



# Liquid-phase hydrogenation of benzene to cyclohexene catalyzed by Ru/SiO<sub>2</sub> in the presence of water–organic mixtures

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## Abstract

The liquid-phase hydrogenation of benzene to cyclohexene was studied using a Ru/SiO<sub>2</sub> catalyst prepared by reduction of ruthenium(III) chloride impregnated in a hydrophilic non-porous silica. In a biphasic water/benzene system at 423 K and 5 MPa of hydrogen pressure, a 14% cyclohexene yield was obtained at 60% benzene conversion. Increased cyclohexene yields and selectivities were observed in the presence of ethylene glycol/water and glycerol/water mixtures, which consist mainly of hydrated organic molecules that can enhance the hydrophilicity around the ruthenium particles favoring the cyclohexene desorption.

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## 1. Introduction

Asahi Chemical Industry Co. has developed a technology for highly selective partial hydrogenation of benzene to cyclohexene thus establishing a new process for producing cyclohexanol [1]. In this process the theoretical consumption of hydrogen is reduced to one-third and fewer undesirable by-products are formed in comparison to the conventional process for making adipic acid and/or

$\epsilon$ -caprolactone through hydrogenation of benzene followed by direct oxidation of cyclohexane to cyclohexanol and cyclohexanone [2,3].

The partial hydrogenation of benzene to cyclohexene is performed in a batch reactor under stirring using non-supported ruthenium particles as catalyst in a water/benzene biphasic system. In order to obtain high cyclohexene yields (48% of cyclohexene yield at 60% of benzene conversion) large amounts of zinc sulfate have to be added to the aqueous phase (Ru:Zn molar ratio of 1:6). This salt is chemisorbed on the ruthenium particles surface changing their characteristic from hydrophobic to hydrophilic. In this manner, a water layer surrounds the ruthenium particles and favors

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cyclohexene desorption from the catalyst surface, due its very low solubility in water, increasing the cyclohexene yield [1,4,5]. One drawback is the possible corrosion of the reactor due to acidic pH of the aqueous phase and the gradual deactivation of the catalyst [5,6]. Lately, the development of new catalytic materials or the addition of organic substances in the aqueous phase have been investigated to substitute zinc salts and increase cyclohexene yield and selectivity. Mizukami et al. [6,7] used a supported ruthenium catalyst, with small amounts of copper, prepared by the sol-gel method and obtained 31.4% yield of cyclohexene at 83.3% of benzene conversion in the absence of zinc sulfate in the aqueous phase. Imamura et al. [8] performed the reaction in liquid ammonia at 393 K and 3 MPa of hydrogen using lanthanides as catalysts. They obtained cyclohexene selectivities higher than 90%, however, for benzene conversions smaller than 10%. When the reaction temperature was decreased to 323 K cyclohexadienes were preferentially formed. Deng and co-workers [9–11] described that ruthenium boride catalysts, prepared by reduction of ruthenium salts with borohydrides, were more selective for reducing benzene to cyclohexene than ruthenium catalysts obtained by hydrogen reduction. However the use of these catalysts makes the addition of zinc sulfate in the aqueous phase necessary in order to achieve high cyclohexene yields. A new supported amorphous ruthenium boride catalyst was recently developed, resulting in high cyclohexene yield (33%) in the absence of zinc sulfate in the aqueous phase. The addition of a small amount of zinc to the as-prepared catalyst enhanced cyclohexene yield and selectivity [11]. Scholten and co-workers [12,13] found for the gas-phase and liquid-phase hydrogenation of benzene over non-supported ruthenium catalyst, that the addition of small quantities of organic compounds containing a hydroxyl or an amine group (modifiers) increase the cyclohexene yield and selectivity. The action of modifiers in the liquid phase was explained by the formation of a hydrogen bond between cyclohexene and the modifier [13]. Majahani and co-workers [14], using  $\text{Ru}/\text{Al}_2\text{O}_3$  as catalyst, showed that small quantities of monoethanolamine in the aqueous phase give better selectivities than zinc sulfate, however, the

best cyclohexene yield was 13% under the studied conditions. Nagahara et al. [15] studied the partial hydrogenation of benzene in the presence of different alcohols (butanols, allyl and benzyl alcohol) in the aqueous phase. A high selectivity to cyclohexene (70%) was obtained at 30% of benzene conversion by addition of small amounts of benzyl alcohol. We report here the results of liquid-phase hydrogenation of benzene catalyzed by ruthenium particles supported on hydrophilic non-porous silica ( $\text{Ru}/\text{SiO}_2$ ) in the presence of water–organic mixtures and explain the increase of cyclohexene yield and selectivity based on the structure of the water–organic mixtures.

## 2. Experimental

### 2.1. Synthesis and characterization of $\text{Ru}/\text{SiO}_2$ catalyst

In order to obtain a catalyst with 2 wt% of ruthenium, hydrophilic fumed silica Aerosil 200 (Degussa) was impregnated with a solution of  $\text{RuCl}_3 \cdot 1.5\text{H}_2\text{O}$  (Aldrich) in water:ethanol (1:1 v/v), dried at 343 K for 10 h and reduced at 673 K in a hydrogen flow for 2 h. Transmission electron microscopy (TEM) was carried out using a Carl Zeiss CEM 902 apparatus with a Proscan high-speed slow-scan CCD camera and digitalized (1024 × 1024 pixels, 8 bits) using the AnalySis software.

### 2.2. Catalytic tests

The hydrogenation reactions were made in a 100 ml SS316 Parr Stirred Reactor (Parr Instrument Co., USA) equipped with pressure gauge, thermocouple, gas inlet valve, liquid sample valve, internal stirring system consisting of a motor drive magnetically coupled to an internal stirrer shaft with attached turbine-type impeller, and electric heater with controls. Hydrogen gas (99.995%, White Martins) was supplied from the cylinder and introduced into the base of the reactor. The entrance tube also served as a sampling tube for the liquid phase. In a typical experiment a known amount of catalyst, 25 ml of water (or water/or-

ganic mixture) and 25 ml of benzene (Fluka) were added and the reactor was closed. To remove the air present in the reactor, it was purged three times with hydrogen. Initially the stirring was adjusted to 300 rpm and heating was started. When the temperature reached 423 K, hydrogen was charged into the reactor (5.0 MPa). After this, the stirring was adjusted to 1000 rpm and the reaction was considered to start. The values of hydrogen pressure and the agitation speed were used to conduct the experiments in the chemically controlled regime [4,16]. The reaction was monitored removing samples of the benzene phase after interrupting the stirring of the slurry, which were analyzed by gas chromatography.

### 2.3. Chromatographic analysis

The samples were analyzed in a gas chromatograph Shimadzu GC17A, equipped with a capillary column Carbowax 20M (30 m × 0.25 mm × 0.25 μm) coupled to a FID detector. The quantification of the benzene, cyclohexene and cyclohexane was made using calibration curves.

### 2.4. Definitions

Benzene conversion (*C*)

$$= \frac{\text{mol of reacted benzene}}{\text{mol of initial benzene}} \times 100$$

Cyclohexene selectivity (*S*)

$$= \frac{\text{mol of cyclohexene formed}}{\text{mol of reacted benzene}} \times 100$$

Cyclohexene yield (*R*)

$$= \frac{\text{mol of cyclohexene formed}}{\text{mol of initial benzene}} \times 100$$

## 3. Results and discussion

In the liquid-phase hydrogenation of benzene in the absence of zinc salts, good yields of cyclohexene could be obtained using ruthenium particles supported on hydrophilic oxides, like silicas and

aluminas [4]. It was shown, for the supported ruthenium catalysts, that the dispersion and the size of the ruthenium particles influence the catalytic activity but not the cyclohexene selectivity [17,18]. The selectivity is influenced by the nature of the support and the pore sizes. The larger average pore size of the support, the higher is the selectivity towards cyclohexene [18]. We utilized as support the hydrophilic silica Aerosil 200, whose surface area is almost entirely external and is not derived from any porosity. The transmission electron micrograph of the Ru/SiO<sub>2</sub> catalyst (Fig. 1) shows the ruthenium particles dispersed on the small spherical-shaped silica particles with sizes in the range of 1–5 nm.

A preliminary study [19] of the liquid-phase hydrogenation of benzene using the Ru/SiO<sub>2</sub> catalyst showed that in the absence of water the reaction is very fast and only cyclohexane is formed. In the presence of water the reaction rate decreases and, under the studied conditions, the best cyclohexene yield (14%) was obtained at 423 K and 5 MPa of hydrogen in the absence of additives. The addition of zinc sulfate in the aqueous phase (Ru:Zn molar ratio between 1:5 and 1:10) only decreases the reaction rate and does not increase the cyclohexene yield and selectivity as described for the unsupported ruthenium catalysts [1,4]. Probably the zinc ions adsorb preferentially on the weak acidic silanol groups [20] of the support and do not modify the environment around the ruthenium particles. Similar results were observed using ruthenium supported catalysts, where the addition of zinc sulfate was not as effective to enhance the cyclohexene yield [11,14].

The results of liquid-phase hydrogenation of benzene in the presence of water–organic mixtures are shown in Fig. 2 and Table 1.

It can be seen that the addition of ethylene glycol and glycerol in the aqueous phase increases the cyclohexene yields and selectivities. The use of methanol results in a decrease on cyclohexene yield even though the initial cyclohexene selectivity values are similar to the obtained with ethylene glycol and glycerol. The addition of ethanol and triacetin (1,2,3-propanetriol triacetate) cause a decrease in the cyclohexene yields and selectivities.

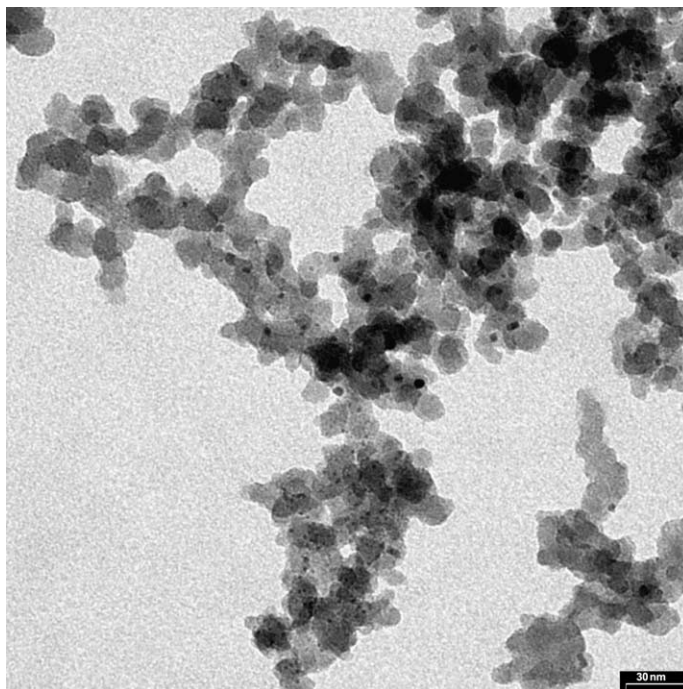


Fig. 1. Transmission electron micrograph of the Ru/SiO<sub>2</sub> catalyst.

From these results we can see that molecules containing more hydrophilic –OH groups increase the cyclohexene yields and selectivities, while molecules with more hydrophobic alkyl groups cause a decrease on these values. The best cyclohexene yields and selectivities were obtained using

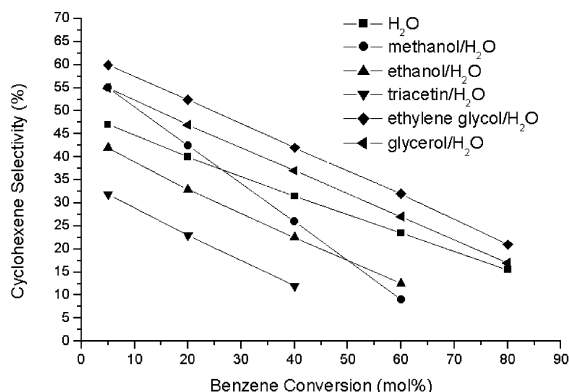


Fig. 2. Benzene conversion  $\times$  cyclohexene selectivity in the liquid-phase hydrogenation of benzene catalyzed by Ru/SiO<sub>2</sub> in the presence of water–organic mixtures (1/1, v/v).

an ethylene glycol/water mixture. On the other hand, the total substitution of water by ethylene glycol decreases the cyclohexene yield to 11%. Thus the presence of water is essential to obtain good yields. The best yields are obtained using 5–50% (in volume) of ethylene glycol in the aqueous phase while above 75% a decrease was observed.

Probably these results can be explained by the structure of the water–organic mixtures. Ethylene glycol has no hydrophobic groups and in water the hydroxyl groups interact with the surrounding water molecules thus forming hydrated organic molecules [21]. In the case of methanol, the role of the hydrophilic interactions is more pronounced due to its small hydrophobic moiety. The formation of water–methanol hydration complexes is more pronounced than larger water cavities accommodating methanol molecules (hydrophobic association) [22]. In water–ethanol mixtures at high ethanol concentrations the water molecules become incorporated by ethanol [23]. Like zinc sulfate the hydrated organic molecules in ethylene

Table 1

Liquid-phase hydrogenation of benzene catalyzed by Ru/SiO<sub>2</sub> in the presence of water–organic mixtures (25 ml of benzene, 25 ml of water/organic (1/1, v/v), 0.100 g of catalyst, 423 K and 5 MPa of hydrogen)

System	Maximum yield of cyclohexene (mol%)	Conversion of benzene (mol%)	Cyclohexene selectivity (%)	Reaction time (min)
Water	14	60	23	40
Ethylene glycol/water	19	60	32	100
Glycerol/water	16	60	27	240
Methanol/water	10	35	29	150
Ethanol/water	9	42	21	70
Triacetin/water	5	30	17	80

glycol/water and glycerol/water probably enhance the hydrophilicity around the ruthenium particles increasing cyclohexene yields and selectivities. In the presence of methanol/water, the high initial cyclohexene selectivity values can also be explained by the presence of water–methanol hydration complexes. On the other hand, the cyclohexene formed is probably more soluble in methanol/water than in water and is further hydrogenated causing a strong decrease in the cyclohexene selectivity. The decrease of cyclohexene yields and selectivities in the presence of ethanol/water and triacetin/water can be explained by the hydrophobic interactions of these molecules.

#### 4. Conclusions

In the liquid-phase hydrogenation of benzene using Ru/SiO<sub>2</sub> as catalyst the addition of ethylene glycol and glycerol in the aqueous phase increase the cyclohexene yield and selectivity. These solutions consist mainly of hydrated organic molecules that can enhance the hydrophilicity around the ruthenium particles favoring the cyclohexene desorption.

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