Platinum catalyzed hydrogenation of 2-butyne-1,4-diol

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Abstract

Hydrogenation of 2-butyne-1,4-diol (B_3D) using 1% Pt/CaCO$_3$ catalyst was carried out to give 2-butene-1,4-diol (B_2D) or butane-1,4-diol (B_1D) selectively or a mixture of two diols eliminating the formation of acetal, aldehyde, and alcohols as side products. In presence of ammonia, nearly complete selectivity to B_2D was obtained in a batch reactor while, in a fixed bed reactor total selectivity to B_1D was obtained. Effect of concentration of ammonia, metal loading and catalyst pre-treatment on catalyst activity and selectivity has been investigated in a batch reactor. The formation of B_1D and B_2D is explained on the basis of associative or dissociative adsorption of B_3D via carbene and carbyne type intermediates which react with adsorbed hydrogen to give the corresponding products. A kinetic model based on Langmuir–Hinshelwood (L–H) type mechanism has been proposed which shows a good agreement with experimental data.
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1. Introduction

Catalytic hydrogenation of 2-butyne-1,4-diol (B_3D) is an industrially important reaction for the manufacture of *cis* 2-butene-1,4-diol (B_2D) and butane-1,4-diol (B_1D). The olefinic diol, B_2D is a starting material for the manufacture of endosulfan [1], Vitamins A and B$_6$ [2] while, butane diol has a wide range of applications in the polymer industry and as a raw material for the manufacture of tetrahydrofuran [3]. The earlier processes reported in the literature for butynediol hydrogenation use Ni or Ni–Cu-based catalysts under severe operating conditions (15–30 MPa pressure and 413–433 K temperature) [4]. Noble metals such as Pd, Ru, alone or with different poisons such as Zn, Pb, Cd, Cu and organic amines were also tried to obtain good

selectivity for B_2D [1,5–11]. With Pd/C as a catalyst, 60–70% selectivity to B_2D was obtained which further increased to 97–99% by addition of another metal or metal salts such as lead or lead acetate [8]. Rosso et al. [11] have reported the use of 5% Ru/C catalysts for hydrogenation of B_3D to give B_1D as a major product. Higher selectivity to saturated product B_1D, is reported by using a catalyst system without any poison, however, in such cases several side products such as γ-hydroxy butryaldehyde, *n*-butryladehyde, *n*-butanol, crotyl alcohol and acetal are known to be formed. Recently, Telkar et al. [12] have reported the kinetics of selective hydrogenation of B_3D to B_2D using supported palladium catalyst. Since both B_2D and B_1D are large scale commercial products, it would be most desirable to hydrogenate B_3D to give either B_2D or B_1D selectively or a desired mixture of B_2D and B_1D by tailoring the catalyst and operating conditions. Hydrogenation of B_3D is of fundamental significance,

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due its adsorption characteristics leading to the formation of active species and their role in determining the product distribution. The aim of this work was, therefore, to study the product distribution in hydrogenation of B_3D, using Pd and Pt based catalysts. Among the several Pd- and Pt-based catalysts screened for hydrogenation of B_3D, $Pt/CaCO_3$ was found to avoid the formation of isomerized products. A kinetic model based on Langmuir–Hinshelwood (L–H) type mechanism has been proposed which indicates that the reaction takes place between adsorbed B_3D and H_2 for the Pt catalyst. Activity and selectivity pattern for $Pt/CaCO_3$ catalyst in both batch and continuous operations was also studied. Batch hydrogenation experiments were conducted in an autoclave while, continuous hydrogenation was carried out in a fixed bed reactor in which both liquid reactant and H_2 gas were continuously fed to the reactor. A possible reaction pathway has also been proposed to explain the observed selectivity pattern for Pt catalyzed hydrogenation of B_3D.

2. Experimental

2.1. Catalyst preparation

The palladium and platinum supported catalysts were prepared as follows. The required quantity of $PdCl_2$ or $PtCl_4$ was dissolved in minimum amount of water, if necessary small quantity of dilute HCl was added to ensure the complete dissolution of the precursor. Under stirring conditions, the slurry of support prepared in water was added to the above solution, and temperature was maintained at 353 K. After 1 h, formaldehyde was added under stirring. Then the reaction mixture was cooled, filtered to obtain the catalyst, which was then dried at room temperature.

2.2. Batch measurement

The hydrogenation of B_3D over Pd- and Pt-supported catalysts was carried out in a 600 ml capacity autoclave (Parr interments Co., USA), which was equipped with arrangements for cooling, gas inlet/outlet and sampling of liquid phase. Automatic temperature control, variable agitation speed, safety rupture disc, high temperature cut off and pressure recording by a transducer were also provided. A reservoir for H_2 gas was used along with a constant pressure regulator for supply of hydrogen at a constant pressure to the reactor. The hydrogen consumption was measured from the pressure drop observed in the hydrogen reservoir.

In a typical hydrogenation experiment, 150 ml of 20% aqueous B_3D solution, 1.2 ml of ammonia solution (30% w/w) and 0.13 gm of Pd- or Pt-supported catalyst were charged to the reactor. The contents were first flushed with nitrogen and then with hydrogen. After the desired temperature was attained the system was pressurized with hydrogen at required pressure. The reaction was started by switching the stirrer on. The progress of the reaction was monitored by the observed pressure drop in the reservoir as a function of time. After the reaction was over as indicated by a constant hydrogen pressure in the reservoir, the reactor was cooled to room temperature and excess hydrogen was vented out safely and the reactor contents were removed for subsequent analysis.

2.3. Continuous measurement

Continuous hydrogenation experiments were also carried out in a fixed bed reactor supplied by "Geomechanique", France. For this purpose, 1% $Pt/CaCO_3$ powder catalyst was pelletized in the form of pellets of 2 mm diameter, which were used for fixed bed experiments. The reactor consisted of a stainless tube of 0.3 m length and 1.2×10^{-2} m, i.d. The reactor was provided with two thermocouples to measure the temperature at two different points, one at the entrance of the reactor and other at the center of the catalyst bed. The reactor was equipped with mass flow controller, pressure indicator and other control devices. A liquid storage tank was connected to the metering pump through a volumetric burette in order to measure the liquid feed rate. The other end of the reactor was connected to a gas–liquid separator through a condenser.

In a typical hydrogenation experiment, 0.04 kg of catalyst pellets were charged in a reactor, wherein the sections above and below the catalyst bed were packed with inert packing (carborundum). The reactor was flushed thoroughly with nitrogen and then with hydrogen at room temperature, before starting the reaction. After attaining the desired temperature, the reactor was pressurized with hydrogen, the liquid feed started and the samples were withdrawn from time to time.

The liquid samples withdrawn were analyzed by gas chromatograph with thermal conductivity detector using PEG 1500 (length: 3 m, i.d.: 3 mm), and Helium (30 ml/min) as a carrier gas.

3. Result and discussions

3.1. Catalytic activity

Pd and Pt catalysts on various supports were screened for their activity and selectivity in B_3D hydrogenation in a batch slurry reactor and the results are presented in Table 1. High turn over frequency (TOF) was achieved for Pd/C and Pd/Al$_2$O$_3$ catalysts giving B_1D as a major product. The total selectivity to B_1D and B_2D together was in the range of 75–80%. In addition to B_1D and B_2D, other side products formed were γ-hydroxy butyraldehyde, n-butyraldehyde and n-butanol. In case of Pd-Pb/CaCO$_3$ catalyst (Lindlar type) the selectivity to B_2D obtained was 77% without formation of any B_1D, however, other side products were still formed to the extent of 23%. Pt/CaCO$_3$ catalyst gave interesting results (Table 1, entry 4), with higher selectivity (83%) to B_2D and the products formed were only B_1D and B_2D without any other products. Fig. 1 shows a typical concentration–time profile of B_3D hydrogenation using Pt/CaCO$_3$ catalyst, in which the only products formed were B_1D and B_2D. Addition of small amount of ammonia with Pt/CaCO$_3$ catalyst gave nearly complete selectivity to B_2D with a decrease in TOF, by about 20%. The activity of 1% Pt/CaCO$_3$ catalyst for both without and with ammonia was substantially (>60%) higher than that for 1% Pd/CaCO$_3$ catalyst, under the same reaction

conditions [12]. Also the formation of γ-hydroxy butyraldehyde, n-butyraldehyde and n-butanol for Pt/CaCO$_3$ catalyst was not observed unlike in case of Pd catalysts, possibly due to the presence of β-hydride phase [13,14].

The B_3D being an acetylenic compound is adsorbed strongly on the catalyst surface through two σ metal carbon bonds [14,15]. The solid catalyst (Pt/CaCO$_3$) was treated with B_3D and the reaction mixture containing both B_3D and B_2D separately in an autoclave at 323 K. The catalyst samples were then isolated, FTIR of these samples in the form of KBr pellets were observed. It can be seen from Fig. 2a, that in case of pure B_3D adsorbed on the catalyst, the peak at 3333 cm^{-1} is due to the –OH while peaks at 1500 and 1128 cm^{-1} are due to characteristic stretching of alkyne (–C≡C–) group, respectively. These remain unchanged for a catalyst sample exposed to a mixture of B_3D and B_2D as shown in spectra (b) indicating the absence of any adsorbed B_2D. However, the original peak at 1500 cm^{-1}, due to B_3D has shifted to 1494 cm^{-1}. This clearly indicates the strong adsorption of B_3D molecule on the catalyst surface, which is also evident from concentration–time profile shown in Fig. 1, in which the further hydrogenation of B_2D to B_1D does not start until B_3D is almost completely reacted. B_3D adsorbed on the catalyst surface can lead to the formation of several types of species, which can be of dissociative or associative in nature and can exist at the same time on the catalyst surface [16]. Since, such species have very short lifetime, it is very difficult to characterize them. The probable reaction pathway for the formation of B_1D and B_2D in absence of ammonia and under the conditions of the present work is shown in Scheme 1. According to this scheme, the

Table 1

Results on catalytic performance over Pd- and Pt-supported catalysts in hydrogenation of butynediol to butenediol[a]

Serial no.	Catalyst	TOF ($\times 10^{-4}$, h^{-1})	Selectivity (%)		
			B_1D	B_2D	Others
1	1% Pd/Al$_2$O$_3$	2.02	75.0	6.0	19.0
2	1% Pd/C	2.92	70.0	5.0	25.0
3	5% Pd-2.5% Pb/CaCO$_3$	1.92	0.0	77.0	23.0
4	1% Pt/CaCO$_3$[b]	2.40	17.0	83.0	0.0
5	1% Pt/CaCO$_3$	1.98	0.0	100.0	0.0

[a] Reaction conditions: temperature, 323 K; pressure, 2.48 MPa; concentration of B_3D, 2.26 kmol/m^3; concentration of catalyst, 0.86 kg/m^3; agitation speed, 13.3 Hz; concentration of NH$_3$, 17.5 mmol; total volume, 1.5×10^{-4} m^3.
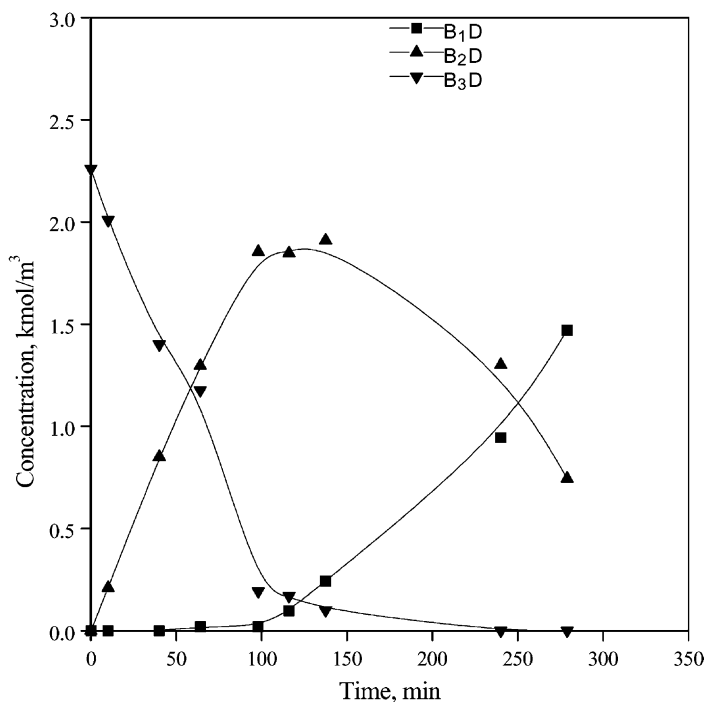
[b] Without ammonia.

Fig. 1. Typical concentration time profile for B_3D hydrogenation. Reaction conditions: temperature, 323 K; pressure, 2.4 MPa; initial concentration of B_3D, 2.26 kmol/m^3; active concentration of catalyst, 6.66×10^{-3} mmol; agitation speed, 13.3 Hz; total volume, 1.5×10^{-4} m^3.

dissociative and associative adsorption of B_3D, would give rise to the formation of carbyne and carbene type intermediates. Formation of B_1D is possible either directly from carbyne type intermediate or via B_2D hydrogenation through carbene species. Carbyne and carbene type of intermediates have very short life time, however, the existence of ethylidyne intermediate on Pt(1 1 1) surfaces has been established by Somorjai et al. [17] and other investigators [16–19] in acetylene hydrogenation. Formation of carbyne type species is more favored by accessible multiple sites and at high H_2 partial pressures.

As shown in Fig. 3, selectivity to B_1D increased with increase in H_2 pressure indicating more formation of carbyne species, which is also in accordance with the earlier reports [16,19]. Nearly complete selectivity to B_2D was achieved when Pt/CaCO$_3$-NH$_3$ catalyst system was used, possibly due to ammonia occupying the available vacant sites on the catalyst surface, which are responsible for the formation of carbyne species.

In the present work, studies on the effect of concentration of ammonia on activity and selectivity pattern of Pt/CaCO$_3$ was also carried out and it was found that as the selectivity to B_2D increased from 83% to nearly 100% with increase in concentration of ammonia, from 0 to 0.004% (mol ratio of ammonia to Pt $= 4.8 \times 10^3$) the activity, expressed in terms of TOF decreased from 2.5×10^4 to 1.6×10^4 h^{-1}. This indicates the inhibition of formation of carbyne type species by blocking the available vacant sites by NH$_3$, causing increase in B_2D selectivity.

Some experiments were carried out using 1% Pt/CaCO$_3$ catalyst pre-treated with B_3D solution. For this purpose, known quantities of fresh catalyst and 20% aq. B_3D solution were stirred under nitrogen atmosphere at 323 K for the desired time duration after which the reaction was continued. The results on the catalyst pre-treatment with hydrogen and B_3D on activity (TOF) and B_2D selectivity are shown in Fig. 4. These results show that the catalyst pre-treated with B_3D solution gave higher TOF ($\geq 25\%$) than
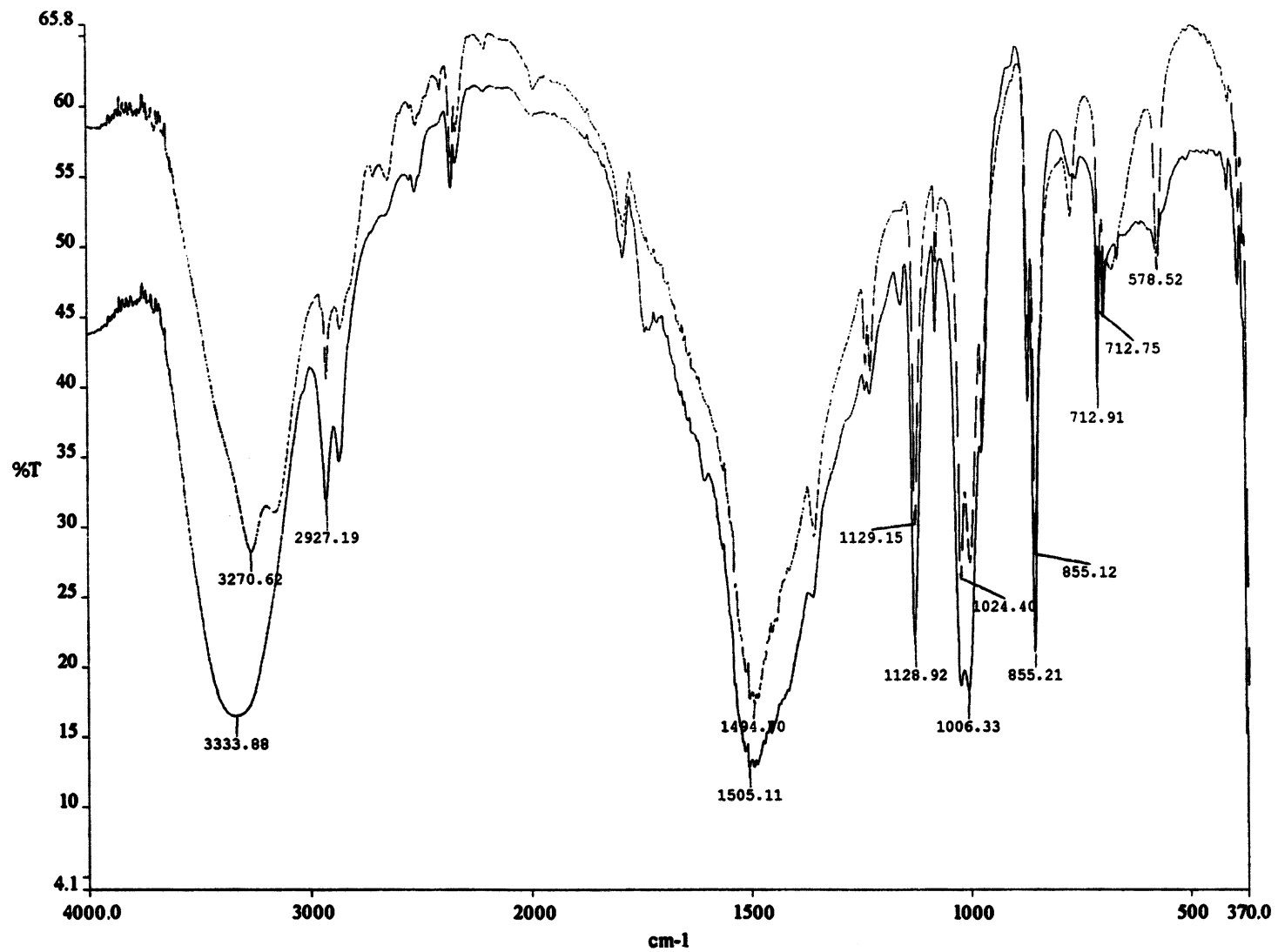
Fig. 2. IR spectra of adsorbed B$_3$D and B$_2$D on the catalyst.
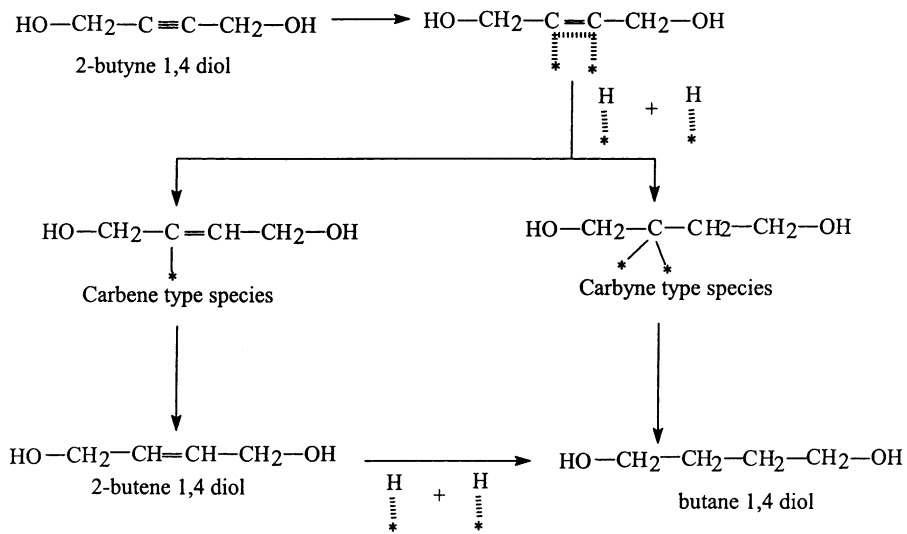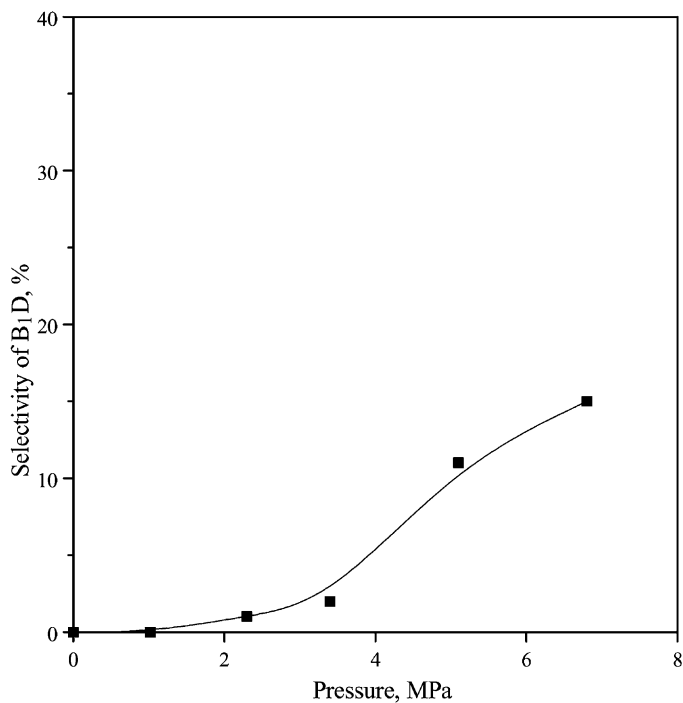
Scheme 1. Hydrogenation of B_3D in absence of ammonia.

Fig. 3. Effect of pressure on B_1D formation. Reaction conditions: temperature, 323 K; initial concentration of B_3D, 2.26 kmol/m^3; active concentration of catalyst, 6.66×10^{-3} mmol; concentration of NH_3, 17.5 mmol; agitation speed, 13.3 Hz; total volume, 1.5×10^{-4} m^3.
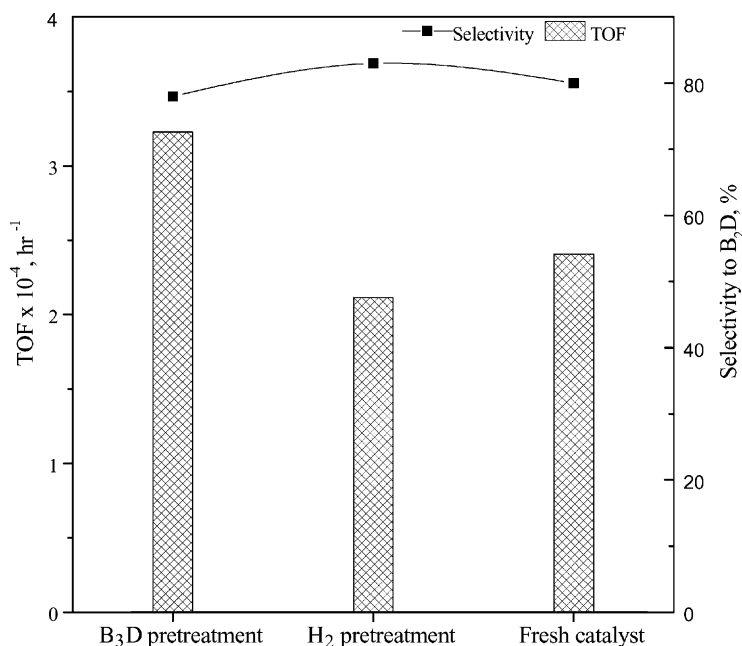
Fig. 4. Effect of catalyst pre-treatment on activity and selectivity. Reaction conditions: temperature, 323 K; pressure, 2.4 MPa; initial concentration of B_3D, 2.26 kmol/m^3; active concentration of catalyst, 6.66×10^{-3} mmol; concentration of NH_3, 17.5 mmol; agitation speed, 13.3 Hz; total volume, 1.5×10^{-4} m^3, pre-treatment time, 60 min.

that of fresh catalyst while, the selectivity to B_2D remained almost constant. This observation is quite different from that observed for Pd catalyst [12], in which B_3D pre-treatment of the catalyst that led to slight ($\approx 10\%$) decrease in the catalyst activity. This indicates different types of adsorption characteristics of B_3D on Pd and Pt catalysts.

Hydrogenation experiments were carried out with varying platinum content ranging from 0.5 to 2%. It was found that the TOF decreased from 1.5×10^4 to 1×10^4 h^{-1} while the selectivity remained almost constant with increase in the metal loading from 0.5 to 2%. The decrease in activity with higher metal loading can be due to lower metal dispersion at higher metal loading.

Since the catalyst used in this reaction was a noble metal catalyst, it was important to study the reuse of this catalyst. In these experiments, the catalyst charged for the first reaction was filtered out and again recharged to the reactor for subsequent runs. The catalyst was found to retain its activity even after the tenth recycle without affecting the selectivity to

B_2D (Fig. 5). The overall TON for the catalysts was found to be 5.24×10^5.

3.2. Kinetic studies

Some preliminary experiments were carried out to select a range of reaction conditions suitable for studying the reaction kinetics, to establish the product distribution and material balance. The range of reaction conditions under which the present study was carried out is given in Table 2. The only product formed was B_2D, in hydrogenation of B_3D, in presence of 1%

Table 2
Range of operating conditions

Condition	Range
Temperature (K)	323–353
Pressure (MPa)	2.4–6.87
Catalyst concentratiom (kg/m^3)	0.8–4
B_3D concentration (kmol/m^3)	1.13–4.45
Ammonia concentration (kmol/m^3)	0–0.215

Fig. 5. Catalyst recycle studies for 1% Pt/CaCO$_3$. Reaction conditions: temperature, 323 K; pressure, 2.4 MPa; initial concentration of B$_3$D, 2.26 kmol/m^3; active concentration of catalyst, 6.66×10^{-3} mmol; concentration of NH$_3$, 17.5 mmol; agitation speed, 13.3 Hz; total volume, 1.5×10^{-4} m^3.

Pt/CaCO$_3$ with ammonia as a catalyst system and the material balance of the reactants (H$_2$ and B$_3$D) consumed and the product (B$_2$D) formed agreed to the extent of 95–98% as per the stoichiometry given below:

$$HO-CH_2-C{\equiv}C-CH_2-OH + H_2O$$
2-butyne-1,4-diol

$$\xrightarrow{\text{Catalyst}} HO-CH_2-CH{=}CH-CH_2-OH$$
2-butene-1,4-diol

A typical plot of H$_2$ absorption versus time is shown in Fig. 6. A second-order polynomial was used to fit the curve, and the slope at zero time was taken as the initial rate of hydrogenation. Reproducibility of the rate measurement was found to be within 3–5% error as indicated by a few repeated experiments. The analysis of the initial rate data is useful in understanding the dependency of the reaction rate on individual reaction parameters and also in the evaluation of mass transfer effects. The effect of individual parameters on the initial rate are discussed below:

3.2.1. Effect of catalyst concentration

The effect of catalyst loading on the initial rate of reaction was studied in the range of 0.86–4 kg/m^3 at 323 K. The initial rate was found increase from 0.235×10^{-4} to 1.25×10^{-4} kmol/m^3/s when the catalyst loading increased from 0.86 to 4 kg/m^3. This linear dependence with respect to catalyst loading indicates the absence of external gas–liquid mass transfer resistances. A few experiments were carried out to study the effect of agitation speed on initial rate of hydrogenation; in which the initial rate were found to be independent of agitation speed. This result also supports the above conclusion of the absence of external gas liquid mass transfer resistance under the conditions of present work.

3.2.2. Effect of pressure

Fig. 7 represents the effect of hydrogen pressure on initial rate of reaction for different temperatures using 1% Pt/CaCO$_3$-NH$_3$ catalyst system. As can be seen from this figure, the rate of reaction increased linearly with increase in H$_2$ partial pressure. This linear
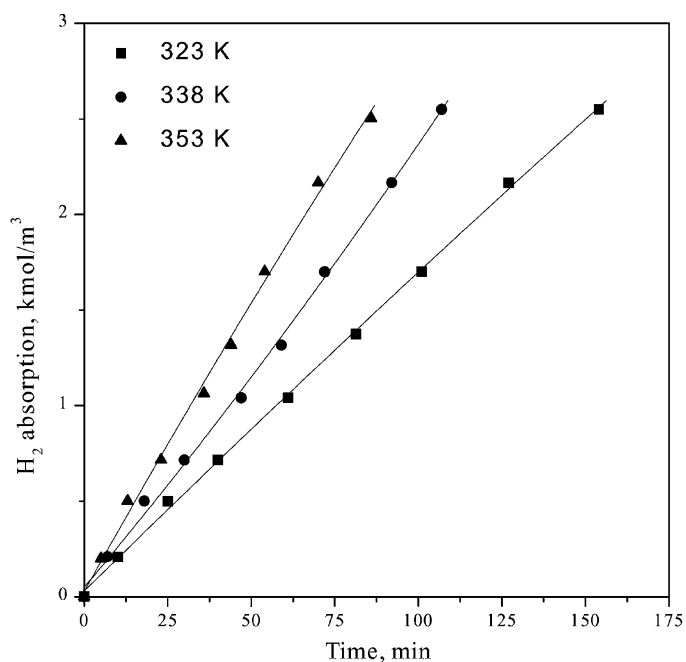
Fig. 6. H_2 absorption vs. time data at different temperatures. Reaction conditions: pressure, 2.4 MPa; initial concentration of B_3D, 2.26 kmol/m^3; active concentration of catalyst, 6.66×10^{-3} mmol; concentration of NH_3, 17.5 mmol; agitation speed, 13.3 Hz; total volume, 1.5×10^{-4} m^3.
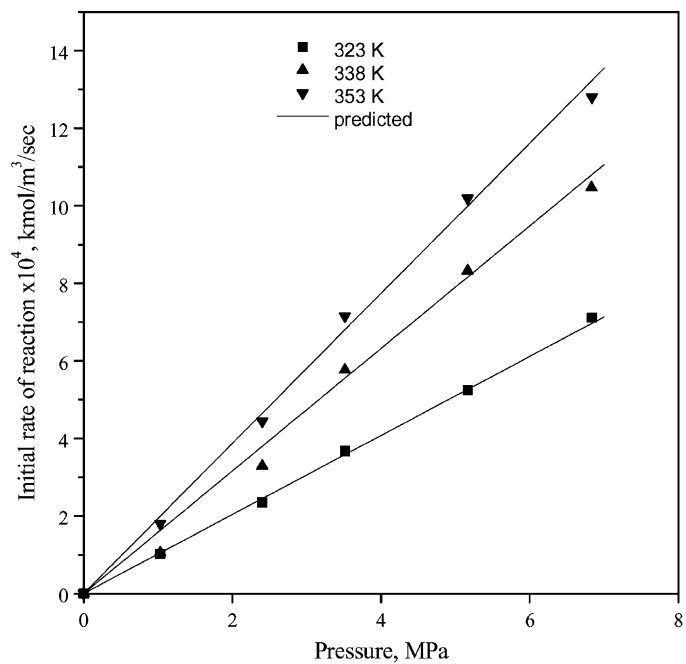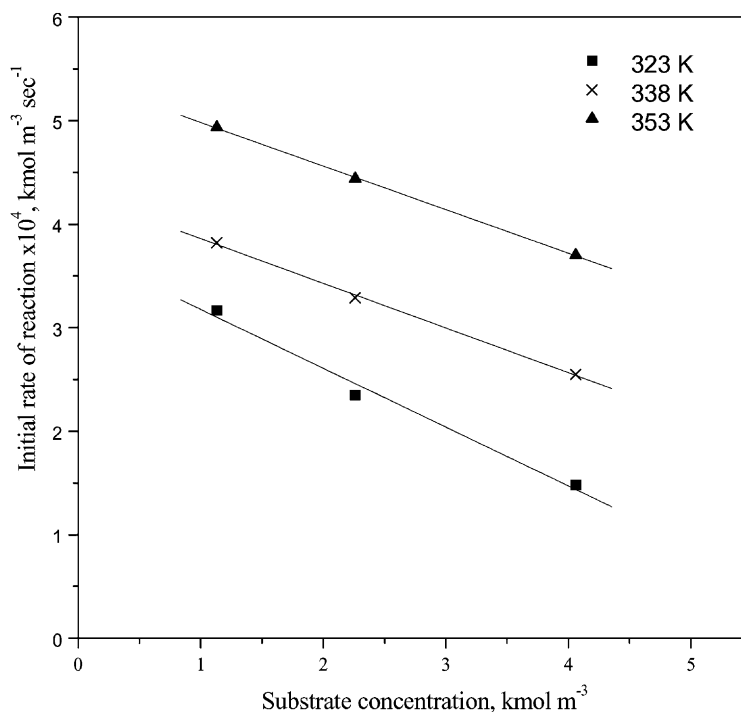

Fig. 7. Effect of H_2 pressure on initial rate of reaction. Reaction conditions: initial concentration of B_3D, 2.26 kmol/m^3; active concentration of catalyst, 6.66×10^{-3} mmol; concentration of NH_3, 17.5 mmol; agitation speed, 13.3 Hz; total volume, 1.5×10^{-4} m^3.

Fig. 8. Effect of concentration of B_3D on initial rate of reaction. Reaction conditions: pressure, 2.4 MPa; active concentration of catalyst, 6.66×10^{-3} mmol; concentration of NH_3, 17.5 mmol; agitation speed, 13.3 Hz; total volume, 1.5×10^{-4} m^3.

dependence of initial rate of reaction on H_2 pressure is different from that observed for Pd catalyst [12].

3.2.3. Effect of concentration of substrate

The effect of substrate concentration on initial rate of reaction is presented in Fig. 8, for three different temperatures (323, 338 and 353 K). The rate was found to decrease with an increase in initial concentration of B_3D, which indicates that the adsorption of B_3D is important and needs to be considered in the proposed rate equation.

3.2.4. Kinetic model

Based on the observed reaction trends with respect to effect of H_2 pressure and substrate concentration on initial rate of reaction, following rate equation was found to represent the observed experimental data suitably:

$$R = \frac{wk_1 A^* B}{(1 + K_B B + K_C C)^2} \tag{1}$$

where w is the concentration of catalyst (kg/m^3), k_1 the reaction rate constant ((m^3)^2/(kmol)kg s), A^* the concentration of H_2 in the reaction mixture (kmol/m^3), B the concentration of B_3D (kmol/m^3), C the concentration of ammonia (kmol/m^3), K_B the adsorption coefficient for B_3D, (m^3/kmol), K_C the adsorption coefficient for ammonia (m^3/kmol), R the rate of reaction (kmol/m^3/s).

The above equation is based on the L–H type mechanism [20,21]. The rate data were fitted to the above rate equation using a nonlinear least square regression analysis. The optimized values of the rate parameters obtained for 95% confidence limit are given in Table 3.

Table 3
Kinetic parameters for rate Eq. (1)

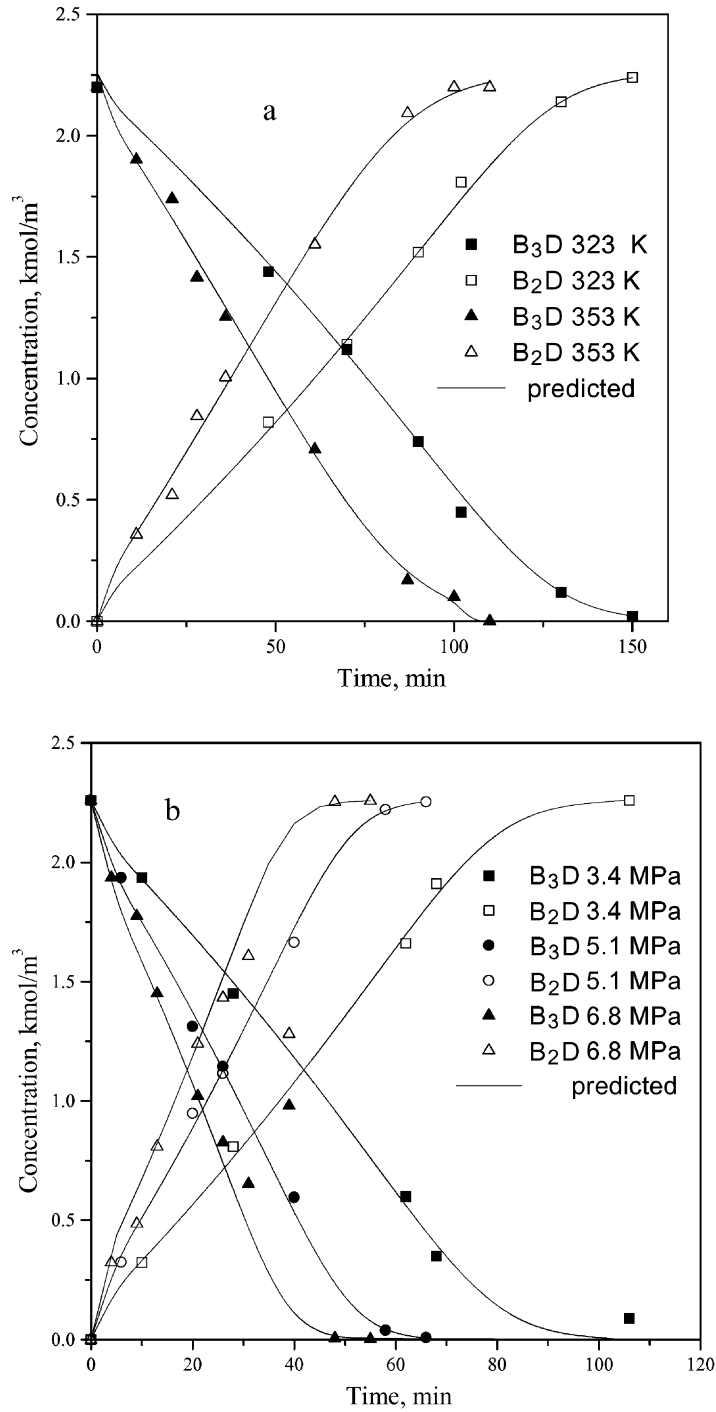| Temperature	k_1 ((m^3)^2/ (kmol)kg s)	K_B (m^3/kmol)	K_C (m^3/kmol)
323	7.228 ± 0.31	10.550 ± 0.52	57.206 ± 3.4
338	23.255 ± 1	13.30 ± 0.73	124.920 ± 6
353	33.367 ± 1.5	14.504 ± 1	143.105 ± 10

Fig. 9. Concentration time profiles (a) at different temperatures and (b) at different pressures. Reaction conditions: initial concentration of B_3D, 2.26 kmol/m³; active concentration of catalyst, 6.66×10^{-3} mmol; concentration of NH_3, 17.5 mmol; agitation speed, 13.3 Hz; total volume, 1.5×10^{-4} m³.
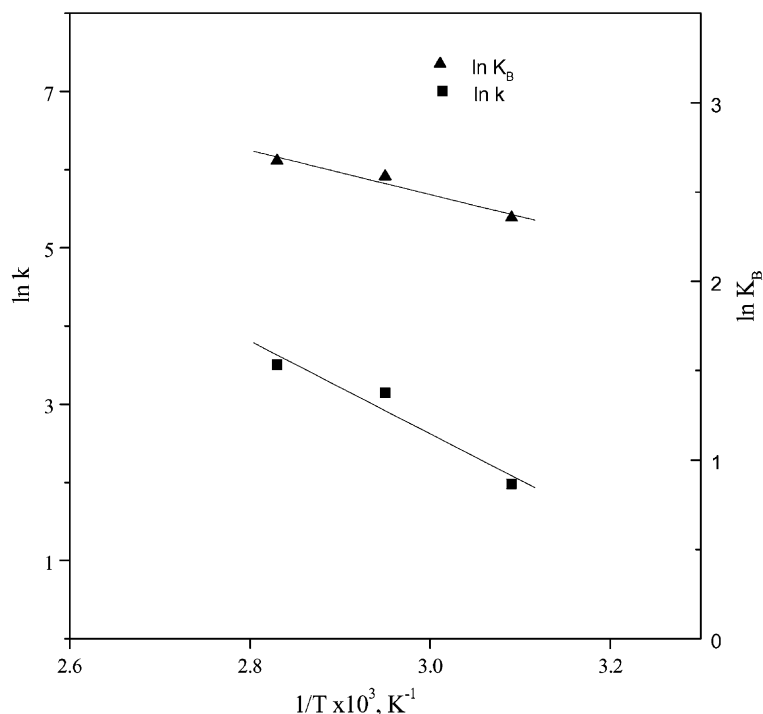
Fig. 10. Arrhenius plot. Reaction conditions: pressure, 2.4 MPa; initial concentration of B_3D, 2.26 kmol/m^3; active concentration of catalyst, 6.66×10^{-3} mmol; concentration of NH_3, 17.5 mmol; agitation speed, 13.3 Hz; total volume, 1.5×10^{-4} m^3.

The experimental and the predicted rates by Eq. (1) were found to agree well as shown in Fig. 7 for the data in the pressure and temperature range of 1–7 MPa and 323–353 K, respectively. The suitability of this rate model (Eq. (1)) was further tested by comparing the predicted and experimental concentration versus time data, under different temperature and pressure conditions. As shown in Fig. 9a and b, all time-data also agreed well with the model predictions indicating the validity of the rate Eq. (1) over a wide range of conditions. The temperature dependence of the rate constant and K_B is shown in Fig. 10, from which the activation energy was calculated as 63.27 kJ/mol. The adsorption coefficient for B_3D showed unusual trend of increase in the values of adsorption coefficients with increase in temperature (Fig. 10). The heat of adsorption calculated from the Arrhenius plot of $\ln K_B$ versus $1/T$ was found to be -21.45 kJ/mol. The negative value of heat of adsorption ($-\Delta H$) indicates the endothermic chemisorption [22].

3.3. Hydrogenation of B_3D in a fixed bed reactor

Hydrogenation of B_3D was also carried out in a fixed bed reactor in which the hydrogen and aqueous solution of B_3D were contacted in a co-current down flow mode using 1% Pt/CaCO$_3$ catalyst in the form of pellets of 2 mm diameter. The reaction was carried out in a temperature range of 323–373 K and the feed flow rate was in the range of 20–60 cm^3/h. The selectivity pattern in continuos flow reactor was completely different from that observed in a batch slurry reactor. As can be seen from Table 4, selectivity to B_1D was always higher at different conversion levels (ranging from 10–100%) in a fixed bed operation than that for batch operation (entry 4, Table 1 and Fig. 2) at 323 K. There are several factors affecting the selectivity pattern in a fixed bed operation, some of which are: (i) higher intra particle diffusion resistance due to the bigger catalyst pellet size, (ii) mass transfer resistance can also be higher due to lower gas and liquid

Table 4
Activity and selectivity pattern of 1% Pt/CaCO$_3$ catalyst in a fixed bed reactor[a]

Serial no.	W/F (h)	Conversion (%)	Selectivity to B$_1$D (%)
1	0.26	10	30
2	0.52	21	38
3	1.04	50	60
4	5.23	100	70

[a] Reaction conditions: weight of catalyst, 0.1 kg; H$_2$ flow, 20 nl/h; H$_2$ pressure, 2.53 MPa.

velocities as compared to the well mixed situation in case of stirred batch operation, (iii) partial wetting of the catalyst particles, due to the evaporation and carry over of solvent, particularly at higher temperatures, (iv) formation of B$_1$D via carbyne type species, as discussed in Section 3.1. One or a combination of these factors can lead to a complete change in B$_1$D selectivity trend in a fixed bed mode of operation [23]. This is being further investigated in detail.

4. Conclusion

Platinum catalyzed hydrogenation of B$_3$D was found to give a mixture of B$_1$D and B$_2$D without formation of other side products, unlike the palladium catalyst. A mechanistic pathway for the formation of B$_1$D and B$_2$D has been proposed, based on the formation of carbyne and carbene type intermediates on the catalyst surface. Initial rate data were collected under various reaction conditions and L–H type rate equation has been proposed to represent the experimental data. Selectivity pattern in case of fixed bed operation was completely reversed from that observed for batch slurry operation.

Acknowledgements

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