Catalysis Today xxx (xxxx) xxx



Contents lists available at ScienceDirect

# Catalysis Today



journal homepage: www.elsevier.com/locate/cattod

# Nanoreactors based on hydrophobized tubular aluminosilicates decorated with ruthenium: Highly active and stable catalysts for aromatics hydrogenation

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### ARTICLE INFO

Keywords: Nanoreactors Hallovsite nanotubes Ruthenium nanoparticles Hydrophobicity Silvlation Aromatics

### ABSTRACT

Industrial hydrogenation catalysts must be not only selective and active but also resistant to feedstock impurities, including water. We report the strategy of preparing catalytic core-shell nanoreactors based on hydrophobized aluminosilicate nanotubes loaded with ruthenium. The modification of halloysite with alkyltriethoxysilanes enhances hydrophobicity of the clay nanotubes (water contact angle up to  $122^{\circ}$ ) and enables their selective loading with 4-nm ruthenium particles. Such a core-shell tubular nanoreactors provide shielding of active sites from deactivation by admixed water and prevent metal leaching. Produced mesoscale catalysts were active in the hydrogenation of aromatics both in organic and aqueous media at 80 °C and a hydrogen pressure of 3 MPa. Benzene hydrogenation in the biphasic system with water resulted in a complete conversion with 100 % selectivity to cyclohexane over halloysite modified by C18-triethoxysilane supported ruthenium catalyst with turnover frequency (TOF) of 4371 h<sup>-1</sup>. This catalytic system remained stable after ten cycles of benzene hydrogenation, providing 98 % conversion. The demonstrated synthetic strategy is promising for the design of industrial catalysts for the hydroprocessing water-containing organic feedstock and may be upscaled due to the abundant availability of halloysite clay nanotubes.

### 1. Introduction

Conventional industrial heterogeneous catalysts mostly comprise a support and active phase immobilized on the surface or within the pore system and represented by micro or nanoparticles [1-5]. These active sites assure chemicals' transformation with enhanced reaction rates. Catalyst's support is often multipurpose and could be functional (acid or base-catalyzed reactions, feedstock molecules pretreating) or non-functional (provides resistance to attrition, shape-selectivity, active particles formation, stabilization, and protection) [5-9]. The commonly used supports are alumina, silica, titania, and aluminosilicates,

including zeolites [10-13]. These supports are characterized by high specific surface area, narrow particle size distribution, and good thermal and chemical stability in the presence of water and various pH conditions [14-17].

Despite numerous studies of catalysts supports, the search for promising new materials combining advantages of synthetic aluminosilicates with low cost and availability of natural clays is relevant [18–21]. Among natural aluminosilicates, halloysite clay nanotubes are the most promising supports for functional materials and catalysts with advanced properties [7,22-25]. The unique features of halloysite are opened tubular structure with 50–70 nm diameter, 0.5–1.0 µm length,

https://doi.org/10.1016/j.cattod.2020.10.001

Received 14 August 2020; Received in revised form 19 September 2020; Accepted 5 October 2020 Available online 12 October 2020 0920-5861/© 2020 Elsevier B.V. All rights reserved.

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and oppositely charged outer and inner surface of different chemical composition (SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub>). These features open the way for nanoarchitectural constructions with optimized system properties [26–28]. The most interesting is the selective loading of metal nanoparticles either onto the outer surface or inside the lumen of these clay tubes [29–31]. This approach is promising for the design of catalysts resistant to the deactivation by the impurities in the feedstock. Such core-shell catalysts are nanoreactors, ensuring the selective transport of reactant molecules to the active sites encapsulated in the tubes. The chemical reaction catalyzed by such encased metal sites and the efficient removal of desired products from the reactor cavity were demonstrated [32,33].

The idea of shielded core-shell catalysts, where active sites are hidden inside the reactors, is actively pursued; for example, dendritic polymers and micelles were employed as "nanoreactors" [34,35]. However, these formulations' recycling stability and scalability were not achieved. The mesoporous silica also may be considered as nanoreactors, and it is closer to the industrial applications [36,37]. Porous silica particles with palladium active sites were modified with perfluorodecyltriethoxysilane to ensure their hydrophobicity and transport of hydrogen via the gas phase in the gas-liquid-solid triphase process [38]. However, large-scale production of such modified silica is unfeasible due to the prohibitively high cost of perfluoroalkylsilanes. The mesoporous silica or aluminosilicates of any type (MCM-41, SBA-15, 16, HMS) are formed by multiple channels, where the composition of each pore after modification and deposition of metals cannot be ensured and properly characterized [6,8,16,39].

With the appropriate nano/micro-scale roughness, the alkylmodified surfaces provide the contact angles sufficient for the superhydrophobic effect, combining efficiency and feasibility [40]. The industrial applicability of this approach was recently shown in superhydrophobic wire mesh demister employed in the gas-liquid separator [40], antimicrobial superhydrophobic cotton fabrics [41], and aluminum-alloy surfaces [42]. The required surface roughness is readily obtainable using the low-cost natural clay nanotubes such as palygorskite [43] and halloysite [44]. Aluminosilicate halloysite clay is a promising material for nanoreactor synthesis due to its unique tubular structure formed by kaolinite layers rolling into tiny tubes [3,7,20, 45–47].

Hydrogenation of aromatics is the essential process of petroleum chemistry. For example, benzene is hydrogenated to cyclohexene and cyclohexane, which are further converted into caprolactam, cyclohexanol, and adipic acid. The same route for toluene provides methylcyclohexane that is oxidized to methyladipic and glutaric acids [48–50]. On the other hand, in refineries, motor fuel hydroprocessing, including dearomatization, is a large-scale process, with permanently increasing applications [51–53]. The benzene hydrogenation is the most common model reaction to test the supported metal catalysts [54,55]. Ruthenium-containing catalysts are widely studied for the hydrogenation of aromatics to cycloalkanes in the liquid phase [55]. Despite these catalysts' high activity, they are sensitive to the presence of water in a feedstock. Many works are devoted to the partial benzene hydrogenation to cyclohexene caused by water or organic/inorganic additives [55, 56]. The reasons for decreasing benzene conversion to cyclohexane via stopping the reaction by water addition were discussed as competitive adsorption on Ru-active sites, different solubility, and mass transfer of reactants, hydrogen, and products within organic and aqueous phases [55.57-59].

In this work, we present an architectural approach for metal core ceramic shell nanoreactors based on natural aluminosilicate nanotubes loaded with ruthenium. The key feature for the catalyst's high stability and efficiency is the modification of the nanotubes with alkyltriethoxysilanes providing hydrophobic outermost surface and selective loading of noble metal particles in the tubes' lumens. The synthetic method proposed ensures the formation of the core-shell tubular mesocatalyst with high activity in the aromatics hydrogenation, water tolerance, and good recyclability.

### 2. Experimental

Following reactants were used: halloysite (HNT) (Sigma-Aldrich), propyltriethoxysilane (PTES), octyltriethoxysilane (OTES), and octadecyltriethoxysilane (ODTES) (Sigma-Aldrich), ruthenium (III) chloride (Aldrich, 45–55 % Ru), sodium borohydride (85 %, Sigma-Aldrich). Benzene, toluene, ethylbenzene, hydrogen peroxide (37 %), 2-propanol, each chemically pure, were purchased from Ekos-1 (Moscow, Russia). Pure gases (Ar, H<sub>2</sub>, He, N<sub>2</sub>) were supplied by NIIKM (Moscow, Russia) and additionally purified by passing them through cold traps filled with CaA zeolite.

### 2.1. Halloysite (HNT) silanization

Halloysite was pretreated by boiling with hydrogen peroxide for 2 h to remove all organic impurities. After cooling and decantation, HNT was washed and dried at 100 °C. The halloysite surface was modified with propyl-, octyl-, and octadecyltriethoxysilane to prepare catalysts with different hydrophobicity. For this purpose, silanes (0.5 mL) were added dropwise to toluene dispersion of halloysite (3 g in 20 mL) and stirred for 18 h. The modified HNT was centrifuged, washed with toluene, and dried at 60 °C for 12 h. The resulted materials were named correspondingly HNT-C<sub>3</sub>, HNT-C<sub>8</sub>, HNT-C<sub>18</sub>, indicating elongation of alkyl chains (3, 8, and 18) attached to the tubes outermost surface.

### 2.2. Synthesis of HNT/Ru core-shell catalysts

A weighed ruthenium (III) chloride (60 mg) was dissolved in 40 ml of distilled water. This solution was added to 1 g of the support (pristine HNT, and modified HNT-C<sub>3</sub>, HNT-C<sub>8</sub>, HNT-C<sub>18</sub>); resulting mixture was sonicated for 10 min and treated with microwave radiation at 800 W for 3 min. This material was decanted and washed with distilled water. The reduction of  $Ru^{3+}$  to  $Ru^{\circ}$  was performed using 0.5 M aqueous solution of sodium borohydride (excess). After reduction, the Ru-nanoclay catalyst was centrifuged, washed with distilled water to remove the products of sodium borohydride decomposition and air-dried for 24 h at 50 °C. The resulted metal-clay materials were named Ru@HNT-0, Ru@HNT-C<sub>3</sub>, Ru@HNT-C<sub>18</sub>.

### 2.3. Physicochemical characterization

The structure and morphology of the catalysts were studied by transmission electron microscopy (TEM) using a JEM-2100 setup (Jeol, Tokyo, Japan). The samples were placed on the copper grid and analyzed under an accelerating voltage of 200 kV. The micrographs were processed using Image-Pro Plus 6.0 software. Particle size distribution was analyzed using 5 microphotographs based on the counting of 500 particles.

Hydrogen temperature-programmed reduction (H<sub>2</sub>-TPR) was carried out on an AutoChem HP2950 (Micromeritics, USA). Before experiments, the catalyst samples were calcined in air at 400 °C for 4 h to transfer ruthenium into the oxide form. The test sample with a weight of ~0.1 g was placed in a quartz reactor and kept in an argon flow at 400 °C for 1 h. Then the reactor was cooled down to 60 °C, and the sample is heated in the 8 % H<sub>2</sub>+Ar gas mixture (30 mL/min) at 10 °C/min up to 400 °C.

Specific surface area (S<sub>BET</sub>), volume (V<sub>p</sub>), and diameter (D<sub>p</sub>) of pores were determined by low-temperature nitrogen adsorption/desorption using a Gemini VII 2390 t (Micromeritics, USA) instrument at 77 K. Before the measurements, the samples were treated in vacuum at 80–300 °C for 4 h. The specific surface was calculated according to the Brunauer–Emmett–Teller (BET) method in a relative pressure range of 0.04 to 0.25 from the desorption data. The volume of pores and their diameter were estimated in terms of the Barrett–Joyner–Halenda model.

The elemental composition of the catalyst formulations was determined using an ARL Perform'X X-ray fluorescence spectrometer (Thermo Fischer, USA). Processing and refinement of the results were



Fig. 1. AFM (a), SEM (b), and TEM (c) micrographs of the pristine nanoclay, and the scheme (d) of the hydrophobization and ruthenium deposition.

performed with the UniQuant method. The three-phase contact angle of the samples was measured with the DSA100 apparatus (Kruss, Germany). The sample was pressed into a tablet (at ca. 100 bar) and placed into the water-jacketed cuvette filled with cyclohexane. The sample was thermostated at 20 °C. Then a water droplet ( $1.0-1.2 \mu$ L) was added onto a sample tablet surface, and the contact angle was measured for 30 s.

### 2.4. Catalytic experiments

Evaluation of the catalytic activity in hydrogenation of aromatics was performed with a 5000 Multiple Reactor System (Parr, USA) with stainless steel batch reactors, Teflon inlet, and magnetic stirrer. The reactor was loaded with 60 mg of the catalyst and aromatic substrate (benzene, toluene or ethylbenzene) to keep a constant substrate/Ru molar ratio of 2000. In case of biphasic hydrogenation tests, the same quantity of aromatics and distilled water were added. Catalytic tests were run at a hydrogen pressure of 3.0 MPa and 80 °C.

After reaction, the reactor was cooled down, the pressure was dropped to atmospheric, and the catalyst was separated from reaction products via centrifugation, washed 3 times with ethanol, and dried at 50 °C overnight. Recycling experiments were performed as for fresh catalyst: a sample of spent catalysts (60 mg) with aromatic substrate (benzene, toluene, ethylbenzene or mixture with water) were placed in

autoclave, sealed, filled with hydrogen and the tests were run at pressure of 3.0 MPa and 80  $^\circ$ C. Hydrogenation products were analyzed on a Chromos GC-1000 gas chromatograph equipped with a flame ionization detector and a MEGA-Wax Spirit column.

The catalyst' activity in hydrogenation (turnover frequency, TOF) was calculated as the amount of reacted aromatic substrate in definite time (conversion of 40–80 %) per mole of ruthenium specific surface area, according to the formula: TOF =  $2000 \times C_{subs}/t_i$ , where 2000 - a molar ratio of substrate/Ru,  $C_{subs}$  – substrate conversion,  $t_i$  is the time, for which substrate conversion ( $C_{subs}$ ) was evaluated. Each experiment was carried out three times at the same conditions, with the results differing by no more than 2 % from the corresponding average value. The measurement error did not exceed 1 %.

### 3. Results and discussion

### 3.1. Optimization of the core-shell tubule system build-up

The AFM, SEM, and TEM micrographs of pristine halloysite (HNT) and the scheme of ruthenium-containing catalysts preparation are presented in Fig. 1. This nanoarchitectural approach comprises the design of the outer hydrophobic shell, which prevents adsorption of Ru-cations onto negative nanotubes outermost surface and forces them into the



Fig. 2. Time-dependent contact angles (a) and Sessile drop micrographs for Ru@HNT-C<sub>18</sub> (b), Ru@HNT-C<sub>8</sub> (c), and Ru@HNT-C<sub>3</sub> (d). The solid lines are log-polynomial fits for triplicate measurements, shades are 95 % prediction intervals, points are measured data series closest to the fit. Scale bars are 0.5 mm.



Fig. 3. TEM micrographs (a,c,e,g) and Ru-particles size distributions (b,d,f,h) of Ru@HNT-0 (a,b), Ru@HNT-C<sub>3</sub> (c,d), Ru@HNT-C<sub>8</sub> (e,f), Ru@HNT-C<sub>18</sub> (g,h) catalysts.

hydrophilic lumens. We optimized the hydrophobic shell formation using alkyltriethoxysilanes with the tail length of  $C_3$ ,  $C_8$ , and  $C_{18}$ . Therefore, these samples are referred to as: #1 unmodified nanoclay (reference catalyst Ru@HNT-0), and three formulations used hydrophobized tubes surface, as follows, #2 modified with propyltriethoxysilane, PTES (Ru@HNT-C<sub>3</sub>), #3 modified with octyltriethoxysilane, OTES (Ru@HNT-C<sub>8</sub>), and #4 with octadecyltriethoxysilane, ODTES (Ru@HNT-C<sub>18</sub>). Microwave-assisted Ru deposition was applied for all samples following the same procedure described in [5,7,32,45,49].

The hydrophobicity of resulting materials increases with the length of the alkyl attached to the halloysite surface, as indicated by higher water–cyclohexane–solid contact angle, Fig. 2 [60]. The Ru@HNT-0 contact angle was estimated as rather low (< 10°); it was difficult to get a precise value due to the water droplet's rapid imbibition by the HNT tablet. The silanized samples showed increasingly high contact angles, from 50 to 122°. The silanization prevents adsorption of the

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#### Table 1

The composition and structural characteristics of pristine halloysite, Ru@HNT-0, and Ru@HNT-C<sub>3-18</sub> samples.

Sample	Metal content, wt.%, $\pm 0.1$	Textural characteristics					Du avana a mantiala
		$S_{BET}, m^2$ /g, $\pm 1$	Average pore volume, cm $^3/g,\pm 0.1$	Average pore diameter, nm, $\pm 0.1$	ATES <sup>1</sup> alkyl	Ru location <sup>2</sup>	size, nm, $\pm 0.1$
Halloysite	-	64	0.33	6.4	none	n/a	_
Ru@HNT-0	1.8	58	0.30	6.2	none	mostly outer sites	1.3
Ru@HNT-C3	2.5	53	0.28	6.1	propyl	mixed inner / outer	3.4
Ru@HNT-C8	2.7	49	0.26	5.9	octyl	inner sites	3.7
Ru@HNT-C18	2.7	47	0.25	5.8	octadecyl	inner sites	4.8

<sup>1</sup> Alkyl-triethoxysilane modifying agent.

<sup>2</sup> Based on TEM data.

water molecules by a modified HNT sample, and the longer the alkyl moiety of the used silane, the higher is the contact angle, as it was also indicated for other silane coatings on silica [61,62]. These data confirm the comparable enhancement of grafting density of alkyl chains onto the halloysite nanotubes: Ru@HNT-C<sub>18</sub>>Ru@HNT-C<sub>8</sub>>Ru@HNT-C<sub>3</sub>>Ru@HNT-C<sub>3</sub>>Ru@HNT-O (non-modified).

Due to the increased hydrophobicity of the modified Ru@HNT-C<sub>3-18</sub> catalysts, their catalytic activity should be different in the presence of admixed water. We may expect that the samples Ru@HNT-C<sub>8</sub> and Ru@HNT-C<sub>18</sub> will prevent water contact with the active sites of the catalysts due to their contact angle being higher than 90°, determining their preferential wettability with the organic phase [60].

Modification of the nanotubes may alter ruthenium nucleation on the HNT surface. Fig. 3a presents the TEM image of Ru@HNT-0 obtained using the microwave-assisted deposition of ruthenium ions on unmodified HNT followed by reduction. Such a synthesis allows for ultrafine Ru nanoparticles with a size of  $\sim$ 1.3 nm seeded mostly on the outer HNT surface, because the inner lumen is charged positively, and ruthenium cations intercalation to the inner cavity is hindered [32,63]. Under the given electrostatic conditions, Ru<sup>3+</sup> mainly interacts with the negatively charged outer surface of the unmodified HNT-0 sample.

Fig. 3c–g show the morphology of hydrophobized Ru@HNT-C<sub>3</sub>, Ru@HNT-C<sub>8</sub>, and Ru@HNT-C<sub>18</sub>. In contrast to Ru@HNT-0, these samples have Ru-particles located mainly inside the lumen, and their average diameter increased to 3-5 nm. The preferential binding of the alkylsilanes onto the outer silica surface of the nanotubes leaves only the inner alumina surface available for the loading of ruthenium. Thus, we can expect the formation of larger Ru particles on silanized supports due to the less available halloysite surface for the nucleation and hindered mass transport of the metal cations from aqueous media [47,64]. The particle size distributions of Ru@HNT-C<sub>3</sub>, Ru@HNT-C<sub>8</sub> samples are quite similar, with an average of 3.4–3.7 nm. An increase in the average particle size to 4.8 nm was noticed for the Ru@HNT-C<sub>18</sub> sample modified with the silane with the longest alkyl tail (Fig. 3, g, h). It could be explained by the higher hydrophobicity of octadecyl-modified halloysite hindering the contact with the ruthenium precursor solution, and thus fewer nucleating sites available for the formation of the nanoparticles.

The location, dispersion, and availability of active sites impact on the activity and stability of hydrogenation catalysts. The proposed synthesis approach opens the possibility of manipulating hydrophobicity and, as a result, controlling the location of the metal particle deposition. An increase in Ru content was achieved by clay nanotubes' surface modification with silanes, as shown in Table 1.

The Ru-catalysts based on halloysite hydrophobized with alkylsilanes (propyl-, octyl-, and octadecyltriethoxysilane) grafted to the nanoclay surface have similar metal content, surface area, pore volume, and diameter. The modification with silanes provides almost quantitative loading of ruthenium ( $\approx$ 91 % from theoretical), while for the Ru@HNT-0 sample synthesized on unmodified clay nanotubes, this parameter does not exceed 60 %. Nitrogen low-temperature adsorption shows that the volume and diameter of pores monotonically decrease with an elongation of the grafted alkyl chains of silanes, Table 1. The silanization changes the route of the Ru nanoparticles formation on the halloysite surface, Fig. 3. The metal cations are efficiently pushed inside tubes resulting in the selective formation of Ru° encased in the clay nanotubes.

The temperature-programmed reduction experiments also confirm the differences in the ruthenium particle formation. The TPR-H<sub>2</sub> profiles obtained for HNT/Ru samples and their quantification (based on deconvolution) are presented in Fig. 4 and Table 2. The ruthenium content was calculated based on hydrogen consumption caused by a complete reduction of RuO<sub>2</sub>. All the TPR-H<sub>2</sub> profiles of ruthenium catalysts have an intense peak at 123  $\pm$  2 °C corresponded to RuO<sub>2</sub> adsorbed on the outer surface of the nanotubes [32]. For the Ru@HNT-0



Fig. 4. TPR-H<sub>2</sub> profiles for the samples Ru@HNT-0 to Ru@HNT-C<sub>3-18</sub> and their deconvolution.

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### Table 2

Data of quantification TPR-H<sub>2</sub> spectra for Ru@HNT-0 to Ru@HNT-C<sub>3-18</sub> samples. Ruthenium content is based on TPR-H<sub>2</sub> data.

Comple	Tomporature of reduction °C	Hydrogen consumption for $P_{\rm HO}$ reduction much $(a + 0.01)$	Ruthenium content, wt.%, $\pm 0.01$	
Sample	remperature of reduction, C	Hydrogen consumption for $KuO_x$ reduction, minor/g, $\pm 0.01$	Per the peak of reduction	
Ru@HNT-0	125	0.25	0.13	1.40
Ru@HNT-C3	123/146/>200	0.13/0.34/0.02	0.65/1.7/0.1	2.45
Ru@HNT-C8	120/144/>200	0.09/0.39/0.04	0.45/1.97/0.2	2.62
Ru@HNT-C18	124/157/>200	0.09/0.34/0.10	0.45/1.71/0.5	2.66



Fig. 5. Aromatics hydrogenation in organic (a,c,e) and biphasic water-containing (b,d,f) systems over Ru@HNT-0 and Ru@HNT-C<sub>3-18</sub> catalysts.

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#### Table 3

Turnover frequencies (TOFs) for aromatics hydrogenation over Ru@HNT-0 to Ru@HNT-C\_{18} catalysts.

Substrate	Catalysts	Organic phase TOF, $h^{-1}$ , $\pm 10$	Biphasic TOF, $h^{-1}$ , $\pm 10$
	Ru@HNT-0	4200	2136
Ru@HNT-C <sub>3</sub> 3840	3840	2379	
Delizene	Ru@HNT-C8	4871	2833
	Ru@HNT-C18	8090	4371
	Ru@HNT-0	6582	1660
Toluono	Ru@HNT-C3	3240	2308
Toruelle	Ru@HNT-C8	3178	3233
	Ru@HNT-C18	2760	2583
	Ru@HNT-0	1543	776
Ethylbonzono	Ru@HNT-C3	1663	1287
Ethyidelizelle	Ru@HNT-C8	2161	1256
	Ru@HNT-C18	2666	1218

sample, hydrogen consumption occurs only at this temperature, indicating that all the ruthenium nanoparticles deposited on the outer surface. This observation is in full agreement with TEM images, Fig. 3. Calculated Ru content is lower than measured by XRF (1.80 vs. 1.35 wt. %) corresponding to the available active sites for interaction with hydrogen [65]. Rising the silane alkyl chain length in the course of Ru site-dependent synthesis, results in increase of the number of the nanoparticles inside the lumen (Table 1, Fig. 3).

As Table 2 shows, for the Ru@HNT-C<sub>8</sub> and Ru@HNT-C<sub>18</sub> samples, the first peak area decreases with a simultaneously rise in hydrogen consumption at 144–157 °C that could be ascribed to the reduction of small (diameter  $\leq$ 2 nm) Ru-particles located in the lumen. For the Ru@HNT-C<sub>18</sub> sample with the longest alkyl chain, one may observe the much higher hydrogen consumption in the high-temperature range (above 200 °C). Based on the structural characteristics, we may explain this part of the profiles as a reduction of ruthenium oxides strongly bonded with the inner alumina layer in the clay lumen [45,49]. For the Ru@HNT-C<sub>18</sub> sample, it may also be caused by particle enlargement.

According to TPR-H<sub>2</sub> data, ruthenium content in Ru@HNT-0 to Ru@HNT-C<sub>18</sub> samples is 1.40–2.65 wt. %; the longer the alkyl in the silane, the more ruthenium oxide was reduced at higher temperatures. Hydrogen consumption (RuO<sub>x</sub> reduction) at temperatures >200 °C monotonically increases from 0.02 to 0.04 and 0.10 mmol/g for the samples hydrophobized with C<sub>3</sub>-, C<sub>8</sub>-, and C<sub>18</sub>-alkylsilanes. These data are in agreement with the results of elemental analysis (Table 1) and confirm that the modification of the halloysite surface with ATES promotes the deposition of Ru nanoparticles inside nanotubes' lumen.

Based on structural characteristics, TPR-H<sub>2</sub>, and TEM analysis, we confirm the selective loading of Ru inside clay tubes modified with alkyltriethoxysilanes. The halloysite hydrophobization achieved by the alkyl grafting provides a selective deposition of ruthenium cations inside the nanotubes. The proposed method results in ruthenium nanoparticle core shielded by clay nanotubes allowing for effective reactors for aromatics hydrogenation even with water impurity. Encasing catalytic metal nanoparticles in the ceramic shells prevents their aggregation at high temperature and catalysts maintain the high activity at 400–500 °C, as was demonstrated for halloysite-based automotive exhaust catalysts [23,33,66].

### 3.2. Catalytic testing

The catalytic properties of Ru@HNT samples were compared in the hydrogenation of aromatics both in hydrocarbon and in biphasic hydrocarbon-water media (volume ratio 1:1). We evaluated the initial hydrogenation activity (as a slope of "conversion-time" curves), the final aromatics conversions at the end of the test (200 min), and the influence of added water on the characteristics above. The results for the hydrogenation of benzene, toluene, and ethylbenzene are summarized in Fig. 5 and Table 3.

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Table 4

Ru content and textural properties of Ru@HNT-C18 catalyst after recycling.

Descale	Dec contont sut 0/	Textural properties			
#	$\pm 0.1$	$\frac{S_{BET},\ m^2/g,}{\pm\ 1}$	$\begin{array}{l} V_{pore,}~cm^{3}/g,~\pm\\ 0.05 \end{array}$	$D_{pore}$ , nm, $\pm 1$	
0	2.7	47	0.25	5.8	
1	2.6	47	0.26	5.9	
2	2.6	49	0.26	6.0	
3	2.6	50	0.26	6.0	
5	2.5	50	0.26	6.0	
10	2.4	51	0.27	6.0	

The silanized catalysts provided a high activity, expressed in high TOFs (Table 3), and complete aromatic substrates conversions (Fig. 5). In all experiments, a selectivity to complete hydrogenation products (cyclohexane, methylcyclohexane, ethylcyclohexane) was 100 %. As to the non-modified ruthenium sample Ru@HNT-0, benzene and toluene conversions stopped at  $\sim$ 80 %, and for ethylbenzene did not exceed 70 % typical for other supported ruthenium catalysts [14,49,55,59]. Despite the similar ruthenium content for all Ru@HNT-C3 to Ru@HNT-C18 samples, the higher catalytic activity was observed for Ru@HNT-C<sub>18</sub> due to the highly dispersed nanoparticles inside the tubes (Tables 1,2). It should be noted that the conversion curve for ethylbenzene over the Ru@HNT-C3 sample is middling between the Ru@HNT-C<sub>18</sub> and the Ru@HNT-0. This could be explained by the location of the nanoparticles: for Ru@HNT-0 and Ru@HNT-C3 both outside/inside and for Ru@HNT-C8 and Ru@HNT-C18 – inside the tubes only (Fig. 3). This difference is distinctly manifested in biphasic organic-water systems during benzene, toluene, and ethylbenzene hydrogenation. The estimated ratio of activity Ru@HNT-C<sub>18</sub> to Ru@HNT-0 is about two, and the final conversion difference is 30-60 %. The samples hydrophobized with C3-C8 alkyl tails have intermediate characteristics.

For the catalyst Ru@HNT-0 with the outer location of metal nanoparticles, benzene hydrogenation is incomplete even in pure hydrocarbon media, and reaction being stopped at 70–80 % conversion. This "stop effect" is pronounced in biphasic systems where final aromatics conversion was not higher than 40 %. Therefore, water negatively affects hydrogenation on the external surface of HNT/Ru. In contrast, the "stop effect" is eliminated for the catalysts Ru@HNT-C<sub>8</sub> and Ru@HNT-C<sub>18</sub>, where Ru-particles are located inside the nanotubes. As to the "stop effect" observed, it may be induced by concurrent adsorption of water on Ru-nanoparticles [7,31,48,55]. In all the biphasic systems, we observed that water addition decreases both the initial activity and the conversion. Based on TEM (Fig. 3) and catalyst testing data in organic and organic-water systems, we conclude that the activity and water tolerance of the nanoclay catalysts are much improved for the samples where Ru is located inside the halloysite nanotubes.

Notably, the hydrophobized ruthenium containing nanosystems based on halloysite clay provided superior catalytic activity compared to montmorillonite, hydrotalcite, and carbon nanotubes supported ruthenium counterparts (TOFs are 270, 1300, and 649 h<sup>-1</sup> at 100, 120, and 70 °C respectively, with 100 % selectivity to cyclohexane at complete benzene conversion) in organic media [67–69]. In aqueous media, these catalysts lose activity due to strong adsorption of water molecules over ruthenium active sites. As well, cyclohexene' diffusion gradient prevents further hydrogenation, which resulted in benzene conversion and selectivity loss [45,55]. This catalyst worsening was not observed for hydrophobized shielded core-shell nanoreactors, which only partially decreased activity upon shifting to water containing media, but retained the complete conversion of the aromatic substrate at 100 % selectivity to the product of complete hydrogenation (Table 4 and Fig. 5).

Finally, we have investigated the stability of the most efficient  $Ru@HNT-C_{18}$  catalyst in the recycling mode of benzene hydrogenation. As shown in Fig. 6, the catalytic activity expressed in TOF only slightly



Fig. 6. Kinetics curves (a) and the final conversions (b) for recycle tests of Ru@HNT-C18 catalyst in a biphasic system benzene-water (50 vol. %).

decreases with the cycle number. This could be explained in partial metal leaching that is confirmed by Ru content decreases from 2.7 to 2.4 wt.% (Table 4).

The differences between conversion-time curves for 1–3 cycles are negligible, and conversion for 3 h remains unchanged (100 %). With the number of cycles, the conversion rate decreased by 2 % and equaled to 98 % in the tenth cycle. Notably, after ten cycles, ruthenium content was 2.4 %, making Ru@HNT-C<sub>18</sub> highly active and stable nanoreactors for aromatics hydrogenation both in organics and biphasic with water systems.

#### 4. Conclusions

The mesoporous hydrophobized ruthenium-containing catalysts templated on natural clay nanotubes were synthesized and tested in aromatics hydrogenation both in organic and biphasic media containing 50 vol % water. By measuring the contact angle, it was established that the longer is the alkyl moiety of the used silane, the greater is the water contact angle: from 50 to  $122^{\circ}$  for alkyl chains from 3 to 18. The hydrophobic shell allowed the loading of Ru-particles selectively inside the nanotubes, producing active, stable, and recyclable mesocatalyst. The longest silane alkyl chains shell (C<sub>18</sub>) provided practically complete Ru loading (2.7 wt. % Ru vs. 3.0 theoretical value) for the modified halloysite nanotubes. As a result, 4.6–5.0 nm in diameter metal particles were synthesized selectively in the lumen of the tubes. This was confirmed by TEM images and TPR-H<sub>2</sub> measurements, resulting in the peak of hydrogen consumption shifting to a high-temperature area.

The proposed nano-architectural approach resulted in the ruthenium particle core shielded by clay nanotubes with high catalytic activity in hydrogenation of aromatics. This core-shell formulation remarkably enhanced the catalyst water tolerance and stability. Octadecyltriethoxysilane modified clay nanotubes support for ruthenium catalyst (Ru@HNT-C<sub>18</sub>) was the most active in benzene hydrogenation both in organic (TOF =8090 h<sup>-1</sup>) and biphasic system with water (TOF =4371 h<sup>-1</sup>), demonstrating a complete conversion and selectivity to cyclohexane of 100 %. This system allowed for ten cycles of catalytic hydrogenation with complete conversion of aromatics and could be scaled up for industrial applications due to the low cost and availability of natural clay nanotubes.

#### CRediT authorship contribution statement

Aleksandr Glotov: Supervision, Conceptualization, Investigation, Methodology, Writing - review & editing. Andrei Novikov: Writing original draft, Visualization, Conceptualization. Anna Stavitskaya: Writing - original draft, Visualization, Conceptualization. Vladimir Nedolivko: Investigation, Writing - original draft. Dmitry Kopitsyn: Investigation, Data curation. Alexandra Kuchierskaya: Investigation. Evgenii Ivanov: Formal analysis, Resources. Valentine Stytsenko: Writing - original draft. Vladimir Vinokurov: Supervision, Methodology. **Yuri Lvov:** Conceptualization, Supervision, Project administration, Writing - review & editing.

#### **Declaration of Competing Interest**

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

### Acknowledgments

This work was funded by the Ministry of Science and Higher Education of the Russian Federation (Grant No. 14.Z50.31.0035). The authors thank A. Vutolkina, Ya. Chudakov, M. Artemova, E. Smirnova, and E. Novikova (all are from Gubkin University) for their input and R. Fakhrullin for AFM imaging of halloysite.

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