized to oxoMAT or isomerized to form HMR 1. It was demonstrated in [13], that isomerization occurs over alumina surface, while it is not the case in the presence of supported Au particles. The impact of isomerization reaction increases with decreasing of the gold catalyst activity. The reaction over the washed spent catalyst resulted in lower catalyst activity compared to the fresh one. Moreover, the selectivity to oxoMAT decreased significantly in case of washing the spent catalyst by organic solvents, such as propan-2-ol and acetone. The reason for that is most likely deactivation during the washing procedure of gold particles responsible for the

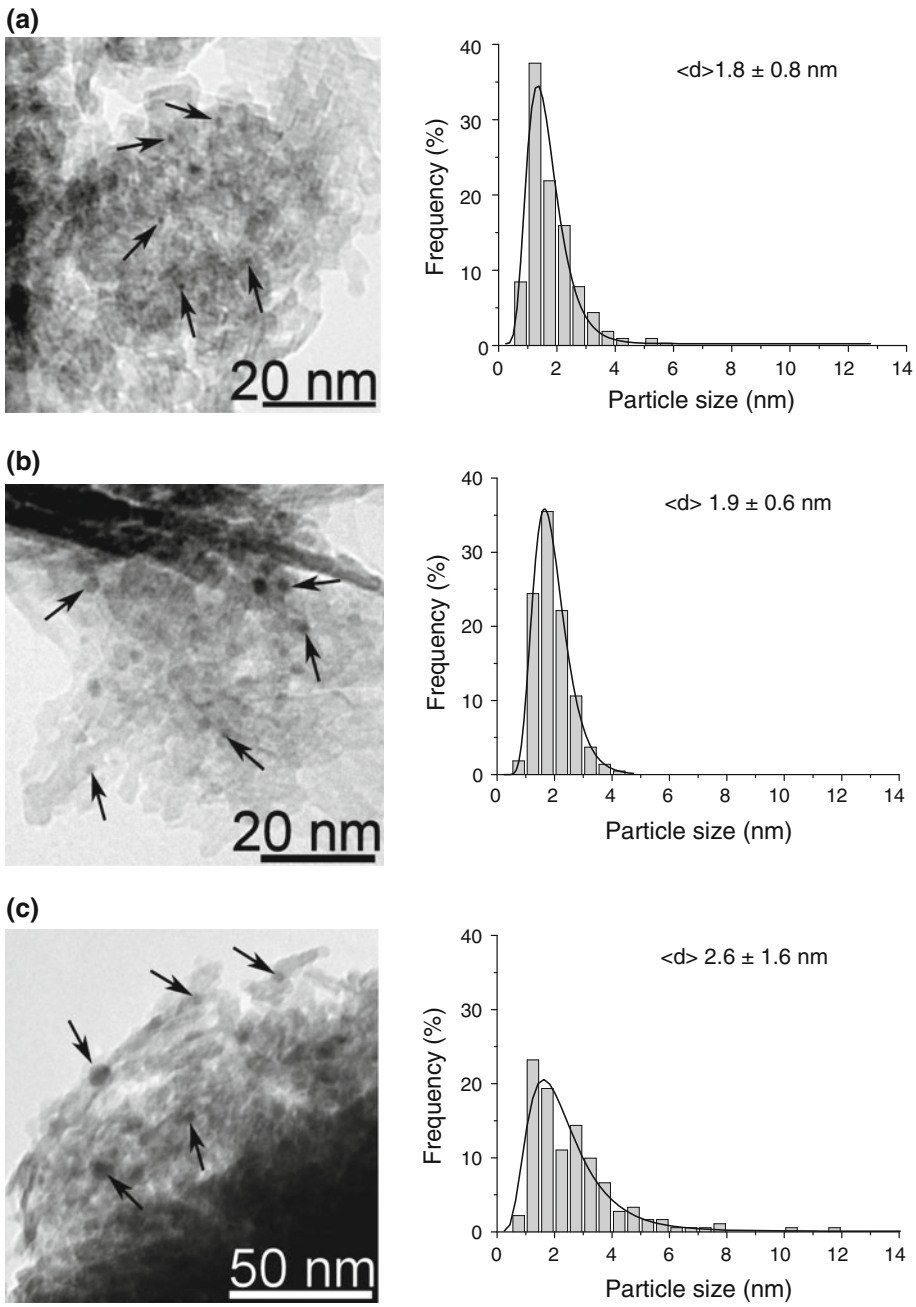


Fig. 6 TEM images and particle size distribution histograms of 2 wt% Au/Al_2O_3 catalysts: **a** before the reaction, **b** after the reaction of HMR oxidation, **c** after the reaction of HMR oxidation and calcination at 400 °C

oxidation reaction. Catalyst calcination and calcination after the washing with water were found to be the most efficient approaches for catalyst regeneration.

The in situ catalyst washing was applied in order to exclude catalyst losses and additional deactivation of the catalyst by exposure to air and light, which are known to decrease gold catalyst activity [20]. The results are compared with the two consequent experiments without a washing procedure (Fig. 8). Kinetic curves obtained in two runs over the fresh catalyst were very similar, for that reason, only one of them is displayed in Fig. 8. The initial reaction rates over washed and non-washed catalysts were similar, while the non washed catalyst was deactivating faster.

Attempts to extract organic compounds by different solvents were shown to be ineffective in the catalyst regeneration, although some improvements of catalytic activity were achieved.

3.3.2 Calcination

Calcination of the spent catalysts was performed either at 300, 400 or 500 °C. According to the TPO technique equipped with mass-spectrometer and DSC-TGA

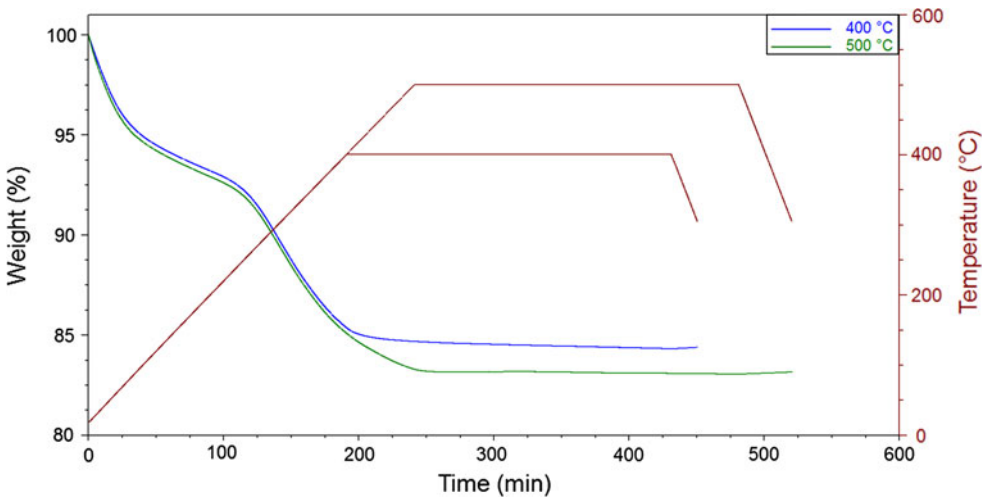


Fig. 7 DSC–TGA curve showing the weight decomposition of spent 2 wt% Au/Al_2O_3 at increasing temperature

Table 1 Selective oxidation of HMR over fresh and spent 2 wt% Au/Al_2O_3 catalysts under synthetic air flow at 70 °C

Catalyst Au/Al_2O_3	$k \times 10^2$, $s^{-1} \times g_{Au}^{-1}$	Conversion after 4 h (%)	Selectivity after 4 h (%)			
			OxoMAT	HMR 1	Coni	ConA
Fresh	9.5 ± 1.8	56	100	0	0	0
Spent						
No treatment	1.0 ± 0.2	17	20	80	0	0
Calcined at 300 °C after 1 run	5.5 ± 1.1	32	50	50	–	–
Washed by H_2O, 100 °C						
Re-used 1 time	2.0 ± 0.4	25	42	58	0	0
Re-used 2 time	0.9 ± 0.2	8	64	36	0	0
Calcined at 300 °C after 2 run	3.0 ± 0.5	40	66	34		
Re-used 3 time						
Washed by acetone, 56 °C						
Re-used 1 time	1.8 ± 0.4	25	21	40	2	37
Re-used 2 time	1.8 ± 0.4	25	7	47	2	43
Washed by propan-2-ol, 83 °C						
Re-used 1 time	1.0 ± 0.2	14	13	87	0	0
Re-used 2 time	0.5 ± 0.1	10	30	70	0	0

measurements, at temperatures of 300–450 °C the combustion of adsorbed organics was observed. Increasing of the calcination temperature resulted in catalyst surface reconstructions due to gold particles sintering and changes of the alumina phase [21]. HMR oxidation performed over the spent catalysts treated at 400 and 500 °C resulted in the 32 and 28 % conversion of HMR, respectively, and 100 % selectivity to oxoMAT (Table 1). The effect of catalyst calcinations was compared to the activity of water-washed catalyst and non-treated spent catalyst (Fig. 8). Catalyst calcinations resulted in higher yield of oxoMAT. Furthermore, calcinations of the spent catalyst at higher temperature (500 °C) resulted in slightly lower HMR conversion, than after calcinations at 400 °C. This observation suggests that increasing of calcinations temperature is not efficient for catalyst regeneration. It is worth to note, that calcinations at 300 °C improved catalyst activity, while the selectivity to oxoMAT decreased to 66 %. The optimal calcination procedure was found to be performed at 400 °C.

Nevertheless, the catalyst activity of the calcined spent catalyst was almost two times lower than the activity of the fresh one. The reason for this is a combination of several factors. Besides incomplete oxidation of strongly adsorbed organics and experimentally detected Au particles sintering (see Sect. 3.2.2) also leaching of Au during the reaction (see Sect. 3.2.3) can contribute to the overall decline of catalyst activity.

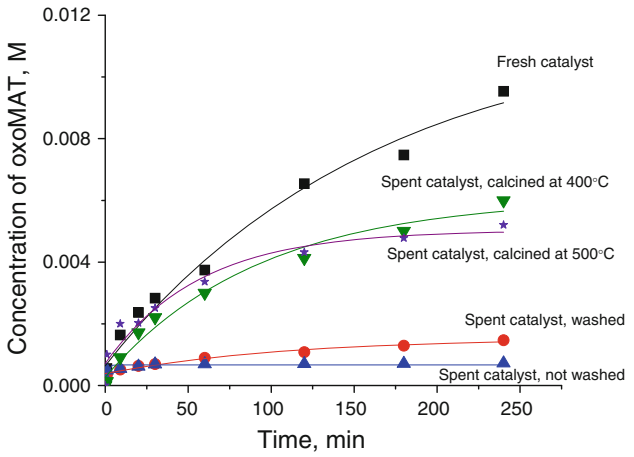


Fig. 8 OxoMAT concentration profile during HMR selective oxidation over 2 wt% Au/Al_2O_3 catalysts: fresh, spent/calcined, spent/washed and spent/non-washed

4 Conclusions

The nature of gold catalysts deactivation during the oxomatairesinol synthesis by oxidative dehydrogenation of hydroxymatairesinol was investigated. The main reason for decreasing of catalyst activity was found to be adsorption on gold surface of organic components from the substrate and the reaction product. A minor impact of other factors, such as catalyst leaching and gold particles agglomeration, can also be the reason for catalyst activity decrease. The most successful approach to regenerate the catalyst is calcination in an oxidizing atmosphere.

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