Hydrogenolysis of sorbitol over Ni, Pt and Ru supported on SBA-15

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Hydrogenolysis of sorbitol (15% aqueous solution) has been carried out in a batch reactor over Ni (6 wt%), Pt (1 wt%) and Ru (1 wt%) supported on SBA-15 and carbon coated SBA-15 (SBA-15(C)). For comparison, the three metals have also been supported on activated carbon (AC). The catalysts are characterized by XRD, N_2 and H_2 adsorption measurements. Addition of $Ca(OH)_2$ to the reaction mixture increases conversion and selectivity for the dihydroxy compounds, 1,2-propanediol (PD) and ethylene glycol (EG). Based on yield of dihydric alcohols (PD+EG), the performance of the catalysts at 220 °C and 60 bar in the presence of $Ca(OH)_2$ is in the order: Ru-AC ~ Ru-SBA-15(C) > Ru-SBA-15 ~ Ni-SBA-15, the yields being 40, 39, 31 and 29 wt%, respectively.

The transformation of cellulose from biomass into value added chemicals that are presently being made from petrochemical feed-stocks has assumed great significance owing to depleting petroleum reserves and the need to use renewable feed-stocks. It is hoped that cellulose will be converted into intermediate platform chemicals that can be transformed into many final products[1-8]. One such platform chemical sorbitol, which may be produced from starch and cellulose, can be converted into different products, such as ethylene glycol (EG), propane diols (PDs) and glycerol (G) that are important commodity chemicals[9].

Many studies on the transformation of sorbitol into EG, PDs and G have been reported [10-15]. Clark *et al.*[10] carried out sorbitol hydrogenolysis using Ni on

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Kieselguhr and reported 40% glycerol yield. Chao *et al.*[11] carried out the reaction in a fixed bed reactor over Ni/SiO_2 and obtained 30% conversion to glycerol. Sohounloue *et al.*[12] investigated sorbitol hydrogenolysis over Ru/SiO_2 in basic medium and proposed a retro-aldol condensation mechanism. Montassier *et al.*[16] investigated the influence of S-poisoning of Ru/carbon during the hydrogenolysis of sorbitol. He proposed that the main C–C bond cleavage reaction in sorbitol hydrogenolysis was a retro-Michael reaction under the action of adsorbed nucleophilic species. Zhao *et al.*[15] carried out sorbitol hydrogenolysis over 3% Ru supported on carbon nanofiber based catalysts and reported 85.7% conversion and 51.3% selectivity for the three products, EG and PD (44% yield). Ye *et al.*[17] have reported a PD + EG yield of 48.5% (91.1% conversion and 53.2% selectivity) over Ce (0.5%)-Ni (20%)/Al_2O_3, which possessed reasonably good reusability. We had earlier reported studies on Ni, Pt and Ru supported on two different supports, NaY[18,19] and fly ash[20].

We present herein our investigations on the activity of Ni, Pt and Ru supported on mesoporous silica, SBA-15, and SBA-15 modified by depositing carbon in its pores for the hydrogenolysis of sorbitol. For comparison, the metals were also supported on activated carbon and their activity evaluated.

Experimental

SBA-15 and carbon coated SBA-15 (SBA-15(C)) were prepared following the procedures reported by earlier workers[21]. The template, P123 ($EO_{20}PO_{70}EO_{20}$, Aldrich; 4 g) was dissolved in a solution containing 30 g H_2O and 120 g of 2 *M* HCl at 35 °C. TEOS (tetraethyl orthosilicate, 8.5 g) was added to the clear solution and the mixture was stirred at 35 °C for 24 h. It was then aged at 80 °C for 24 h, during which a precipitate was produced. The precipitate was recovered, washed, and air-dried at room temperature. Two different calcination procedures were adopted to prepare SBA-15 and SBA-15(C); calcination in air at 550 °C for 6 h produced a white sample of SBA-15 and calcination in N_2 at 550 °C for 6 h yielded the grey sample, SBA-15(C). During both the calcinations, the temperature was raised from room temperature to

550 °C at a rate of 1 °C/min. The grey colour of SBA-15(C) is attributed to the formation of carbon film on the pore walls of SBA-15 due to decomposition of the template (P123) during calcination in N_2. The C-content of the sample (SBA-15(C)) was 4 wt%.

Ni (6 wt%), Ru (1 wt%) and Pt (1 wt%) were loaded on SBA-15 and SBA-15(C) by impregnation. The metal salt loaded SBA-15 samples were dried at 120 °C for 6 h, calcined at 450 °C (6 h) and reduced at 400 °C (4 h) in H_2. In the case of the SBA-15(C) samples, reduction was carried out directly after drying without calcination.

Ni (6%), Pt (1%) and Ru (1%) were supported on activated carbon (AC), procured from SD Fine Chem, India, by impregnation using solutions of the requisite salts, viz., $Ni(NO_3)_2$, H_2PtCl_6 or $RuCl_3$, by an incipient wetness method. The metal salt loaded samples were dried at 110 °C for 12 h, and then calcined at 450 °C (4 h). Finally, the catalysts (Ni(6%)-AC, Pt(1%)-AC and Ru(1%)-AC) were reduced at 400 °C for 4 h.

XRD patterns of the calcined catalysts were obtained using a Rigaku Miniflex II instrument with Cu Kα (λ = 1.5418 Å). Surface areas and pore volumes of the samples were obtained by N_2 adsorption at liquid N_2 temperature (Micromeritics, ASAP 2020). Metal dispersion measurements were carried out on the reduced sample (0.2 g) by pulsed chemisorption of H_2 at 25 °C using a commercial instrument (Micromeritics, Autochem II, Chemisorption Analyzer). The samples were reduced at 450 °C for 2 h and flushed with Ar at the same temperature for 2 h prior to H_2 chemisorption.

Hydrogenolysis of sorbitol was carried out in a 300 mL stainless steel (SS) autoclave (Parr 4843) using 100 g of an aqueous solution of 15 wt% sorbitol. After the aqueous mixture of sorbitol was introduced into the autoclave and briefly purged with N_2, the H_2-reduced catalyst (powder) was added. The sealed autoclave was purged well by flowing H_2 at room temperature. The typical reaction conditions were as follows: 15% sorbitol in water; catalyst: 0.5 g; temp: 220 °C; pressure: 60 bar; time: 6 h; stirring speed: 300 rpm; After 6 h, the autoclave was cooled rapidly with cold water. The product mixture was then collected, weighed, filtered and analyzed. The liquid product mixture was analyzed by HPLC (LC20AT, Shimadzu) equipped with a RI detector (RID-10A, Shimadzu). The separation of the product mixture was achieved using a NH_2 column (Phenomenex) at 25 °C. Doubly distilled water was used as the mobile phase at a flow rate of 0.5 mL min^{-1} and a typical analysis run lasted 20 min. The polyhydric alcohols were analysed in a gas chromatograph (GC) with a capillary column (FFAP).

Results and discussion

The physicochemical characteristics of the catalysts are presented in Table 1. The total surface areas were calculated, using the BET equation. The surface areas of the supports are 702 and 561 and 1159 m^2/g for SBA-15 and SBA-15(C) and AC, respectively (Table 1). The external surface areas (S_{Ext}) of the samples calculated by the t-plot method are, 551 and 440 and 386 m^2/g, respectively, for the above supports (Table 1). In SBA-15 and 15(C), the

Table 1—Textural properties and metal dispersion of the catalysts

Catalyst	S_{BET}[a] (m^2/g)	S_{EXT}[b] (m^2/g)	PV_{tot}[c] (cm^3/g)	Avg pore dia. (Å)[d]	a_o (Å)[e]	Metal dispersion, % (crystallite size, nm)[f]
SBA-15	702	551	0.93	64.9	96.15	-
Ru(1%)-SBA-15	505	399	0.73	61.5	101.63	46 (2.4)
Pt(1%)-SBA-15	427	373	0.72	59.3	107.80	56 (1.7)
Ni(6%)-SBA-15	600	501	0.91	64.2	108.46	3 (29.)
SBA-15C	561	440	0.77	62.4	101.05	-
Ru(1%)-SBA-15C	560	428	0.74	64.5	105.87	74 (1.5)
Pt(1%)-SBA-15C	455	403	0.73	60.0	99.37	38 (2.4)
Ni(6%)-SBA-15C	381	325	0.71	64.3	105.25	29 (3.0)
AC	1159	386	0.68	37.5	-	-
Ru(1%)-AC	797	263	0.46	36.9	-	47 (2.3)
Pt(1%)-AC	882	304	0.51	37.0	-	36 (2.6)
Ni(6%)-AC	662	138	0.35	34.1	-	32 (2.7)

[a]Surface area using BET method; [b]S_{BET}–S_{Micro} (from t-plot); [c]Total pore volume ($p/p_o \sim$ 0.99); [d]using BJH method; [e]using $a_o = d_{100}/\sqrt{3}$ (for SBA-15 and SBA-15(C)); [f]Calc. from H_2-chemisorption data using $d = 5\rho/S_M$, where ρ = density of metal and S_M = metal surface area per g of metal.

external area is mainly the area of the pore system, the worm-holes present contributing to the micropore area (between 22-24 %). In AC, though a large fraction (~67%) of the area arises from micropores, a substantial amount of meso and macro-porosity, contributing to 386 m^2/g of area, is also present. The total pore volumes of the supports are 0.93 and 0.77 and 0.68 cm^3/g for SBA-15 and SBA-15(C) and AC, respectively (Table 1). On loading of the metals, the surface areas and pore volumes of all the supports decrease due to hydrothermal treatment during drying and calcination steps. Still, the external surface areas of all the catalysts are substantial. It is believed that the large molecule sorbitol (dimensions: 0.67×0.53×0.29 nm) will be able to diffuse into the mesopores in SBA-15, SBA-15(C) and AC even after substantial hydration. The average pore diameters of the supports and catalysts (obtained by the BJH method) are also presented in Table 1. The N$_2$ adsorption-desorption isotherms of SBA-15 and SBA-15(C) and the prepared supported metal catalysts are similar, revealing uniformity of pores and negligible damage to the pore system on loading of the metals (Fig. 1).

The dispersion of the metals and the average crystallite sizes calculated from H$_2$ adsorption experiments are listed in Table 1. In general, Pt and Ru (1 wt% each) are better dispersed than Ni (6 wt%) over all the supports. The best metal-support combinations for obtaining the highest dispersion for the metal are Ru/SBA-15(C) (74%) and Ni/AC (32%).

Low angle XRD patterns of SBA-15 and SBA-15 (C) reveal the characteristic (100), (110) and (200) lines (Fig. 2). The unit cell value (a_o) for SBA-15 and SBA-15(C) are 96.15 and 101.05 Å, respectively (Table 1). The marginal increase in a_o values on loading of the metals in most cases is probably due to relaxation of the pore system by hydrolysis of the Si-O-Si bonds during impregnation, drying and calcination procedures. The XRD patterns of AC and the catalysts (Fig. 3) reveal lines typically observed for graphitic materials (002 plane at 2θ=23.8° and 101 plane at 43.4°)[22]. Besides, peaks for metallic Ni and Pt are also seen in the reduced samples (Fig. 3).

Dehydration products (olefins) and ketonic/ aldehydic compounds were not detected in the present study. It is likely that any such products formed, were transformed into other compounds by hydrogenation. Similarly, hydrocarbons were not detected in the products, though methane was found in traces
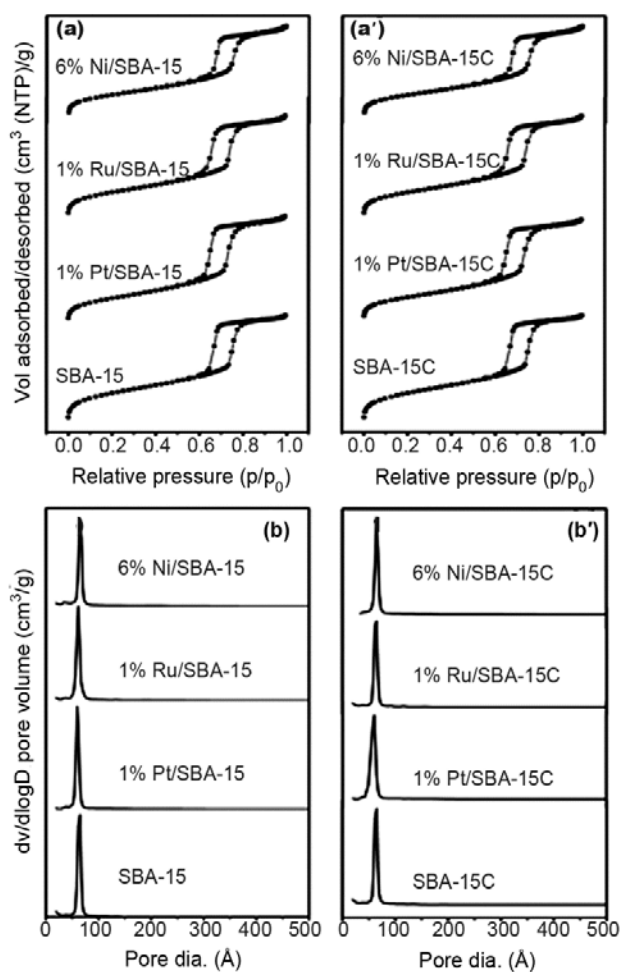

Fig. 1— (a, a′) N$_2$ adsorption-desorption isotherms, and, (b, b′) pore size distribution of the support and supported catalysts.
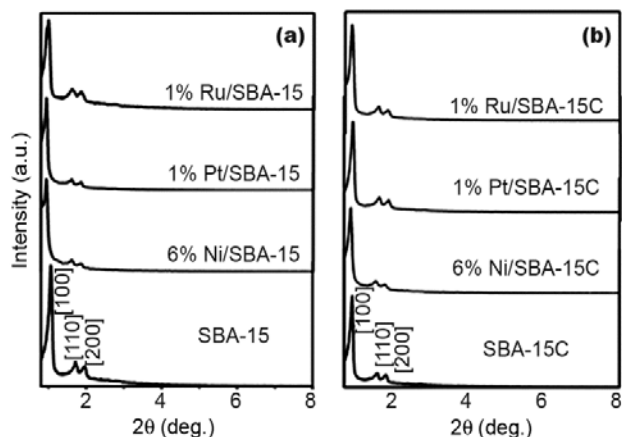

Fig. 2—Low angle XRD patterns of (a) SBA-15 supported catalysts, and, (b) SBA-15(C) supported catalysts.
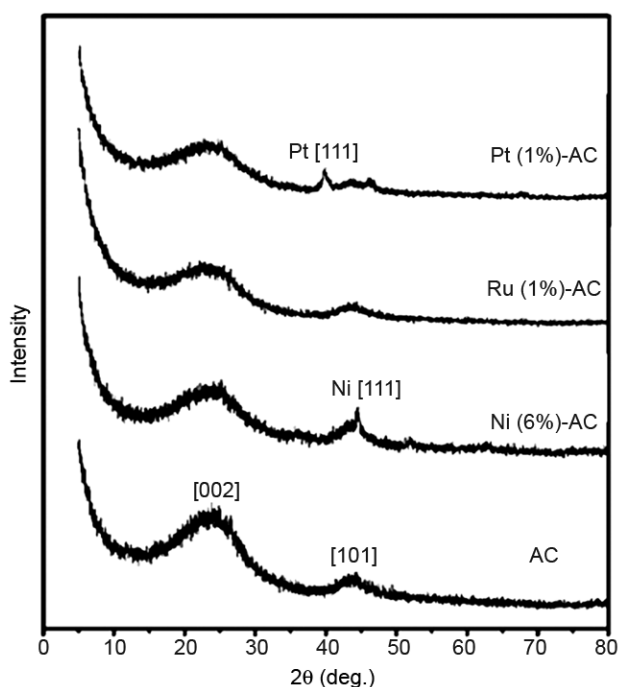
(less than 0.1 wt%) in some runs. Among the two propanediols, only the 1,2-diol was obtained. The mass balances of the runs were better than 98%.

The results of the hydrogenolysis of sorbitol (in water) at 220 °C and 60 bar over Ni, Pt and Ru supported on SBA-15 are presented in Table 2. Ni is the most active catalyst followed by Ru and Pt, the conversions being 35%, 32% and 29%, respectively. The major products of the reaction over this support in the case of all the three metals are the dihydric alcohols 1,2-propanediol (PD) and ethylene glycol (EG), and the polyols (erythritol and xylitol).

The selectivity for the desired dihydric alcohols is in the same order as activity: Ni > Ru > Pt, while the selectivity for glycerol is in the reverse order. When $Ca(OH)_2$ (0.5 g) is added to the reaction mixture, the conversions increase marginally, but the selectivity for PD+EG increases substantially, the increase being 42% to 73% for Ni, 39% to 74% for Ru and 26% to 66% for Pt. Correspondingly, selectivity for glycerol, polyols and other products decreases drastically.

On the carbon coated support (SBA-15(C)), the order of activity of the metals is different from that observed over SBA-15; it is Ru > Pt > Ni (Table 3).

Fig. 3—XRD patterns of activated carbon and the AC supported catalysts.

Table 2— Sorbitol hydrogenolysis over metal loaded SBA-15 in the presence and absence of $Ca(OH)_2$. [React. cond.: 15% sorbitol in water; catalyst: 0.5 g; temp.: 220 °C; pressure: 60 bar; time: 6 h; stirring speed: 300 rpm; $Ca(OH)_2$: 0.5 g]

Catalyst	Sorbitol conv. (%)	Product selectivity (wt%)				
		Glycerol	Dihydric alcohols[a]		Polyols[b]	Others[c]
			1,2 PD	EG		
Ru(1%)-SBA-15	32	14	27	12	22	25
Pt(1%)-SBA-15	29	19	16	10	31	24
Ni(6%)-SBA-15	35	12	29	13	38	8
Ru(1%)-SBA-15+Ca(OH)₂	42	8	72	2	9	9
Pt(1%)-SBA-15+Ca(OH)₂	36	8	63	3	11	15
Ni(6%)-SBA-15+Ca(OH)₂	40	7	69	4	9	11

[a]PD = 1,2-propanediol; EG = ethylene glycol; [b]trihydric (other than glycerol) and higher alcohols; [c]unidentified products.

Table 3—Sorbitol hydrogenolysis over metal loaded SBA-15(C) in the presence and absence of $Ca(OH)_2$. [React. cond.: Same as in Table 2]

Catalyst	Sorbitol conv. (%)	Product selectivity (wt%)				
		Glycerol	Dihydric alcohols[a]		Polyols[b]	Others[c]
			1,2 PD	EG		
Ru(1%)-SBA-15(C)	40	19	25	7	30	19
Pt(1%)-SBA-15(C)	35	28	16	2	35	19
Ni(6%)-SBA-15(C)	13	15	14	4	14	53
Ru(1%)-SBA-15(C)+Ca(OH)₂	49	7	73	7	7	6
Pt(1%)-SBA-15(C)+Ca(OH)₂	51	11	40	7	20	22
Ni(6%)-SBA-15(C)+Ca(OH)₂	30	12	50	5	15	18

[a]PD = 1,2-propanediol; EG = ethylene glycol; [b]trihydric (other than glycerol) and higher alcohols; [c]unidentifiedproducts.

Table 4—Sorbitol hydrogenolysis over metal loaded AC in the presence and absence of $Ca(OH)_2$. [React. cond.: same as in Table 2]

Catalyst	Sorbitol conv. (%)	Product selectivity (wt%)				
		Glycerol	Dihydric alcohols[a]		Polyols[b]	Others[c]
			1,2 PD	EG		
Ru(1%)-AC	27	17	49	7	19	8
Pt(1%)-AC	8	31	18	2	38	11
Ni(6%)-AC	13	16	49	9	19	7
Ru(1%)-AC +Ca(OH)$_2$	52	4	72	5	6	13
Pt(1%)-AC+Ca(OH)$_2$	23	8	47	4	12	28
Ni(6%)-AC+Ca(OH)$_2$	35	8	55	6	12	19

[a]PD = 1,2-propanediol; EG = ethylene glycol; [b]trihydric (other than glycerol) and higher alcohols; [c]unidentified products.

Selectivity for glycerol is in the same order as for the SBA-15 catalysts, Pt > Ru > Ni. Selectivity for the dihydric alcohols is lower than that observed over the SBA-15-supported catalysts. On addition of $Ca(OH)_2$, conversion increases substantially for all the metals, especially Ni and Pt (from 13% to 30% for Ni, from 40% to 49% for Ru, and, from 35% to 51% for Pt). There is also a substantial improvement in selectivity for PD+EG (from 18% to 55% for Ni, 32% to 80% for Ru and 18% to 47% for Pt). This is associated with a corresponding decrease in selectivity for the other products.

The results of the hydrogenolysis of sorbitol over AC-supported catalysts are presented in Table 4. On this support, Ru is more active than Ni followed by Pt. Selectivity for glycerol is in the same order as for SBA-15 and SBA-15(C), Pt > Ru > Ni. Selectivity for the dihydric alcohols is higher than that observed over the other two supports in the case of Ni and Ru. On addition of $Ca(OH)_2$, conversion increases substantially for all the metals (from 13% to 35% for Ni, 27% to 52% for Ru and from 8% to 23% for Pt). There is also an improvement in selectivity for PD+EG (58% to 61% for Ni, 56% to 77% for Ru and 20% to 51% for Pt). This is associated with a corresponding decrease in selectivity for glycerol and polyols.

The activities of the supported metals and their selectivity for PD+EG and glycerol on the four supports, in the absence and presence of $Ca(OH)_2$ were studied. The performances of the catalysts vary depending on the support and the presence or absence of $Ca(OH)_2$. In the presence of $Ca(OH)_2$, AC is a good support for Ru while SBA-15(C) is a good support for Pt. In the presence of $Ca(OH)_2$, both Pt-SBA-15(C) and Ru-AC possess nearly similar activities for conversion of sorbitol (conversions being 52% and 51%, respectively), while the yields of the glycols (PD+EG) decrease in the order:

Ru-AC ~ Ru-SBA-15(C) >Ru-SBA-15 > Ru-NaY (yields being 39 wt%, 38 wt%, 32 wt% and 27 wt%, respectively).

Examining the relative activity of the metals on each support, the orders are not exactly the same in the presence and absence of $Ca(OH)_2$, though substantial similarity in the orders is seen. This confirms that though the reaction occurs mainly on the metal, $Ca(OH)_2$ also plays a role in determining overall conversion. When the relative activity of the metals are arranged based on exposed atoms (calculated from dispersion; Table 1), we get a slightly different ordering; Ni being the most active over SBA-15 followed by Pt. Pt is the most active metal when supported on SBA-15(C) and Ru is the most active one in the case of AC. This ordering based on exposed atoms does not depend on the absence or presence of $Ca(OH)_2$. As the metal plays the major role in the reaction, the order of activity of the metals should be similar over all the supports. However, this is not found to be so, indicating that the support also plays a role in the reaction by influencing the activity of the metal.

In conclusion, in the hydrogenolysis of aqueous sorbitol over Ni, Pt and Ru supported on SBA-15, carbon coated SBA-15 and activated carbon 1,2-Propanediol is the major product. Based on intrinsic activity of the metals obtained at high conversions, SBA-15 appears to be a good support for Ni, while AC is most suited for Ru. In general, Ni and Ru are more selective for C_2 and C_3 glycols than Pt. Though the addition of $Ca(OH)_2$ increases the activity of the catalysts, the metal appears to be mainly responsible for sorbitol conversion and selectivity for C_2 and C_3 glycols. The support has an influence on the reaction, presumably by influencing the activity of the metal.

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