Ruthenium-containing SBA-12 catalysts for anisole hydrodeoxygenation

Agnieszka Feliczak-Guzik, Paulina Szczyglewska, Mietek Jaroniec,
Izabela Nowak

PII: S0920-5861(19)30113-0
DOI: https://doi.org/10.1016/j.cattod.2020.03.006
Reference: CATTOD 12719

To appear in: *Catalysis Today*

Received Date: 12 June 2019
Revised Date: 3 February 2020
Accepted Date: 4 March 2020

Please cite this article as: Feliczak-Guzik A, Szczyglewska P, Jaroniec M, Nowak I, Ruthenium-containing SBA-12 catalysts for anisole hydrodeoxygenation, *Catalysis Today* (2020), doi: https://doi.org/10.1016/j.cattod.2020.03.006

Ruthenium-containing SBA-12 catalysts for anisole hydrodeoxygenation

Agnieszka Feliczak-Guzik, [1] Paulina Szczyglewska, [1] Mietek Jaroniec, [2] Izabela Nowak[1]

Authors

[1]*Adam Mickiewicz University in Poznań, Faculty of Chemistry, Uniwersytetu Poznanskiego 8, 61-614 Poznan, Poland*

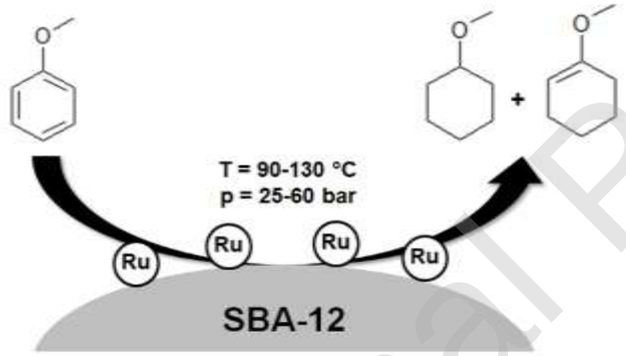
[2]*Kent State University, Department of Chemistry and Biochemistry, Kent Ohio 44242, USA*

Corresponding author

Izabela Nowak

Adam Mickiewicz University in Poznań, Faculty of Chemistry, Uniwersytetu Poznanskiego 8,
61-614 Poznan, Poland
Email: nowakiza@amu.edu.pl

Graphical abstract



Highlights:

- Synthesis of stable Ru-containing mesoporous materials.
- High conversions in the hydrodeoxygenation of anisole.
- Upgrading anisole, a product of thermal conversion of lignin.
- Study of mechanism of the HDO reactions over RuSBA-12.

Abstract

Hexagonally ordered mesoporous silica SBA-12 catalysts containing various amounts of Ru (1 or 3 wt.%) were obtained by wet impregnation. These catalysts were thoroughly characterized by X-ray diffraction (XRD), transmission electron microscopy (TEM), and low-temperature nitrogen adsorption/desorption (N_2 ads/des). Anisole conversion was measured over catalysts at different process conditions, where the process temperature was 90-130 °C and the hydrogen pressure – 25-60 bar. Prior the experiments the process was optimized, i.e., the amount of catalyst used in the reaction and the time of reaction were adjusted. This study shows a significant effect of hydrogen pressure and process temperature on the hydrodeoxygenation of anisole, the conversion of which increased (16-100%) with both increasing parameters. For all the catalysts studied, the highest selectivity was obtained to two main reaction products, methoxycyclohexane and 1-methoxycyclohexene. Along with increasing conversion of anisole, the selectivity to the main reaction product - methoxycyclohexane generally increased (65-96%) reducing the amount of 1-methoxycyclohexene (0-27%).

Keywords

ordered mesoporous silica, biomass upgrading, biooil processing

1. Introduction

Depletion of natural energy resources (crude oil, natural gas, solid fuels) has prompted a great interest in the use of renewable energy sources, mainly biomass [1]. Increased interest in the biomass conversion is not only because of the energy related reasons but also ecological reasons, mainly the need to restrict the emission of greenhouse gases [2, 3]. Biomass composed of cellulose, hemicellulose and lignin units [4, 5], thanks to its chemical decomposition and processing abilities is a valuable raw material that can be processed into a number of useful products, e.g., substitutes of crude oil fuels [6, 7]. This aspect is very important because at present transport uses up to 1/5 of energy on the global scale [8, 9].

One of the technologies used for transformation of biomass is fast pyrolysis, which is thermal decomposition of high-molecular chemical compounds to simpler components under anaerobic conditions [10, 11]. At these conditions, the building blocks of biomass undergo degradation leading to the formation of a liquid fraction known as biooil or pyrolytic oil [12].

It is a mixture of over 300 different chemical compounds containing a significant number of oxygen atoms [13], mainly in the form of oxygen lignin derivatives, aldehydes (including heterocyclic furfurals), alcohols, phenols, ketones, carboxylic acids or carbohydrates [6, 14]. Biooil has a high energy potential as it maintains up to 70% of the initial biomass energy [5]. However, it cannot be applied directly as a fuel because of a too high content of water (up to 25 wt.%) and oxygen (up to 40 wt.%), which finally results in a low calorific value [5, 9]. In order to make its properties more resembling those of crude oil, biooil must be subjected to physicochemical processing [15].

A promising pathway to get high quality hydrocarbon fuel from biooil is the catalytic hydrodeoxygenation (HDO) [16-18]. This process is based on the reaction of chemical compounds contained in biooil with gaseous hydrogen, under elevated pressure, elevated temperature and in the presence of a catalyst. Under these conditions the reagents are transformed to simpler compounds, mainly hydrocarbons [18, 19]. This process permits a removal of oxygen atoms from chemical compounds of biooil but also leads to the saturation of multiple bonds of the reagents, which improves the system stability. Finally, the process brings a decrease in the O/C ratio at the simultaneous increase in the H/C ratio, which means that the improved biooil, called a biofuel, can be used as a motor vehicle fuel [9]. The HDO process is usually carried out at a temperature between 200 and 500 °C under hydrogen at a pressure reaching 200 bar [20]. Under such conditions, the majority of chemical compounds are able to convert into their deoxygenated analogues [6]. In the laboratory scale the mechanism of HDO is studied using the so-called model chemical compounds that are identical to those contained in biooil [21]. Very often anisole is selected for investigation because it contains an isolated methoxyl group (-OCH_3) which is the most often met in the chemical structure of biooil [22-24].

High yield of HDO process depends on the catalyst which should by characterized by high activity even at lower pressure and temperature [21, 25]. The most effective catalysts for this process are those with transition metal ions (Pt, Pd, Ru, Rh, Ir, Co, Ni) as the active components because they show high activity in the processes involving hydrogen [26, 27]. Because of their high cost [28], they are usually deposited on supports in order to enlarge the surface area of the active phase and improve the mechanical strength and thermal stability of the system [29]. A particularly interesting group of supports are ordered mesoporous silicas [30-32], characterized by well-developed system of pores with diameters between 2 and 50 nm, high pore volume (~0.7 cm^3/g) and large surface area reaching even 1000 m^2/g [29, 33]. Very attractive silicas are those of SBA (Santa Barbara Amorphous) type materials because they are non-toxic, possess ordered mesoporous structure with interconnected micropores in the mesopore walls and can be easily synthesized by block copolymer soft templating [30, 34].

The best-known representative of the SBA class of materials is SBA-15 silica with two-dimensionally ordered mesopores. Below are some examples from the literature where this material was used as catalyst in the HDO reaction.

A very interesting silica from the SBA group is SBA-12, which has a hexagonal distribution of channels with the $p6_3/mmc$ space group. The specific surface area of this silica often exceeds 1000 m^2/g [35]. The pores of the SBA-12 material have a three-dimensional architecture that essentially facilitates the transport of larger reagent molecules, which in turn provides easier access to active sites. The material in question has not yet attracted much attention , although there is a good chance that it will because, like the SBA-15 silica, it has thick pore walls, thanks to which it is thermally and hydrothermally stable.

Catalytic systems based on mesoporous silicas have been explored by many authors in hydrodeoxygenation of anisole. Yang et al. [36] have studied the mechanism of HDO of anisole catalyzed by a catalyst having nickel atoms on SBA-15 type mesoporous silica. The process was performed at 310 °C under hydrogen pressure of 30 bar for 6 h. The products formed in large amounts at 100% anisole conversion were hexane (selectivity 26%), cyclohexane (30%) and benzene (26%). Results of this experiment proved high activity of the catalyst used because it was possible to obtain a high degree of deoxygenation and anisole hydrogenation.

Similar studies have been carried out by Sankaranarayanan et al. [5] who investigated the catalytic activity of ordered mesoporous silica, specifically SBA-15 with deposited cobalt atoms as the active phase. The process was performed at 220 °C under hydrogen pressure of 50 bar for 2 h. These authors achieved 99% anisole conversion to the following products: methoxycyclohexane (selectivity 72%), cyclohexane (12%), cyclohexanone (1%) and cyclohexene (0.5%). The catalytic system was also very active, although the highest selectivity was achieved to methoxycyclohexane, to the compound with single bonds between carbon atoms but still having oxygen in the structure. Although the results of hydrodeoxygenation of chemical compounds of biooil are good, the search for catalytic systems capable of providing high yields but at possibly lower temperatures and pressures is continued [26]. According to literature, the HDO process is the most effective at elevated temperatures and pressures, but at these conditions it is an energy consuming process, uneconomical from industrial viewpoint [37].

Previously only SBA-15 among the SBA-family materials was used as a support of the HDO catalyst. Here we report data for hydrodeoxygenation of anisole over the ruthenium catalyst deposited on SBA-12 silica at relatively low temperature (90-130 °C) and under low pressure of gas hydrogen (25-60 bar). We studied the effect of the reaction time, the amount of catalyst and the active phase loading on the conversion process. The impact of these parameters on the degree of anisole conversion, types and amounts of the reaction products is discussed. It is the first attempt of using SBA-12 silica with transition metal catalysts in the HDO conversion. Such ordered mesoporous silica with symmetry group $p6_3/mmc$ can be of consideration when outstanding stability and three-dimensional mesopore structure is desired for the proper adsorption/diffusion necessary in heterogeneous catalysis. A comparison with other catalysts is assessed.

2. Experimental

2.1. Synthesis of SBA-12 silica with deposited ruthenium

SBA-12 silica was synthesized by adding structure-directing agent BRIJ 76 surfactant (Sigma Aldrich; 8 g) to a mixture of water (40 g) and 0.1M chloric acid (160 g) and stirring for 2 h. Then, 17.6 g of tetraethyl orthosilicate (TEOS, Fluka, 99% purity) was added and the mixture was stirred for 20 h. After this time, the mixture was poured to PP bottles and placed in a drying apparatus at 80 ºC for 24 h. The solid product was filtered, dried and calcined in order to remove the template at 550 ºC for 6 h. The resulting silica was subjected to wet impregnation in order to introduce different amounts of ruthenium to obtain catalysts with different amount (wt.%) of Ru with respect to the mass of the support (the incremental dosage was 0.5 wt.% up to maximum 3 wt.%, i.e., catalysts with 0.5; 1; 1.5; 2; 2.5 and 3 wt.% were prepared). Ethanol solution of ruthenium(III) chloride was introduced dropwise to the dry SBA-12 support in the amount sufficient to fill the pores and wet the external surface of particles. The content of the beaker was stirred. The beaker was tightly closed with a polyolefin-paraffin foil Parafilm® and left to rest for 24 h to allow penetration of the solution into the pores of SBA-12. Afterwards, the foil was removed and the beaker was placed under fume hood at room temperature until the entire solvent was evaporated under stirring the content from time to time. Next, the catalysts were dried for 1 h at 30 ºC, 1 h at 40 ºC, and 18 h at 60 ºC, followed by reduction in a tube furnace in hydrogen atmosphere. To remove air from the system argon of N5.0 purity (Linde Gas Poland) (50 cm^3/min) was blown to the furnace, then hydrogen (50 cm^3/min) was introduced and after 0.5 h the furnace was switched into the heating mode. The catalysts were reduced at 250 ºC for 3 h (the temperature was established based on the TPR results). The catalysts studied were labelled as y RuSBA-12, where y is the wt.% content of ruthenium in relation to the support.

2.2. Hydrodeoxygenation of anisole

The process of anisole hydrodeoxygenation was carried out in a high-pressure reactor (CAT 24 HEL) placed on a magnetic stirrer and equipped with a thermocouple and manometer to measure the initial pressure in the reactor. The catalysts dispersed on SBA-12 silica support and containing 1 or 3 wt.% ruthenium (labelled as 1% RuSBA-12, 3% RuSBA-12) with respect to the support, were placed in a furnace at 250 °C for 3.5 h under dry argon flow prior to the hydrodeoxygenation in order to remove traces of water. An appropriate amount of the catalyst (0.025, 0.05 or 0.1 g) together with anisole (1 g) was placed in a glass vessel equipped with a magnetic stirrer. No solvent was added as anisole was in the liquid state. The glass vessel with the reaction mixture was placed in a high-pressure reactor, which was tightly closed and flushed with argon of N5.0 purity in order to remove air from the reactor. Then hydrogen of N5.0 purity was introduced to the reactor and then the reactor was filled with hydrogen up to the pressure of 25, 40 or 60 bar. The reaction was conducted at three temperatures 90, 110 or 130 °C, for the time of 1, 2.5 or 4 h. The reaction mixture was stirred at 700 rotations per minute. After the reaction time, the reactor was cooled to room temperature. The reaction mixture was centrifuged (VWR) in order to separate the liquid reaction products from the solid catalyst.

The reaction substrates and products were analyzed using a gas chromatograph made by VARIAN 3900 GC equipped with a capillary column CPWAX57CB (length 25 m, diameter 0.32 mm, film thickness 1.2 µm) and a flame-ionization detector. The products were identified on the basis of comparison of retention times of the compounds obtained with those of the standards. The results were confirmed by the results of gas chromatography analysis using a chromatograph coupled with a mass detector made by VARIAN 4000 GC and a capillary column VF-5MS (length 30 m, diameter 0.25 mm, film thickness 0.25 µm).

3. Characterization of catalysts

The Ru content in all synthesized catalysts was evaluated by inductively coupled plasma (ICP) analysis. In addition, these catalysts were characterized by X-ray diffraction (XRD), transmission electron microscopy (TEM), low-temperature nitrogen adsorption/desorption (N_2 ads/des). The XRD diffractograms were recorded on a diffractometer Bruker AXS D8 Advance, using CuKα (0.154 nm) radiation, in the range 2ϴ=0.6-10° with 0.02° step (small-angle range) and 2ϴ=4-60° with 0.05° step (wide-angle range). TEM images were recorded on a JEOL-2000 TEM microscope at 80 kV.

Low-temperature nitrogen adsorption/desorption isotherms were recorded on Nova Quantachrome instrument at 176 °C, after prior degassing of the sample in vacuum at 350 °C for 24 h. The surface area of the catalysts was determined by the BET (Brunauer – Emmet – Teller) method. The pore volume was determined using the KJS-BJH method based on the BJH (Barret – Joyner – Halenda) algorithm [38, 39].

4. Results and discussion

4.1. Characterization of SBA-12 type materials containing ruthenium

All the materials studied were characterized by using some of the techniques described in chapter 3. This allowed selection two for detailed characterization. Additionally, due to the lack of space, only data for 1 and 3 wt.% are discussed here. Fig. 1 presents the diffractograms recorded for pristine SBA-12 and SBA-12 support with deposited ruthenium, in the small-angle range (Fig. 1a) and wide-range range (Fig. 1b). The small-angle diffractograms show one main reflection at 2ϴ=1.8° corresponding to the plane [002] and a lower-intensity reflection at 2ϴ=1.27°, corresponding to the plane [100]. The material of SBA-12 type structure belongs to the space group ($p6_3$/mmc) and has hexagonal symmetry [40, 41] so the elementary cell parameters were calculated for hexagonal symmetry.

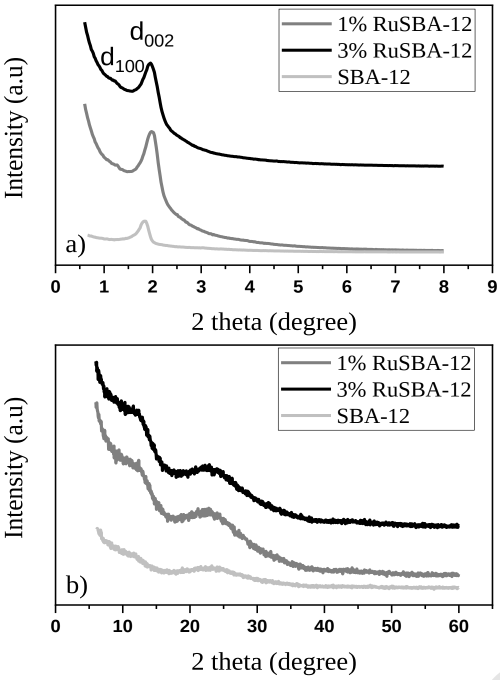
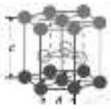


Figure 1. XRD profiles: a) 1% RuSBA-12, 3% RuSBA-12 and SBA-12 (small angle); b) 1% RuSBA-12, 3% RuSBA-12 and SBA-12 (wide angle).

The a and c lengths of the elementary cell for hexagonal RuSBA-12 sample vary in the range 8.0 to 9.6 nm, as shown in Table 1. The unit cell parameters of the SBA-12 (a = 8.0-8.4 nm, c = 8.9-9.1 nm, c/a = 1.63) are in good agreement with previously reported results [42, 43]. After introduction of ruthenium in the amounts smaller than 1 wt.% the values of a and c lengths decrease and then increase when the content of ruthenium increases from 1 to 3 wt.%.

Table 1. Structure and textural properties of SBA-12 and RuSBA-12.

Catalyst	XRD	N_2-physisorption

	Structure	d_{100} (nm)	d_{002} (nm)	Unit cell parameters (nm)		Surface area (m^2/g)	Pore width (nm)
				a	c		
SBA-12	Hexagonal/ p6_3/mmc 	7.2	4.8	8.4	9.6	1002	5.02
1% RuSBA-12		6.9	4.4	8.0	8.9	956	4.96
3% RuSBA-12		7.2	4.5	8.4	9.1	967	4.83

*Unit cell parameter for SBA-12 containing ruthenium: $a = 2d_{100}/\sqrt{3}$ and $c = 2d_{002}$ [39, 41].

The nitrogen adsorption/desorption isotherms recorded for samples 1% RuSBA-12 and 3% RuSBA-12 (Fig. 2) are of type IVa, characteristic of mesoporous materials. Also, the type of hysteresis loop is typical for mesoporous materials [40, 44, 45]. As was mentioned above, the isotherms obtained for the SBA-12 samples studied match the patterns reported for other mesoporous materials with p6_3/mmc symmetry [40]. The additional hysteresis loop recorded for samples with 1 wt.% of Ru can be interpreted as a result of the presence of voids between particles [42, 46]. Surface area of the samples is close to 1000 m^2/g, while the average pore size is 5 nm, as shown in Table 1.

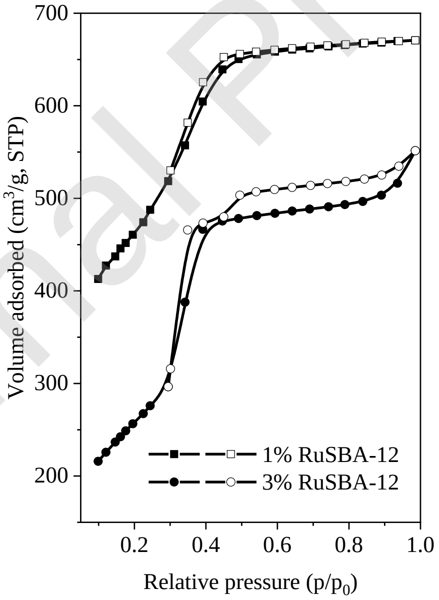


Figure 2. N$_2$ – adsorption/desorption isotherms of 1% RuSBA-12 and 3% RuSBA-12. The isotherm measured for 3% RuSBA-12 is shifted by 200 cm^3/g STP.

The TEM images presented in Fig. 3, confirm the ordered mesoporous structure of the materials studied. They have hexagonal 3D structure with densely packed mesopores (hcp) [47]. No crystalline ruthenium oxide species were observed (wide-angle XRD, TEM), which can suggest that agglomerates at the outer surface were not formed. Thus, Ru probably exists in the catalyst in the form of isolated Ru atoms The results of SEM/EDX analysis (not shown here) confirm homogeneous distribution of ruthenium species.

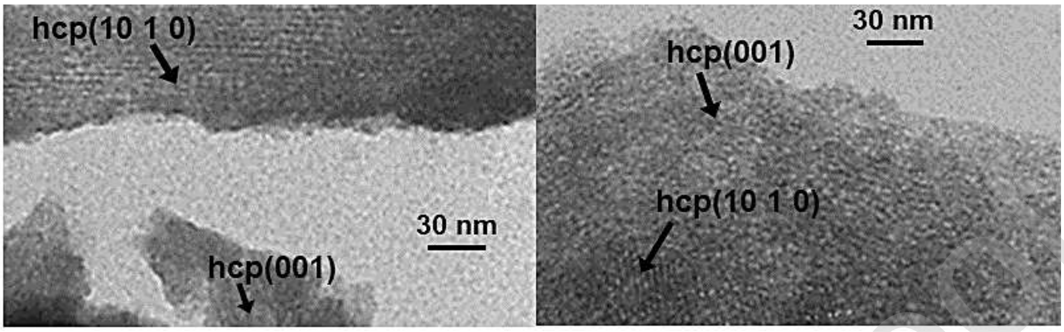


Figure 3. TEM images of 1% RuSBA-12 and 3% RuSBA-12.

4.2. Catalytic activity

Hydrodeoxygenation of organic compounds is the process of obtaining hydrocarbons in the presence of gaseous hydrogen supplied under elevated pressure that takes place at elevated temperature and in the presence of a catalyst, as shown in Fig. 4.

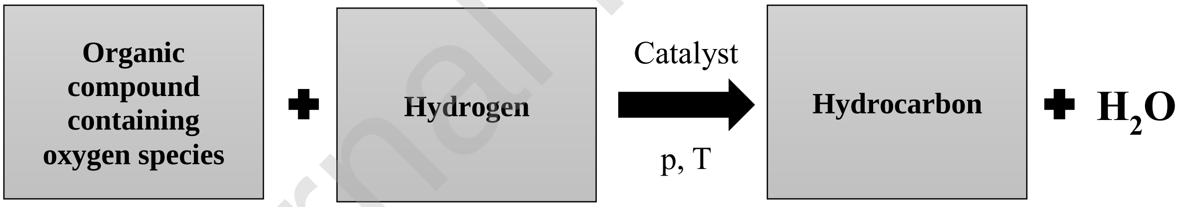


Figure 4. The idea of the hydrodeoxygenation process.

In this study a series of hydrodeoxygenation reactions of anisole were performed using SBA type silica loaded with different amounts of ruthenium catalyst. The reaction does not proceed without a catalyst and proceeds with low conversion with unmodified SBA-12 catalyst (Table 2, entry 19). The effects of the reaction time, the amount of catalyst, hydrogen pressure and temperature were evaluated. According to literature data, the sequence of transformations of anisole molecules under elevated pressure and temperature includes a few reactions such as hydrogenation, dehydration, demethoxylation and demethylation [12, 48]. The type and amounts of products of HDO of anisole depend on many parameters, including the type of catalyst and conditions of the process.

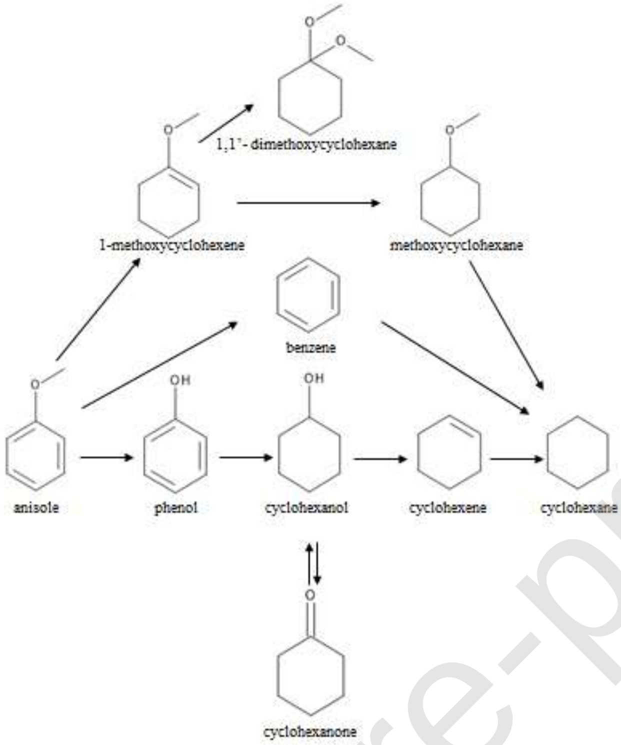


Figure 5. Scheme of the possible routes for anisole hydrodeoxygenation.

The main products of HDO of anisole identified by GC or GC-MS, irrespective of the conditions, are methoxycyclohexane and 1-methoxycyclohexene, as shown in Fig. 6-9. Besides the above main products, the formation of cyclohexane, cyclohexene, benzene, 1,1'-dimethoxycyclohexane, cyclohexanone, cyclohexanol, was confirmed. The selectivities to these products are listed in Table 2. However, these products are not presented on the plots as their total content did not exceed 20%. Based on the identified products of the reaction, three pathways of HDO of anisole to a fully hydrodeoxygenated compound - cyclohexane - are proposed (Fig. 5). The first pathway involves hydrogenation of the aromatic ring, leading to 1-methoxycyclohexene and subsequently to methoxycyclohexane, then the C-O bond between the carbon from the aromatic ring and the oxygen from methoxyl group is broken, which leads to cyclohexane formation. The formation of undesirable product of 1,1'-dimethoxycyclohexane (that contains more oxygen atoms than the initial compound) as a result of methanol attachment to 1-methoxycyclohexene is also possible.

In the second pathway, cyclohexane is obtained via an intermediate product benzene. This pathway starts with direct demethoxylation of anisole to the aromatic structure and then the aromatic ring is hydrogenated.

In the third pathway, the first reaction is demethylation of the substrate, leading to the formation of phenol, which is converted to cyclohexanol via total hydrogenation of the aromatic ring. Cyclohexanol can undergo isomerization to cyclohexanone, dehydration of which gives cyclohexene. Cyclohexene having a double bond in its structure can easily undergo hydrogenation to cyclohexane. Because of possible cyclohexanol dehydration, the reaction can also give dicyclohexyl ether.

Analysis of Fig. 6-9 and Table 2 data suggests that in this study the main pathway seems to be the first one, involving direct hydrogenation of aromatic ring: anisole → 1-methoxycyclohexene → methoxycyclohexane → cyclohexane. The domination of this pathway may be related to the character of transition metal used as a catalyst that prefers hydrogenation of aromatic ring [37] and to the fact that the reactions were run at low temperatures and low pressure, at which the energy needed for hydrogenation of aromatic ring is lower than that needed to break the bond between the carbon atom from the aromatic ring and the methoxyl group or the oxygen atom and carbon from the methyl group [5]. A general conclusion is that in the HDO reaction of anisole catalyzed by SBA-12 silica with deposited ruthenium atoms the hydrogenation of aromatic ring is preferred over demethylation and demethoxylation. The product forming in the largest amount is methoxycyclohexane with higher H/C ratio to be achieved in the process. The teams of Shi [49], Khromov [50] and Sankaranarayanan [5] studied also HDO of anisole and reported the highest selectivity to methoxycyclohexane.

Table 2. By-product distribution for anisole HDO over 1% RuSBA-12 and 3% RuSBA-12 under different conditions.

No.	Reaction conditions/ Catalyst	Selectivity (%)						
		cyclohexane	cyclohexene	benzene	1,1-dimethoxy-cyclohexane	cyclohexanone	cyclohexanol	others
	1 h, 110 °C, 60 bar, 0.05 g of catalyst							
1	1% RuSBA-12	1.0	-	0.1	1.6	0.6	1.1	0.6
2	3% RuSBA-12	1.3	-	-	3.3	0.1	0.5	2.3
	2.5 h, 110 °C, 60 bar, 0.05 g of catalyst							
3	1% RuSBA-12	2.7	0.1	-	3.1	-	1.4	0.5
4	3% RuSBA-12	3.2	0.2	-	2.9	-	1.3	0.5
	4 h, 110 °C, 60 bar, 0.05 g of catalyst							
5	1% RuSBA-12	2.1	0.1	-	1.8	-	1.2	0.8
6	3% RuSBA-12	1.7	0.4	-	-	-	1.1	1.1
	4 h, 110 °C, 60 bar, 0.025 g of catalyst							
7	1% RuSBA-12	0.9	-	0.1	0.5	0.4	0.6	0.3
8	3% RuSBA-12	1.3	0.2	-	1.0	-	0.7	0.7
	4 h, 110 °C, 60 bar, 0.1 g of catalyst							
9	1% RuSBA-12	2.4	0.1	-	3.5	0.1	1.6	3.8
10	3% RuSBA-12	3.5	0.6	-	-	-	1.5	2.8
	4 h, 90 °C, 25 bar, 0.05 g of catalyst							
11	3% RuSBA-12	1.6	0.2	0.2	0.9	0.6	1.3	0.4
	4 h, 90 °C, 40 bar, 0.05 g of catalyst							
12	3% RuSBA-12	1.0	0.1	0.1	-	-	0.9	0.5
	4 h, 90 °C, 60 bar, 0.05 g of catalyst							
13	3% RuSBA-12	0.8	-	-	-	-	0.7	0.5
	4 h, 110 °C, 25 bar, 0.05 g of catalyst							
14	3% RuSBA-12	2.5	0.2	0.3	-	-	1.6	0.8
	4 h, 110 °C, 40 bar, 0.05 g of catalyst							
15	3% RuSBA-12	3.2	0.1	0.1	4.6	0.1	1.6	1.2
	4 h, 130 °C, 25 bar, 0.05 g of catalyst							
16	3% RuSBA-12	4.4	0.2	0.5	5.5	1.2	2.3	5.0
	4 h, 130 °C, 40 bar, 0.05 g of catalyst							
17	3% RuSBA-12	4.6	0.3	-	3.9	-	2.1	2.5
	4 h, 130 °C, 60 bar, 0.05 g of catalyst							
18	3% RuSBA-12	3.8	0.3	-	-	-	1.9	2.3
19	SBA-12	4.5	0.1	-	-	-	1.3	1.5

The reactions without catalyst do not occur (conversion ~ 0%), whereas with pristine SBA-12 (without ruthenium species) occurs with a small (~1.5%) conversion of anisole.. Others: i.e.: 1,1'-dimethoxycyclohexane, dicyclohexyl ether.

The plots illustrating the influence of the reaction time, the amount of catalyst, catalyst loading, pressure and temperature of the reaction are shown below.

4.2.1. Influence of reaction time

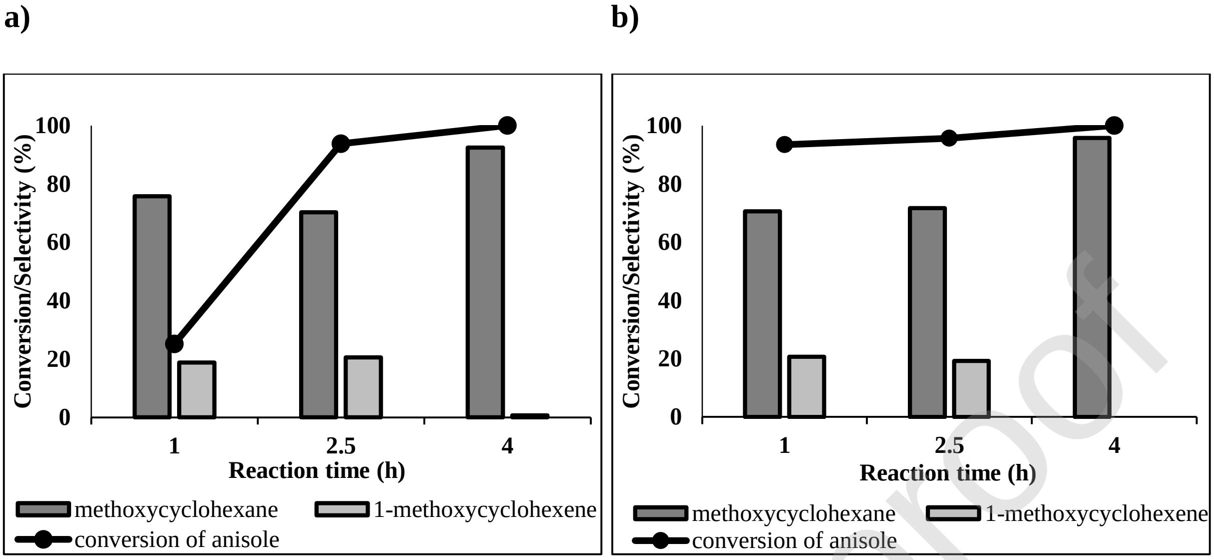


Figure 6. Effect of reaction time on the conversion and product selectivity for anisole HDO over a) 1% RuSBA-12 b) 3% RuSBA-12 catalysts. Conditions: reaction temperature 110 °C, hydrogen pressure 60 bar, amount of catalyst 0.05 g.

Preliminary studies of hydrodeoxygenation of anisole were carried out to establish the optimum time of the process. The reaction was carried out for 1, 2.5 or 4 h at 110 °C, under hydrogen pressure of 60 bar and in the presence of 0.05 g SBA-12 containing 1 or 3 wt.% of ruthenium. Decomposition of the main products of the reaction and the degree of anisole conversion as a function of time are presented in Fig. 6, while the selectivities to the side products are given in Table 2 (entries no. 1, 3, 5 for the catalyst 1 wt.% RuSBA-12, and 2, 4, 6 for the catalyst 3 wt.% RuSBA-12). The results unambiguously show that the quantitative composition of the products and anisole conversion depend significantly on the time of the HDO process. In the experiment with 1% RuSBA-12 catalyst the time of reaction had a great effect on the anisole conversion, which increased from 24% after 1 h to 93% after 2.5 h, to 100% after 4 h (Fig. 6a). Moreover, the catalyst became increasingly selective towards methoxycyclohexane with time of the reaction because the amount of this compound increased. A similar correlation was observed for the process with 3% RuSBA-12, for which after 4 h of the process the selectivity towards methoxycyclohexane increased to 96% (Fig. 6b). Using the 3% RuSBA-12 catalyst, the degree of anisole conversion was smaller than in the presence of 1% RuSBA-12. The conversion of anisole was already high - 93% after 1 h of the process, then after 2.5 h it increased to 95% and after 4 h it was 100%. Greater activity of 3% RuSBA-15 catalyst after 1 h of the process was a direct consequence of a greater content of metal with respect to the substrate. Based on the results of these experiments, we decided to carry out further experiments for 4 h.

4.2.2. Influence of the amount of the catalyst

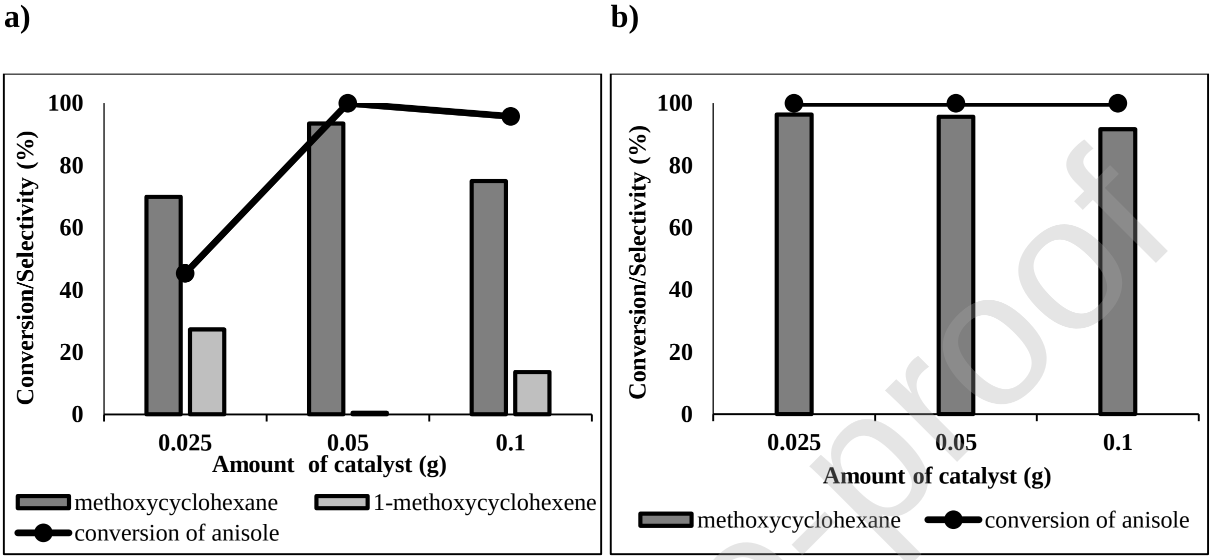


Figure 7. Effect of amount of catalyst on the conversion and product selectivity for anisole HDO over a) 1% RuSBA-12 b) 3% RuSBA-12 catalysts. Conditions: reaction temperature 110 °C, hydrogen pressure 60 bar, reaction time 4 h.

At the next stage, our aim was to establish the optimum amount of the catalyst used in the process. The HDO of anisole was performed at 110 °C under a hydrogen pressure of 60 bar for 4 h, in the presence of 0.025, 0.05 or 0.1 g of samples 1% RuSBA-12 or 3% RuSBA-12. Analysis of HDO of anisole in the presence of sample 1% RuSBA-12 (Fig. 7a) (Tab. 2, items 5, 7, 9) reveals that the greatest catalytic activity was obtained for the catalyst amount of 0.05 g. The use of catalyst in this amount gave the maximum conversion of anisole to 94% of methoxycyclohexane. The reaction in the presence of 0.025 or 0.1 g of the catalyst led to the formation of noticeable amounts of 1-methoxycyclohexene - a compound of a lower content of hydrogen than methoxycyclohexane - and the degree of anisole conversion was lower than when an intermediate amount of catalyst was used, i.e., 0.05g. When 0.1 g catalyst was used in the reaction, a decrease in the anisole conversion and a decrease in the selectivity to methoxycyclohexane were observed compared to the reaction catalyzed by 0.05 g of silica. A decrease in the catalyst activity can be attributed to the physico-chemical properties of the catalyst, and of course the reaction conditions according the Sabatier principle stating that the bond strength between reactants and catalyst should be intermediate (i.e., not too weak, so that the reactants adsorb on the catalyst surface but not too strong to avoid, its poisoning).

For the processes in the presence of 3% RuSBA-12 (Fig. 7b) (Table 2, entries no. 6, 8, 10) no significant effect of the amount of the catalyst was observed as in all reactions the selectivity to methoxycyclohexane was greater than 90% and the anisole conversion was maximum. Based on these results, we decided to use in the further study the catalyst in the amount of 0.05 g.

4.2.3. Influence of catalyst loading

The studies aimed at establishment of the optimum reaction time and optimum amount of the catalyst also provided information on the activity of the catalysts used, 1% RuSBA-12 or 3% RuSBA-12, differing in ruthenium loading. The more selective catalyst with higher anisole conversion was 3% RuSBA-12. Its higher activity can be directly related to the greater content of metal on the support surface. Therefore, further studies on the effect of pressure and temperature on HDO of anisole were performed with the catalyst 3% RuSBA-12.

4.2.4. Influence of hydrogen pressure

The influence of hydrogen pressure on the distribution of the reaction products and the degree of anisole conversion was studied for three pressure values, 25, 40 or 60 bar at three temperatures 90 °C (Fig. 8a), 110 °C (Fig. 8b) or 130 °C (Fig. 8c). Table 2 gives the amounts of products of HDO of anisole besides the main ones (entries no. 6, 11-18). The reaction was performed for 4 h using 0.05 g of 3% RuSBA-12 catalyst. The results imply a significant effect of hydrogen pressure on the character of HDO of anisole. For each temperature, the conversion of anisole increased with increasing hydrogen pressure. Under the hydrogen pressure of 60 bar the aromatic ring hydration occurred in the highest degree. It resulted in the formation of a large amount of methoxycyclohexane and small amount of 1-methoxycyclohexene, which is particularly evident for the processes carried out at 110 and 130 °C. For the reactions performed at 90 °C, the change in hydrogen pressure had practically no effect on the distribution of the main reaction products.

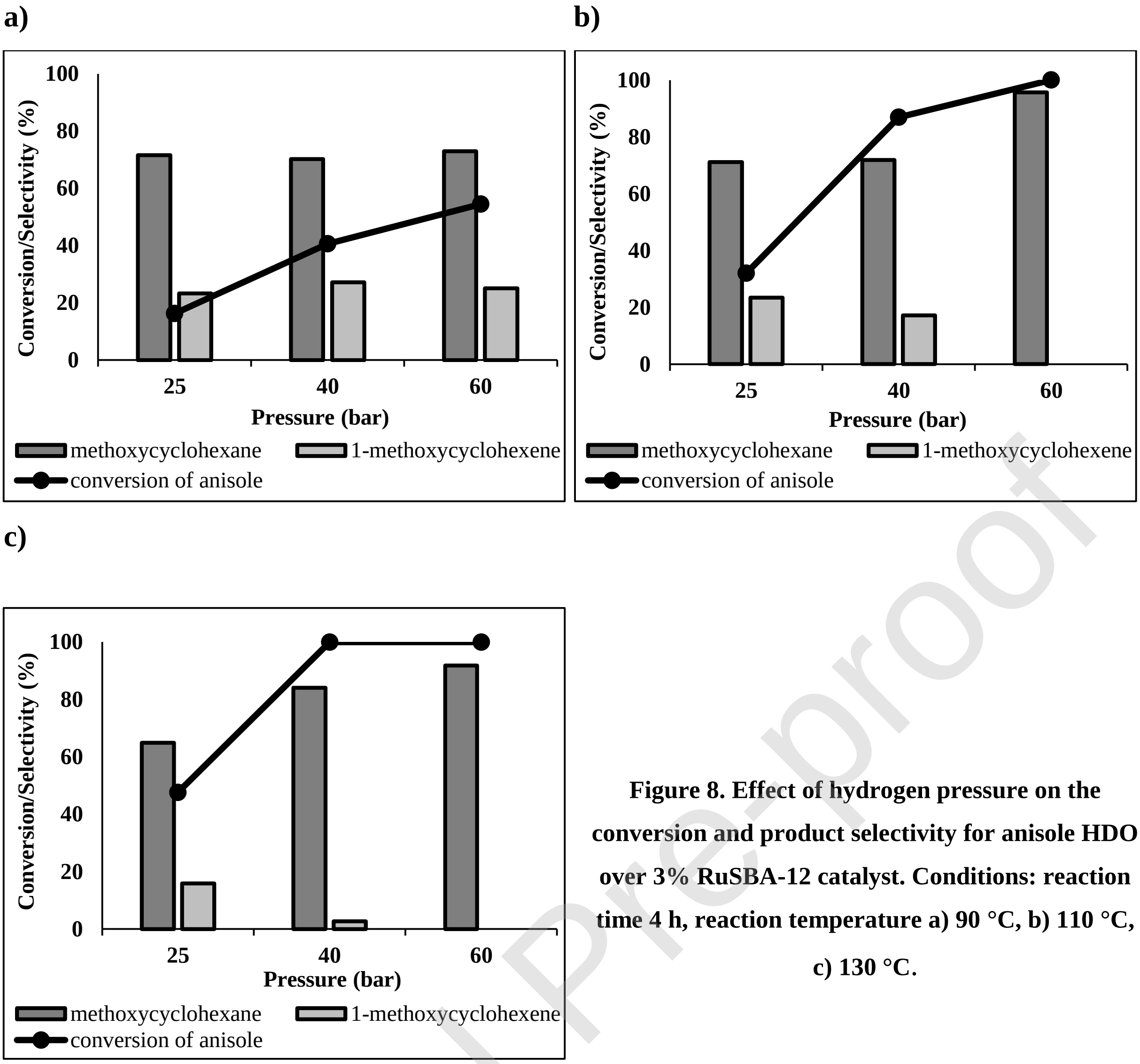


Figure 8. Effect of hydrogen pressure on the conversion and product selectivity for anisole HDO over 3% RuSBA-12 catalyst. Conditions: reaction time 4 h, reaction temperature a) 90 °C, b) 110 °C, c) 130 °C.

4.2.5. Influence of reaction temperature

The influence of temperature on HDO of anisole on its conversion and selectivity of the reaction towards individual reaction products is illustrated in Fig. 9a-c. The experiments were performed at 90, 110 or 130 °C under hydrogen pressures of 25 bar (Fig. 9a), 40 bar (Fig. 9b) or 60 bar (Fig. 9c). Table 2 presents the amounts of the reaction products other than the main ones (entries no. 6, 11-18). These data show that the reaction temperature, similarly as pressure, has a significant influence on the character of the process. At each pressure an increase in temperature caused greater conversion of anisole. However, temperature changes had no effect on the amounts of the particular reaction products. The catalyst became more selective with increasing temperature, which is well visible for the processes at 130 °C.

As can be seen from Fig. 9a-c, anisole conversion at 90 °C is very low and the main products are 1-methoxycyclohexene and methoxycyclohexane. At higher temperature, 110-130

°C, the amount of generated cyclohexane increases (Tab. 2), while the amount of 1-methoxycyclohexene decreases (Fig. 9a-c). In other words, the C_{aryl}-O bonds cleave and anisole is converted preferentially to cyclohexane at higher temperature, which indicates the occurrence of the reaction according to the pathways I and II in Fig. 5.

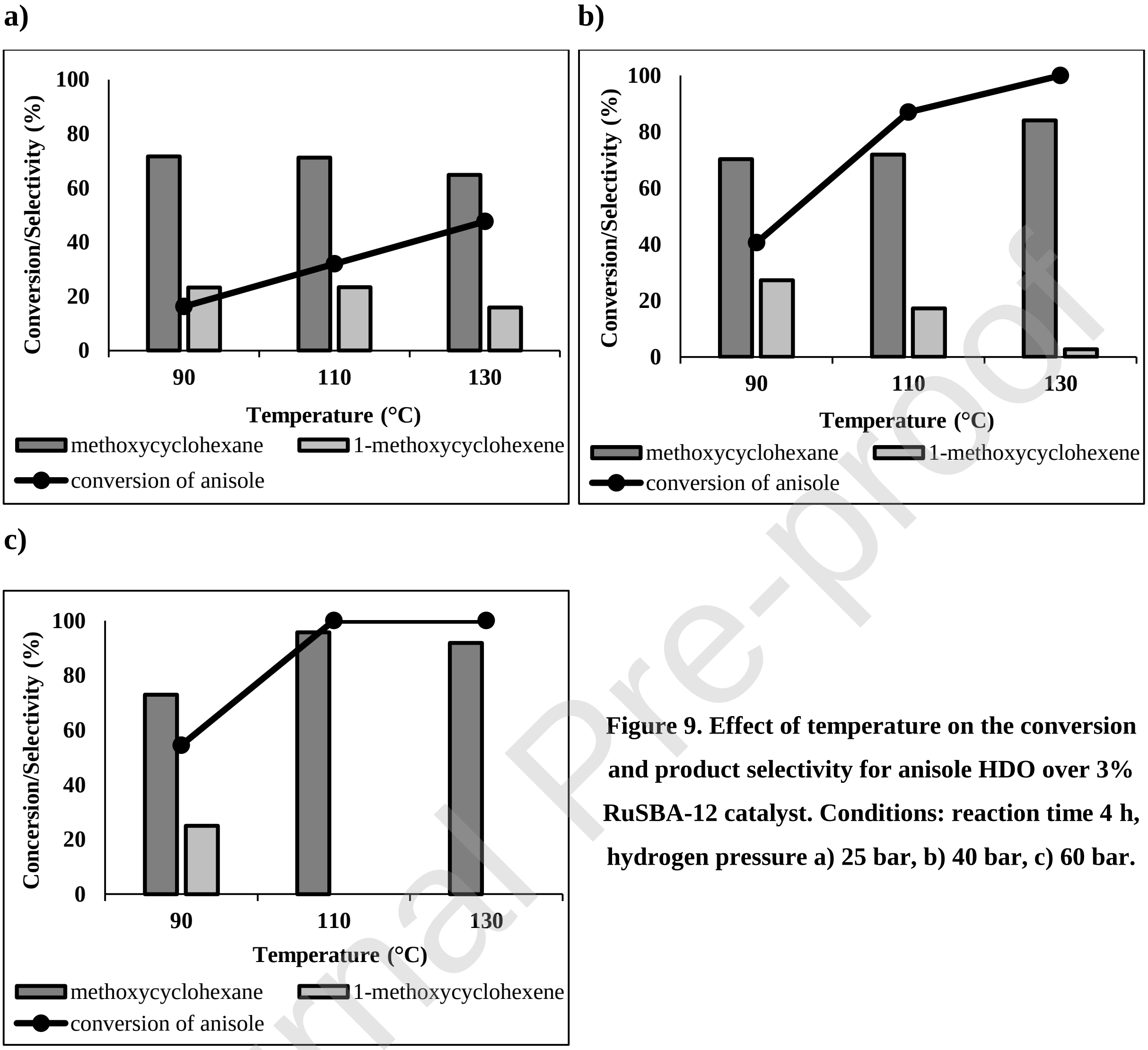


Figure 9. Effect of temperature on the conversion and product selectivity for anisole HDO over 3% RuSBA-12 catalyst. Conditions: reaction time 4 h, hydrogen pressure a) 25 bar, b) 40 bar, c) 60 bar.

4.2.6. Comparison of current experimental results with literature data

The main reaction product in our experiment was methoxycyclohexane - chemical compound with a higher H/C atom ratio than the starting substrate. According to the literature, methoxycyclohexane is very often obtained in this reaction regardless of the type of catalyst used. In accordance with the data collected in the Table 3 (examples 2 and 6), scientists also reported methoxycyclohexane as the main product, however the reaction temperature used was much higher. Moreover, in our experiments, methoxycyclohexane was obtained with higher selectivity and higher conversion of anisole. Some research groups have reported deoxygenated chemicals (Tab. 3, examples 1, 3, 4 ,7, 8), however, several factors contributed to this, such as harsher process conditions and the presence of acid centers. The table below collects more examples from the literature, where anisole was subjected to the hydrodeoxygenation reaction.

Tab. 3. Comparison of the results of anisole hydrodeoxygenation reactions obtained by various research groups

	Catalyst	Reaction conditions		Conversion [%]	Main reaction product and its selectivity [%]	Ref.
		T [°C]	p [bar]			
1	Ni/SBA-15	310	30	100	cyclohexane, 30	[36]
2	Co/SBA-15	220	50	99	methoxycyclohexane, 72	[5]
3	Re-MoO_x/TiO_2	300	60	68	benzene, 28	[51]
4	RuO_2/NiO/Al-SBA-15	400	1	46	benzene, 45	[52]
5	NiMo/SBA-15	300	1	72	1-methoxycyclohexane, 57	[53]
6	Ni/HZSM-5	200	68	3	methoxycyclohexane, 87	[54]
7	Ni_2P/SiO_2	250	15	22	cyclohexane, 64	[55]
8		300		97	cyclohexane, 93	

5. Conclusions

The reaction of hydrodeoxygenation of chemical compounds obtained from biomass degradation is generally considered as a new and attractive method for production of biofuels. Further research needs to be conducted to optimize the process and make it energetically efficient. Studies of hydrodeoxygenation of anisole, chosen as a representative of organic compounds present in biooil, catalyzed by RuSBA-12 at varying pressures (25-60 bar) and temperatures (90-130 °C), permitted the following conclusions: (I) ordered mesoporous silica such as SBA-12 with ruthenium deposited on their surface are highly active in HDO of anisole, (II) larger content of ruthenium on the support surface is directly related to a higher conversion of anisole, (III) the product obtained in the highest amount, irrespectively of the reaction conditions, was methoxycyclohexane, (IV) the pressure and temperature of the process have significant effect on the degree of anisole conversion and the selectivities to the reaction products. The yield of the process increased with increasing pressure and temperature.

Briefly, Ru catalyst catalyzed aromatic C-O bonds to produce aromatic hydrocarbons due to its oxophilicity. The strong metal oxophilicity of Ru favors the direct C_{aryl}-O bond cleavage to benzene, while the weak oxophilic catalyst (e.g. Pt/SiO_2) favors the aliphatic C_{alkyl}-O bond breaking to phenol. Both demethylation and demethoxylation occur over the moderately oxophilic Ru catalysts.

6. Acknowledgements

To Maria, a very outstanding scientist, sincere thanks for all she has done and will continue to do in the future in the field of heterogeneous catalysis. Thank you, for being always ready to share your knowledge.

The authors wish to thank the National Centre for Science for financial support of the studies reported within the research project HARMONIA-5 (no. DEC-2013/10/M/ST5/00652).

7. References

[1] O. Ellabban, H. Abu-Rub, F. Blaabjerg, Renew. Sust. Energ. Rev. 39 (2014) 748-764.

[2] C. Viju, W.A. Kerr, Energ. Policy 56 (2013) 543-548.

[3] A. Zecca, L. Chiari, Energ. Policy 38 (2010) 1-3.

[4] D.M. Alonso, J.Q. Bond, J.A. Dumesic, Green Chem. 12 (2010) 1493-1513.

[5] T. Sankaranarayanan, A. Berenguer, C. Ochoa-Hernández, I. Moreno, P. Jana, J.M. Coronado, D.P. Serrano, P. Pizarro, Catal. Today 243 (2015) 163-172.

[6] Z. He, X. Wang, Catal. Sust. Energ. 1 (2012) 28-52.

[7] L. Caspeta, N.A.A. Buijs, J. Nielsen, Energ. Environ. Sci. 6 (2013) 1077-1082.

[8] M. Mohammad, T.K. Hari, Z. Yaakob, Y.C. Sharma, K. Sopian, Renew. Sust. Energ. Rev. 22 (2013) 121-132.

[9] P.M. Mortensen, J.D. Grunwaldt, P.A. Jensen, K.G. Knudsen, A.D. Jensen, Appl. Catal. A-Gen. 407 (2011) 1-19.

[10] D. Mohan, C.U. Pittman, P.H. Steele, Energy Fuels 20 (2006) 848-889.

[11] W. Mu, H. Ben, X. Du, X. Zhang, F. Hu, W. Liu, Bioresource Technol. 173 (2014) 6-10.

[12] Q. Bu, H. Lei, A.H. Zacher, L. Wang, S. Ren, J. Liang, Y. Wei, Y. Liu, J. Tang, Q. Zhang, R. Ruan, Bioresource Technol. 124 (2012) 470-477.

[13] S. Czernik, A.V. Bridgwater, Energy Fuels 18 (2004) 590-598.

[14] T. Kan, V. Strezov, T.J. Evans, Renew. Sust. Energ. Rev. 57 (2016) 1126-1140.

[15] R. Nava, B. Pawelec, P. Castaño, M.C. Álvarez-Galván, C.V. Loricera, J.L.G. Fierro, Appl. Catal. B-Environ. 92 (2009) 154-167.

[16] M. Saidi, F. Samimi, D. Karimipourfard, T. Nimmanwudipong, B.C. Gates, M.R. Rahimpour, Energ. Environ. Sci. 7 (2014) 103-129.

[17] Y. Wang, T. He, K. Liu, J. Wu, Y. Fang, Bioresource Technol. 108 (2012) 280-284.

[18] T. Yang, Y. Jie, B. Li, X. Kai, Z. Yan, R. Li, Fuel Process. Technol. 148 (2016) 19-27.

[19] Y.C. Lin, C.L. Li, H.P. Wan, H.T. Lee, C.F. Liu, Energy Fuels 25 (2011) 890-896.

[20] C. Zhao, J. He, A.A. Lemonidou, X. Li, J.A. Lercher, J. Catal. 280 (2011) 8-16.

[21] N. Arun, R.V. Sharma, A.K. Dalai, Renew. Sust. Energ. Rev. 48 (2015) 240-255.

[22] W.S. Lee, Z. Wang, R.J. Wu, A. Bhan, J. Catal. 319 (2014) 44-53.

[23] E.H. Lee, R. Park, H. Kim, S.H. Park, S.C. Jung, J.K. Jeon, S.C. Kim, Y.K.J. Park, J. Ind. and Eng. Chem. 37 (2016) 18-21.

[24] X. Zhu, L.L. Lobban, R.G. Mallinson, D.E. Resasco, J. Catal. 281 (2011) 21-29.

[25] S. De, B. Saha, R. Luque, Bioresource Technol. 178 (2015) 108-118.

[26] G. Yao, G. Wu, W. Dai, N. Guan, L. Li, Fuel 150 (2015) 175-183.

[27] C. González, P. Marin, F.V. Diez, S. Ordóñez, Ind. Eng. Chem. 55 (2016) 2319-2327.

[28] Q. Lai, C. Zhang, J.H. Holles, Appl. Catal. A-Gen. 528 (2016) 1-13.

[29] F. Hoffmann, M. Cornelius, J. Morell, M. Frőba, Angew. Chem. Int. Ed. 45 (2006) 3216-3251.

[30] I.T. Ghampson, C. Sepúlveda, R. Garcia, J.L.G. Fierro, N. Escalona, W.J. DeSisto, Appl. Catal. A-Gen. 435-436 (2012) 51-60.

[31] Q. Lu, C.J. Chen, W. Luc, J.G. Chen, A. Bhan, F. Jiao, ACS Catal. 6 (2016) 3506-3514.

[32] S. Ahmadi, Z. Yuan, S. Rohani, C.C. Xu, Catal. Today 269 (2016) 182-194.

[33] P. Kumar, V.V. Guliants, Micropor. Mesopor. Mat. 132 (2010) 1-14.

[34] S. Jin, Z. Xiao, C. Li, X. Chen, L. Wang, J. Xing, W. Li, C. Liang, Catal. Today 234 (2014) 125-132.

[35] Y. Sakamoto, I. Diaz, O. Terasaki, D. Zhao, J. Pérez-Pariente, J.M. Kim, G.D. Stucky, J. Phys. Chem. B 106 (2002) 3118-3123

[36] Y. Yang, C. Ochoa-Hernández, V.A. de la Peña O'Shea, P. Pizzaro, J.M. Coronado, D.P. Serrano, Appl. Catal. B-Environ. 145 (2014) 91-100.

[37] M. Kim, J.M. Ha, K.Y. Lee, J. Jae, Catal. Commun. 86 (2016) 113-118.

[38] M. Kruk, M. Jaroniec, A. Sayari, Langmuir 13 (1997) 6267-6273.

[39] J. Rouquerol, D. Avnir, C.W. Fairbridge, D.H. Everett, J.D. Haynes, N. Pernicone, J.D.F. Ramsay, K.S.W. Sing, K.K. Unger, Pure Appl. Chem. 66 (1994) 1739-1758.

[40] D. Zhao, Q. Huo, J. Feng, B.F. Chmelka, G.D. Stucky, J. Am. Chem. Soc. 120 (1998) 6024-6036.

[41] A. Kumar, D. Srinivas, Catal. Today 198 (2012) 59-68.

[42] Q. Huo, R. Leon, P.M. Petroff, G.D. Stucky, Science 268 (1995) 1324.

[43] J. M. Campelo, T.D. Conesa, M.J. Gracia, M.J. Jurado, R. Luque, J. M. Marinas, A.A. Romero, Green Chem. 10 (2008) 853–858.

[44] M. Thommes, K. Kaneko, A.V. Neimark, J.P. Olivier, F. Rodriguez-Reinoso, J. Rouquerol, K.S.W. Sing, Pure Appl. Chem. 87 (2015) 1051-1069.

[45] A. Kumar, D. Srinivas, P. Ratnasamy, Chem. Commun. 42 (2009) 6484-6486.

[46] A. Feliczak-Guzik, B. Jadach, H. Piotrowska, M. Murias, J. Lulek, I. Nowak, Micropor. Mesopor. Mat. 220 (2016) 231-238.

[47] Y. Sakamoto, I. Diaz, O. Terasaki, D. Zhao, J.P. Pariente, J.M. Kim, G.D. Stucky, The J. Phys. Chem. 106 (2002) 3118-3123.

[48] A. Sanna, T.P. Vispute, G.W. Huber, Appl. Catal. B-Environ. 165 (2015) 446-456.

[49] D. Shi, L. Arroyo-Ramirez, J.M. Vohs, J. Catal. 340 (2016) 219-226.

[50] S.A. Khromova, A.A. Smirnov, O.A. Bulavchenko, A.A. Saraev, V.V. Kaichev, S.I. Reshetnikov, V.A. Yakovlev, Appl. Catal. A-Gen. 470 (2014) 261-270.

[51] I. Tyrone-Ghampson, R. Canales, N. Escalona, Appl. Catal. A-Gen. 549 (2018) 225-236

[52] S. Pichaikaran, P. Arumugam, Green Chem. 9 (2016) 2888-2899

[53] T.L.R. Hewer, A.G.F. Souza, K.T.C. Roseno, P.F. Moreira, R. Bonfim, R.M.B. Alves, M. Schmal, Renew. Energ. 119 (2018) 615-624

[54] W. Li, F. Li, H. Wang, M. Liao, P. Li, J. Zheng, C. Tu, R. Li, Mol. Catal. 480 (2020) 110642

[55] Y. Li, J. Fu, B. Chen, RSC Adv. 7 (2017) 15272-15277