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Cellulose Supported Ruthenium Nanoclusters as an Efficient and Recyclable Catalytic System for Benzene Hydrogenation under Mild Conditions[1]

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Abstract—Ruthenium nanoclusters supported on biopolymer cellulose were prepared by chemical reduction technique and characterized by various experimental tools. The cellulose supported Ru catalyst effectively hydrogenates benzene under mild and solvent free conditions. The complete conversion of benzene to cyclohexane was achieved at 70°C and 2.0 MPa partial pressure of H_2 in 1 h. Effect of various parameters such as reaction temperature, H_2 partial pressure, metal loading and catalyst amount on hydrogenation of benzene was studied in detail. The catalyst was recovered from product and reused upto four times without significant loss in its catalytic activity.

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Hydrogenation of benzene is one of the most frequently used reactions and it has significant importance due to a number of reasons. First, it is used to produce cyclohexane and cyclohexane is one of the key intermediate for the production of nylon-6 and nylon-66 [1–4]. Second, it is useful for environmental protection because stringent limitations are set worldwide on the presence of aromatics in fuels [5]. The presence of aromatics in fuels lowers the cetan number and increases the smoke point of jet fuels [4, 5]. However, due to the resonance stabilization energy benzene is very difficult to hydrogenate compared to terminal olefins and olefins which have internal double bond [1–3]. Conventionally, hydrogenation of benzene occurs under drastic temperature/pressure over metal supported heterogeneous catalyst [6]. Therefore, recent research was aimed at developing efficient catalyst systems for hydrogenation of benzene under mild conditions [7]. On the other hand, beyond increasing the catalyst efficiency, the separation of precious catalyst from reaction media is important as the loss of catalyst is not acceptable due to the economical and environmental considerations. In consequence, various transition metal based heterogeneous catalysts were developed for hydrogenation of benzene utilizing different supports like hydrotalcite [4], zeolites [8], alumina [9], carbon [10] and metal organic frame work [11].

Despite significant advances in the synthesis of transition metal nanoparticles [12–16], the development of special supports which are inexpensive, nontoxic, eco-friendly and bio-degradable remains a subject of scientific and industrial interest. Nowadays focus is on the green and sustainable supports for catalytic applications. In this regard biopolymers like chitosan [17–20], gelatin [21] and starch [22] were explored by many researchers. Biopolymers have very interesting properties like high sorption capacity, stability of metal anions, and physical/chemical versatility that make these solids promising candidates for catalytic supports [23]. Cellulose, the most common and inexhaustible source of organic biopolymer is easily obtainable from wood pulp and 40 billion ton of cellulose is produced per year [24]. Cellulose has a wide range of applications such as immobilization of proteins, antibodies and heparin and the separation of enantiomeric molecules [25]. Insolubility of cellulose in water and in most of organic solvents prompted many researchers to explore cellulose as a support in catalysis which offers advantages of heterogeneous catalysts. Many workers explored cellulose as a support for heterogenized metal nanoparticles used as catalysts in various organic transformations [26–29]. However, to the best of our knowledge cellulose supported Ru nanoparticles catalyst has not been explored in aromatic hydrogenation so far.

In this context, we report herein the synthesis and characterization of ruthenium nanoclusters supported

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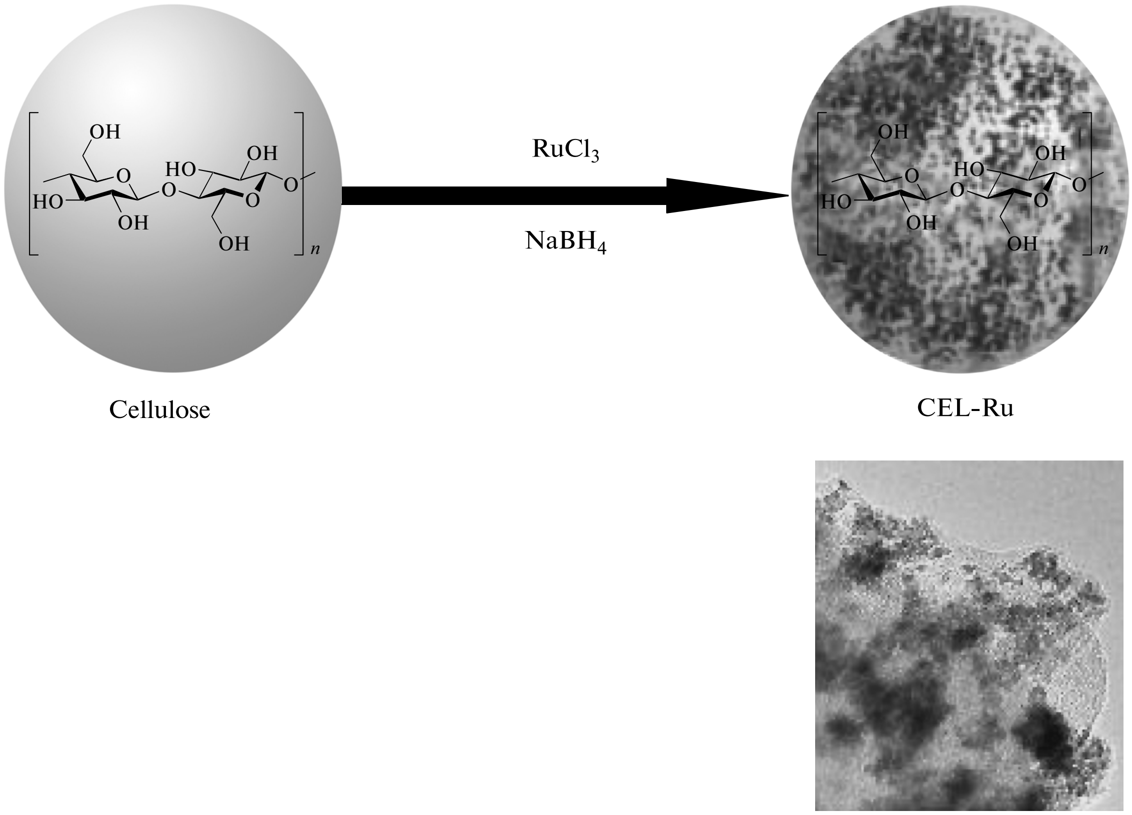

Fig. 1. Synthesis of cellulose supported Ru nanoclusters.

on cellulose and their activity in hydrogenation of benzene to cyclohexane. Moreover, hydrogenation of benzene was conducted under solvent free conditions to avoid the use of toxic and highly inflammable conventional organic solvents to make process environmentally benign. The Ru based catalysts exhibited an improved catalytic activity for hydrogenation of benzene under mild reaction conditions; it was easily recovered from product and effectively recycled.

EXPERIMENTAL

Microcrystalline cellulose was purchased from S.D. Fine Chemicals Ltd. (India). $RuCl_3 \cdot 3H_2O$ and $NaBH_4$ were purchased from M/s Sigma-Aldrich Chemicals (USA) and used as received. Benzene was purchased from Qualigens Fine Chemicals Pvt. Ltd. (India). Methanol and ethanol were purchased from Fisher Scientific Pvt. Ltd. (India). All the chemicals were used as such without further purification. Hydrogen and nitrogen gases (99.9%) used were from Hydro Gas India Pvt. Ltd. (India).

The cellulose supported Ru catalysts were prepared by adsorption-reduction method. To incorporate Ru (2% by weight) on cellulose support, microcrystalline cellulose (1.0 g) and $RuCl_3 \cdot 3H_2O$ (52 mg) were placed together with 5.0 mL ethanol in a two-neck round bottom flask (50 mL) equipped with a mechanical stirrer and a nitrogen inlet. The resulting mixture was stirred at room temperature under an N_2 atmosphere for a period of 12 h. Then, a 0.2 M solution of $NaBH_4$ in ethanol was added dropwise to the reaction mixture with constant stirring; and entire reaction mass was stirred (500 rpm) under N_2 atmosphere for a day at room temperature. Finally, catalyst was separated by filtration, washed with ethanol and dried to give dark grey cellulose supported ruthenium catalyst, CEL-2Ru (Fig. 1). The catalysts having different Ru contents such as CEL-1Ru and CEL-3Ru were also prepared as described above by varying $RuCl_3 \cdot 3H_2O$ amount. Hereafter, designations CEL-1Ru, CEL-2Ru and CEL-3Ru indicate that 1, 2 and 3 weight percent of ruthenium, respectively, were supported on cellulose (CEL) support.

All the hydrogenation reactions were performed in 100 mL stainless steel autoclave reactor (EZE-Seal Reactor, Autoclave Engineers, USA). X-ray powder diffraction (XRD) data was collected on a Miniflex II diffractometer (Rigaku, Japan) using Ni-filtered CuK_α ($\lambda = 1.5418$ nm) radiation with a scanning speed of 0.7 deg/min in the $2° \le 2\theta \le 50°$ range. Fourier transform infrared (FT-IR) spectra were recorded using KBr pellet on GX FT-IR system (PerkinElmer, USA) in the range 400–4000 cm^{-1} with a resolution of 4 cm^{-1}. Surface area measurements were carried out using Micromeritics ASAP-2010 instrument

(Micromeritics, USA). The samples were activated at 120°C for 4 h under vacuum (5×10^{-2} Torr) prior to N_2 adsorption measurements. The BET surface area, pore diameter, and pore volume of the samples were calculated from nitrogen adsorption isotherms measured at 77 K. The metal contents in the catalysts were determined by inductively coupled plasma emission spectrometry (ICPES) (OES, Optical 2000 DV, PerkinElmer) under standard conditions by digesting the sample in minimum amount of concentrated H_2SO_4.

The active metal concentration and dispersion of ruthenium were calculated with the help of the pulse hydrogen chemisorption method. Hydrogen chemisorption tests were performed in Micromeritics Auto Chem II 2920 instrument. For hydrogen chemisorption method sample were degassed in a continuous flow of argon at 120°C for 2 h. Then the catalyst was reduced in a stream of hydrogen and argon at 100°C for 1 h. The composition of this stream was 10% hydrogen and rest was argon. Then several pulses of hydrogen at 75°C were introduced to the sample until the sample was saturated with hydrogen. From this experiment quantity of hydrogen chemisorbed was determined.

Scanning electron microscopy (SEM) images of support and catalyst were measured on a microscope Leo Series VP 1430 ("Carl Zeiss", Germany) with a silicon detector equipped with EDX facility ("Oxford instruments", USA). Analyses were carried out at an accelerating voltage of 18 kV and probe current of 102 AMP. Transmission electron microscope (TEM) images were obtained with a JEOL JEM-2100 microscope (JEOL Ltd., USA) with acceleration voltage of 200 kV using carbon coated 200 mesh copper grids. The samples were ultrasonically dispersed in acetone for 5 min and deposited onto carbon film using capillary and dried in air for 30 min. Thermogravimetric analysis (TGA) was carried out using a TGA/SDTA 851^e equipment (Mettler-Toledo GmbH, Switzerlad) in flowing N_2 (flow rate = 50 mL/min), at a heating rate of 10°C/min and data were processed using $Star^e$ software.

Products were analyzed by gas chromatography (GC) with GC-17A gas chromatograph ("Shimadzu", Japan) using flame ionization detector (FID) having 5% diphenyl- and 95% dimethyl siloxane capillary column (60 m length, 0.25 mm diameter). Column temperature was initially kept at 40°C for 5 min and then raised to 200°C at 10°C/min. Furthermore, reaction mixture was analyzed by GC-MS with GC-MS QP 2010 equipment (Shimadzu) to confirm the products using mass fragmentation patterns.

Catalyst activity tests in hydrogenation of benzene were carried out in 100 mL stainless steel batch reactor. In a typical hydrogenation experiment, required amount of catalyst (CEL-Ru) and substrate benzene were charged into a 100 mL reactor placed in a stainless steel autoclave. The reactor was fitted air tight and flushed with hydrogen three times at room temperature. Then, the reactor was brought to a desired temperature and pressurized with hydrogen. The end of presurizing was considered as the zero reaction time. Hydrogenation reaction was initiated by stirring the entire reaction mass. Constant hydrogen pressure was maintained by supplying hydrogen gas manually through gas inlet valve during the reaction. After a stipulated period, the stirring was stopped and the reactor was abruptly cooled down with the help of ice-water mixture, depressurized, flushed with N_2, opened and the reaction mixture was isolated from the catalyst by decantation to collect a sample for the GC analysis.

RESULTS AND DISCUSSION

The cellulose supported Ru catalysts were characterized by various instrumental techniques. XRD patterns of cellulose and cellulose supported Ru catalysts are shown in Fig. 2a. For CEL-1Ru, CEL-2Ru, and CEL-3Ru XRD patterns are identical to cellulose. No peak due to the presence of Ru or RuO_2 in the catalysts was observed as evidenced by the comparison of the XRD patterns of the catalysts with the diffraction picture of pristine cellulose. Only intensity of the peaks was attenuated. These results indicate that ruthenium particles are highly dispersed [30] on the support. FT-IR spectra of cellulose and cellulose supported Ru catalysts in the 4000–400 cm^{-1} region are presented in Fig. 2b. In, FT-IR spectrum of pristine cellulose, the absorption bands at 3357 and 2906 cm^{-1} are attributed to O–H and methylene ($-CH_2$) groups respectively. The broad peak at 3357 cm^{-1} also indicated that the hydroxyl groups are hydrogen-bonded. The absorption band at 1368 cm^{-1} is due to C–H bending. The band at 1163 cm^{-1} corresponds to anti-symmetric stretching of C–O–C bridge while the bands at 1116 and 1057 cm^{-1} correspond to stretching of skeletal C-O bond. These absorptions bands are characteristics of saccharide structure [17]. FT-IR spectra of the cellulose supported Ru catalysts (CEL-1Ru, CEL-2Ru, and CEL-3Ru) were identical to those of the corresponding cellulose support. This identity confirms that introducn of ruthenium metal does not alter the structure of cellulose. It is also noted that the reused catalyst shows a negligible change in FT-IR pattern (Fig. 2b, CEL-2Ru) so that its behavior is in accord with the catalyst reuse experiments.

SEM images of cellulose (Fig. 3a) and catalyst CEL-2Ru (Fig. 3b) clearly show that the surface morphology of support has a layered structure. Again, SEM images confirm that metal impregnation does not alter the surface morphology of support. The BET surface area of the support and catalysts was found to be ~6.44 m^2/g with 135 Å pore diameter. Hydrogen chemisorptions data (Table 1) showed that the ratio of metal surface atoms in CEL-2Ru and CEL-3Ru catalysts to the total metal number present was lower than

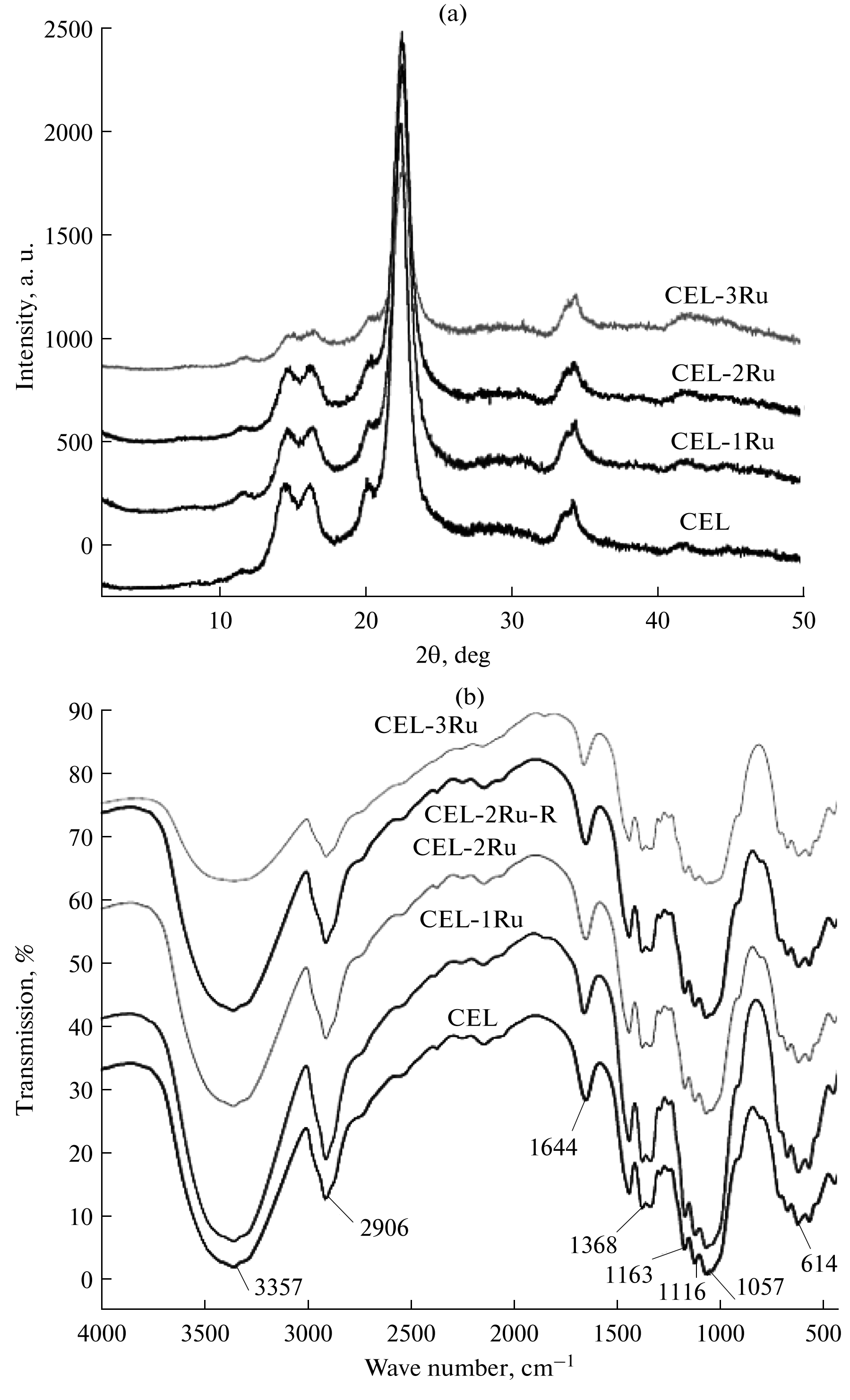

Fig. 2. (a) XRD patterns of support and catalysts; (b) FT-IR spectra of support and catalysts.

the calculated ratio for the samples with metal loading of 2 and 3 wt %. A minor agglomeration of ruthenium nanoparticles may be a reason. TEM data was also in accord with the hydrogen chemisorptions data (Table 1), which indicated presence of slightly bigger size (26 and 29 nm) of ruthenium nanoclusters in CEL-2Ru (Fig. 3c) and CEL-3Ru (not shown) catalysts. Ruthenium contents (weight percentage) in the catalysts determined by chemical analysis using ICP indicated no significant differences related to the theoretical Ru contents in the catalysts; and these contents were in accord with the calculated composition.

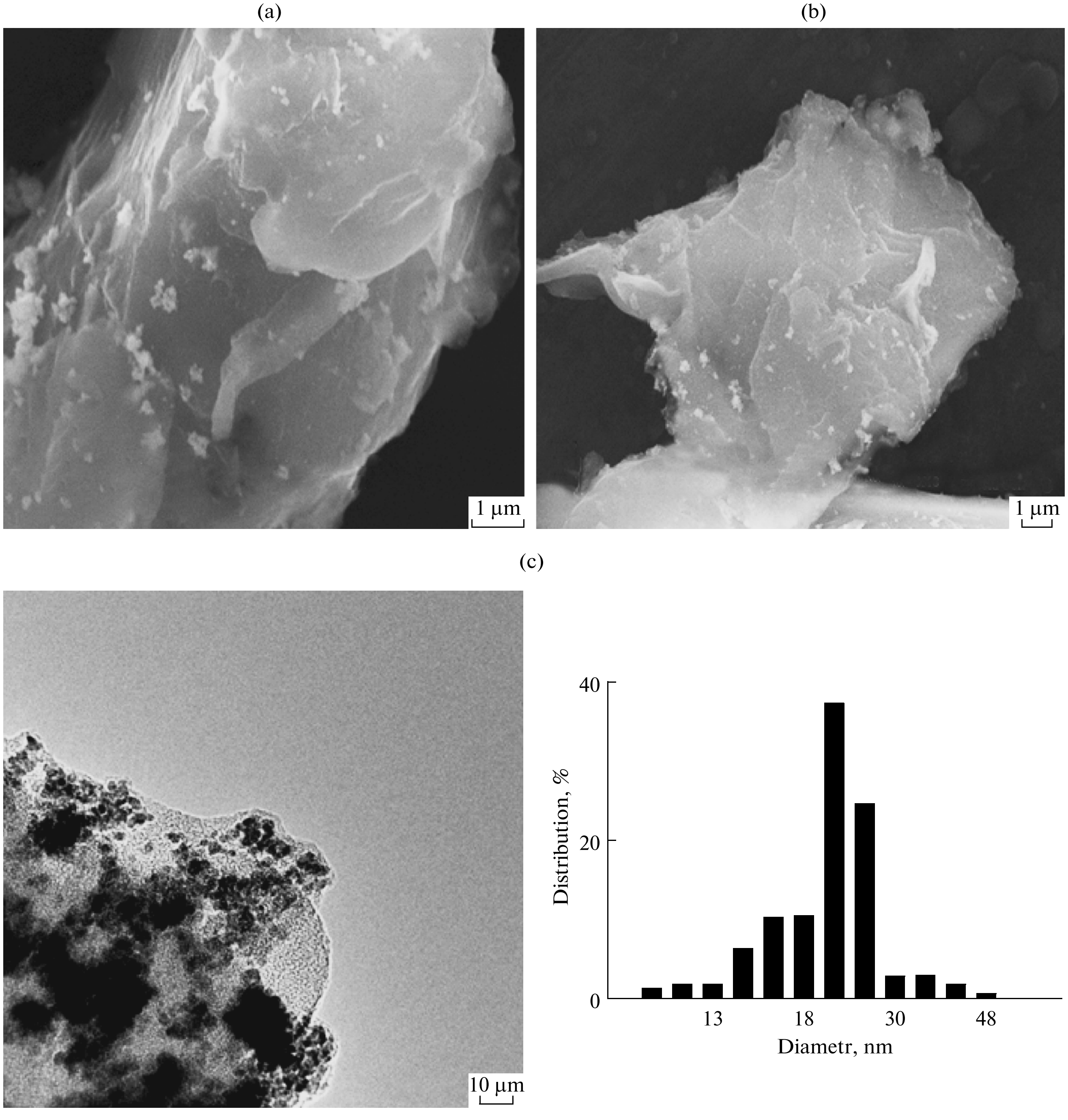

Fig. 3. SEM images of cellulose (a) and CEL-2Ru (b); TEM images of CEL-2Ru (c).

The thermal behaviour of cellulose and cellulose supported Ru catalysts (CEL-1Ru, CEL-2Ru, and CEL-3Ru) is shown in Fig. 4. Pristine cellulose has the only single step indicating a weight loss above 250°C. About 85% of the weight loss is attributed to the decomposition of polysaccharide chain. The cellulose supported Ru catalysts (CEL-1Ru, CEL-2Ru, and CEL-3Ru) displayed thermal behaviour with a two-step weight loss: first weight loss of ~2.5–10% in the range of 50–120°C is due to the physically adsorbed water molecule and second step weight loss of ~84% above 250°C can be ascribed to the decomposition of the polysaccharide framework. The catalysts are thermally stable up to 250°C.

The cellulose supported Ru catalysts were then evaluated in hydrogenation of benzene. The effect of metal loading, amount of catalyst, reaction temperature, hydrogen partial pressure, agitation speed and

Table 1. H_2 pulse chemisorption of catalysts

Entry	Catalyst	H_2 adsorption, μmol/g	Metal dispersion, %	Metallic surface area, m^2/gm of catalyst	Cluster size, nm
1	CEL-1Ru	1.36	1.37	0.33	14.46
2	CEL-2Ru	1.48	0.75	0.36	26.59
3	CEL-3Ru	3.45	1.16	0.85	29.53

reusability of catalyst were studied systematically for the hydrogenation of benzene. Only one product of benzene hydrogenation, i.e. cyclohexane was formed under the studied experimental conditions.

The hydrogenation of benzene was first carried out using catalyst, CEL-2Ru having Ru loading of 2 wt % at 60°C and 2.0 MPa hydrogen pressure. Interestingly, the catalyst, CEL-2Ru effectively hydrogenated benzene (Conv. = 79%) with 100% selectivity of cyclohexane under employed condition. In order to ascertain influence of Ru loading and the role of Ru present in the catalysts, Ru content was varied in cellulose support. The conversion of benzene was found to increase with an increase in the Ru content (Table 2, entries 2–4). This is mainly due to the increase in metal surface area per gram of catalyst (Table 1, entries 1–3) with an increase in metal loading. One experiment was also performed with only pristine cellulose (without Ru) and there was only unreacted benzene, i.e. no conversion of benzene observed after 1 h. On the other hand, the effect of catalyst amount was also studied at 60°C and 2.0 MPa H_2 pressure by varying catalyst amount from 20 to 100 mg of CEL-2Ru catalyst. The conversion of benzene was high at higher amount of catalyst, it decreased then with decreasing amount of the catalyst (Table 2, entries 5–8). At a lower amount of catalyst (20 mg), the benzene conversion was only 26%. The conversion of benzene increased from 26% to 79% with 100 mg of catalyst under identical reaction conditions. Above results clearly confirm an important role of Ru in catalysts and also indicate that the Ru present in the cellulose supported Ru catalysts is the only the active metal centre [4]. For further hydrogenation experiments, the catalyst CEL-2Ru was taken into consideration.

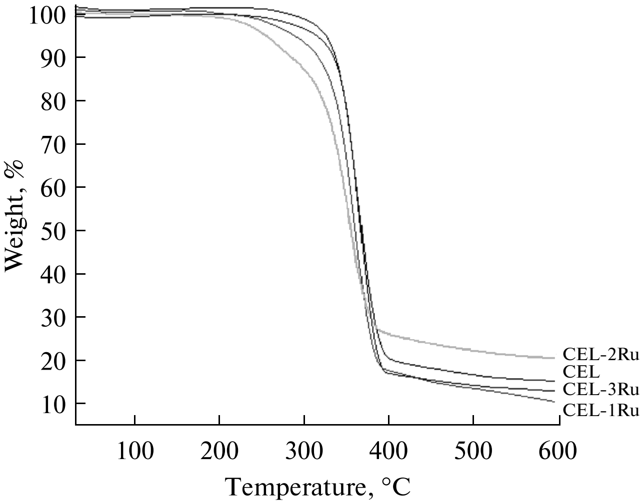

Fig. 4. TGA profiles of support ruthenium catalysts.

The influence of the reaction temperature and partial pressure of hydrogen was then examined in the hydrogenation of benzene using catalyst CEL-2Ru. The reaction temperature was varied from 30 to 80°C at constant hydrogen pressure (2.0 MPa). The conversion of benzene increased with increasing reaction temperature without affecting selectivity to cyclohexane. At a reaction temperature of 30°C, the benzene conversion was 25% with a TOF of 810 (Table 3, entry 1). The conversion and TOF increased by a factor of 4 as the temperature was increased from 30 to 70°C (Table 3, entries 1–5). The conversion of benzene reached 100% with a TOF of 3239 at 70°C (Table 3, entry 5). As the temperature was further increased to 80°C, the conversion reached 100% within 45 min of reaction time with a TOF of 4319 (Table 3, entry 8).

To observe the influence of hydrogen partial pressure on the CEL-2Ru catalyzed hydrogenation of benzene, hydrogenation experiments were carried out by varying the hydrogen partial pressure from 0.5 to 3 MPa at constant temperature (80°C). The conversion of benzene to cyclohexane increased from 36 to 100% (Table 3) with an increase in hydrogen pressure, while TOF increased with an increase in H_2 pressure (Table 3, entries 6–9). At 0.5 MPa hydrogen pressure, conversion was only 36% with a TOF of 1166 h^{-1} (Table 3, entry 6). Increasing H_2 partial pressure from 0.5 to 3.0 MPa, TOF increased by a factor of 4.7 and the complete conversion of benzene was achieved in 35 min with a TOF of 5553 h^{-1} (Table 3, entry 9). A higher hydrogen pressure enhances the oxidative addition of hydrogen on the metal (Ru) sites of the catalyst and increases the concentration of hydrogen

Table 2. Effect of Ru loading and catalyst amount on CEL-Ru catalyzed hydrogenation of benzene to cyclohexane

Entry	Catalyst	Catalyst amount, mg	Conversion, %
1	CEL	100	0
2	CEL-1Ru	100	60
3	CEL-2Ru	100	79
4	CEL-3Ru	100	97
5	CEL-2Ru	80	73
6	CEL-2Ru	60	62
7	CEL-2Ru	40	45
8	CEL-2Ru	20	26

Reaction conditions: benzene = 5 g, temperature = 60°C, H_2 pressure = 2.0 MPa, rpm = 600, reaction time = 60 min.

available for benzene hydrogenation which results in an enhanced conversion of benzene [4].

To determine the effect of sulfur on hydrogenation of benzene catalyzed by CEL-2Ru, hydrogenation experiments were conducted in presence of thiophene (as a sulphur source) under constant 70°C temperature and 2.0 MPa partial hydrogen pressure (Fig. 5). Series of runs was performed with varying concentration of thiophene from 0 to 5 ppm. Even the presence of 1 ppm of thiophene reduced the conversion from 100 to 53%. A further increase in thiophene concentration in reaction mixture caused a decrease in conversion. The poisoning effect of sulphur is interpreted as being due to the influence of its electronegativity on the density of electronic states of metal and is classified as short range phenomenon, i.e. one sulphur atom per metal atom is required to poison a catalyst site [31].

For reusability experiments, the catalyst was filtered from the reaction mixture and dried under vacuum before reuse. Reaction condition for this study was 70°C and 2.0 MPa with 100 mg of catalyst. No significant change in conversion and selectivity to cyclohexane was observed upto four runs (Fig. 6). In order to determine the extent of leaching of Ru, after forth run the reaction mixture was analyzed with ICP-OES instrument having detection limit of ~0.2 ppm with results indicating the absence of Ru in the reaction mixture. This suggests that leaching of Ru, if any, is very low. Therefore catalyst can be recycled without any significant loss in activity under employed reaction condition

The green biopolymer cellulose used as a support to stabilize ruthenium nanoclusters and the resulting catalytic system was found to be an effective heterogeneous catalyst for the hydrogenation of benzene under mild conditions. The cellulose supported Ru catalyst efficiently catalyzed hydrogenation of neat benzene as benzene is difficult to reduce with high selectivity under mild conditions. The catalyst was easily recovered from product by a simple filtration and recycling experiments showed that both the catalytic activity and selectivity of the catalyst to cyclohexane remained unaffected in four consecutive runs. The attractive fea-

Table 3. Effect of reaction temperature and hydrogen partial pressure on CEL-2Ru catalyzed hydrogenation of benzene to cyclohexane

Entry	Temperature, °C	Pressure, MPa	Time, min	Conversion, %	TOF, h^{-1}
1	30	2.0	60	25	810
2	40	2.0	60	33	1067
3	50	2.0	60	49	1587
4	60	2.0	60	79	2559
5	70	2.0	60	100	3239
6	80	0.5	60	36	1166
7	80	1.0	60	58	1879
8	80	2.0	45	100	4319
9	80	3.0	35	100	3553

Reaction conditions: benzene = 5 g, catalyst (CEL-2Ru) = 100 mg, rpm = 600.

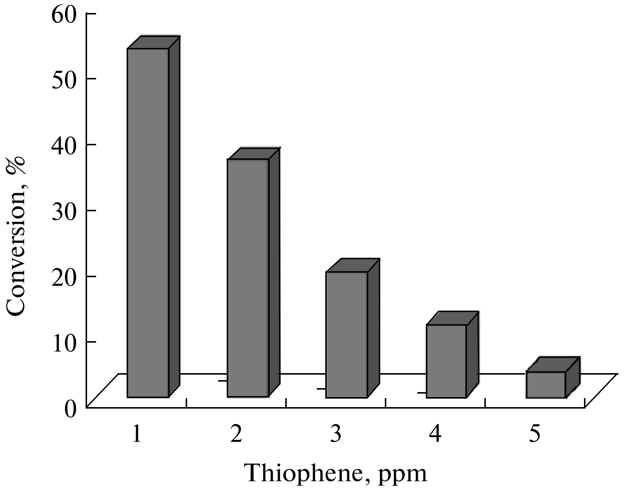

Fig. 5. Effect of sulfur on benzene hydrogenation to cyclohexane catalyzed by CEL-2Ru. Reaction conditions: benzene = 5 g, catalyst (CEL-2Ru) = 100 mg, temperature = 70°C, H_2 pressure = 2.0 MPa, rpm = 600, reaction time = 60 min.

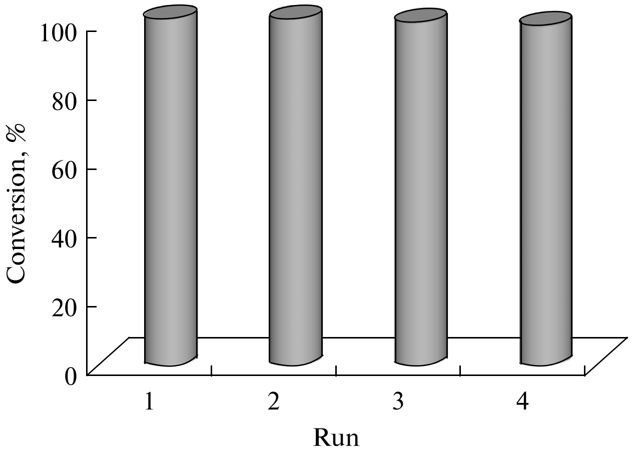

Fig. 6. Reusability of the catalyst for hydrogenation benzene. Reaction conditions are the same as indicated in Fig. 5.

tures of cellulose as support and a high catalytic activity of cellulose supported Ru catalyst in benzene hydrogenation would extend the scope of cellulose as a catalyst support.

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