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Catalyst deactivation in diborane decomposition

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Both thermal and catalytic decomposition of diborane resulting in borane as the main product were investigated under the pressure and temperature ranges of 2–15 bar and 100–300 °C, respectively over Al_2O_3 and Pt/Al_2O_3 in a fixed bed reactor. Catalytic decomposition rate was essentially higher than the thermal decomposition, however the catalyst deactivation was substantial.

KEY WORDS: diborane; catalytic decomposition; deactivation; boron hydrides.

1. Introduction

Diborane (B_2H_6) is a relatively stable, commercially available substance, being a gas at room temperature with the boiling point of −92.6 °C. Diborane is a toxic compound exhibiting a LD_{50} value in humans 30–90 mg/m^3 for 4 h of exposure [1]. It is highly reactive with water and oxygen giving in the presence of water almost instantaneously boric acid:

$$B_2H_6 + 6H_2O \rightarrow 2B(OH)_3 + 6H_2 \tag{1}$$

Diborane is an important product used as a selective reducing agent in organic chemistry. It can be produced for instance via contacting boron trifluoride with sodium borohydride in diethyl glycol dimethyl ether [2].

$$3NaBH_4 + 4BF_3\text{diglyme}2B_2H_6 + 3NaBF_4 \tag{2}$$

Two other routes, where diborane is formed as a product, are the reactions between sulphuric acid and sodium borohydride or sodium borohydride and iodine:

$$2NaBH_4 + H_2SO_4 \quad B_2H_6 + 2H_2 + Na_2SO_4 \tag{3}$$

$$2NaBH_4 + I_2\text{diglyme}B_2H_6 + 2NaI + H_2 \tag{4}$$

Diborane can decompose to pentaborane (B_5H_{11}), decaborane ($B_{10}H_{14}$) as well as to small amounts of tetraborane (B_4H_{10}). After 3 months storage about 8% of diborane was decomposed under 1 bar pressure [3]. In the thermal decomposition of diborane and tetraborane, pentaborane (B_5H_{11}) can be formed [3]. Tetraborane can be slowly formed from the decomposition of diborane as follows [4]:

$$2B_2H_6 \rightarrow B_4H_{10} + H_2 \tag{5}$$

and it is unstable at room temperature and at higher temperatures, i.e. it can decompose to B_4H_8 and B_3H_7 [5]. Pentaborane is additionally formed in the thermal decomposition of diborane at 250 °C and 0.16 bar with the yield of 33% [3]:

$$5B_2H_6 \rightarrow 2B_5H_9 + 6H_2 \tag{6}$$

In the pyrolysis of diborane decaborane ($B_{10}H_{14}$) could be formed at temperatures up to 240 °C [2]. As apparently clear from the short consideration presented above the boron chemistry is very complex. The industrial use of diborane can be thus limited due to its instability and reactivity.

The catalytic decomposition of diborane over several catalysts was reported in the literature. Ni, Fe_2O_3, Cr_2O_3 [6], Ni(100) [7], Ru(0001) [8], silica gels [9,10], silica alumina surfaces [10], Ni/Al_2O_3, Pt [11,12], SiO_2 [13], Al_2O_3 [13,14] and MgO [13] have been used as catalysts in this reaction. Single crystal metal surfaces are very active in diborane decomposition [7, 8,15]. For instance over Ni(100) the formation of B_4H_{10} was observed [7]. Additionally at 227 °C diborane decomposed completely over Ni(100) surface and boron was bonded at the same time to Ni(100) surface [7]. Over Mo(100) surface a complete decomposition of diborane was already noticed below room temperature [15]. Over Ru(0001) surface the hydrogen evolution was visible between −23 and 177 °C from diborane and adsorbed atomic boron was formed on Ru surface, but no desorbed borane (BH_3) or BH_2 was detected by mass spectrometry [8]. Over oxide surfaces different boron hydrides have been detected in diborane decomposition [9,10,13,14]. Traces of B_4H_{10} and B_5H_9 were observed in diborane decomposition over Al_2O_3 [14]. Borane (BH_3) was, however, formed over silica gel surfaces [9,10], by dissociation over hydroxylic surfaces [10]. Furthermore it was stated in [13] that the nature of oxide surface

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determined the type of surface products obtained from diborane decomposition.

The aim of this work was to investigate the thermal and the catalytic decomposition of diborane, which could bring new knowledge of its use, storage and further applications, requiring utilization of heterogeneous catalysts. Additionally catalyst deactivation could be directly investigated in a fixed bed reactor, which was applied in the present study.

2. Experimental

2.1. Experimental setup

The experiments were carried out in a high pressure tubular, fixed bed reactor with a length of 175 mm and the internal diameter of 6.35 mm. The temperature was regulated in the reactor with a thermo element located in the middle of the reactor. The pressure and temperature profiles were recorded during the experiments. In the beginning of an experiment, when the reactor was heated to the desired temperature, argon (99.999%, AGA) was flowing through the reactor. When the desired temperature was reached, the argon flow was decreased and a desired flow of diborane (4130 ppm B_2H_6 in Ar, Praxair, Belgium) was started. The reaction pressure was increased to the desired level. When the steady state conditions were reached the inlet streams were analyzed by GC (HP 5890 Series II) equipped with DB-wax column (length 30 m, inner diameter for a column 0.32 mm, film thickness 0.5 μm) and J&W Scientific DB-1 (length 60 m, inner diameter 0.53 mm, film thickness 5 μm). The experiments at different temperatures and pressures were carried out over the same catalyst by changing gradually the temperature by 50 °C starting the thermal decomposition from room temperature and the catalytic experiments from 100 °C under desired pressure level. When 300 °C was reached another pressure level was adjusted and the temperature was gradually decreased by 50 °C. At each temperature under 1.8 bar total pressure three different time-on-stream values (4, 8 and 12 min) were recorded after which the temperature was raised by 50 °C. After reaching 300 °C, at which only 4 min time-on-stream was recorded, the pressure was increased to 6.5 bar and the temperature was decreased by 50 °C. In the quantification of the products the response factor one was used for products due to the lack of commercial product gases. The gas chromatograph was equipped with an automated sampling valve (VICI E60-230), which was electrically regulated enabling the sampling with a certain time interval. Additionally the outlet flow was analyzed by GC-MS. The peak identification in gas chromatogram was based on the GC-MS analysis by comparing the mass spectrum from the diborane decomposition with NIST reference mass spectra for diborane, tetraborane, pentaborane and decaborane [16]. Due to the extreme toxicity of diborane the mass flow of diborane was not calibrated. Instead a calibration factor for it was calculated against argon flow with the aid of the instruction manual for the regulator [17]. The calibration factors for diborane and for argon were 0.546 and 1.398, respectively. The gas flows were calculated by taking into account the weight percentage of diborane (4130 ppm) and argon (99,587 ppm) in the gas mixture and using following equation:

$$\dot{V}_{B_2H_6} = \dot{V}_{Ar} \frac{100}{\frac{\text{vol.\%1}}{R.f.1} + \frac{\text{vol.\%2}}{R.f.2}} \frac{1}{R.f.2} \qquad (7)$$

where vol.%1 and vol.%2 are weight percentages for diborane and for argon in the gas mixture, respectively. Furthermore the response factors for diborane and for argon are $R.f.1 = 0.546$ and $R.f.2 = 1.398$, respectively. The flow rate for diborane was 110 cm^3/min. This low flow rate was used in order to get a complete absorption of the toxic diborane into 25% methanol – 75% water mixture after the reactor.

The decomposition of diborane was investigated both in an empty reactor and in the presence of catalysts. In the former experiments the pressure was 1.4 bar for a temperature range of 22–300 °C. The catalytic decomposition of diborane was investigated over two different catalysts within the temperature and pressure range of 100–250 °C and 1.5–10 bar, respectively. Prior to the experiments both catalysts, i.e. Al_2O_3 (La Roche, 289 $m^2/g_{cat.}$) and 5 wt% Pt/Al_2O_3 (F 214, Degussa AG, Hanau) were reduced with flowing hydrogen at 300 °C for 60 min and cooled down to room temperature under hydrogen flow. Plugging of the reactor by the formed reaction products was noticed at some temperature and pressure conditions. Typically 0.2 g of catalyst with particle sizes of 90–125 μm was used in experiments. The catalyst bed was placed between quartz sand beads, which were additionally supported by quartz wool.

3. Results and discussion

3.1. Thermal decomposition of diborane

The thermal decomposition of diborane resulted in four different products visible in the gas chromatogram with retention times of 3.4, 3.5, 4.1 and 5.3 min. These peaks corresponded to borane, diborane, triborane and tetraborane, respectively [16]. The product distribution in samples taken after 4 min time-on-stream was based on the area percentage of the peaks in the chromatogram (figure 1). The product identification was carried out by mass spectrometry. The molecular masses of different boranes are the following ones: BH_3 13.8 g/mol, B_2H_6 27.7 g/mol, B_3H_7 39.49 g/mol, B_3H_9 41.5 g/mol, B_5H_9 63.1 g/mol and B_6H_{10} 74.9 g/mol. By analyzing the m/z-ratio between the fragments 11/24 and 48/

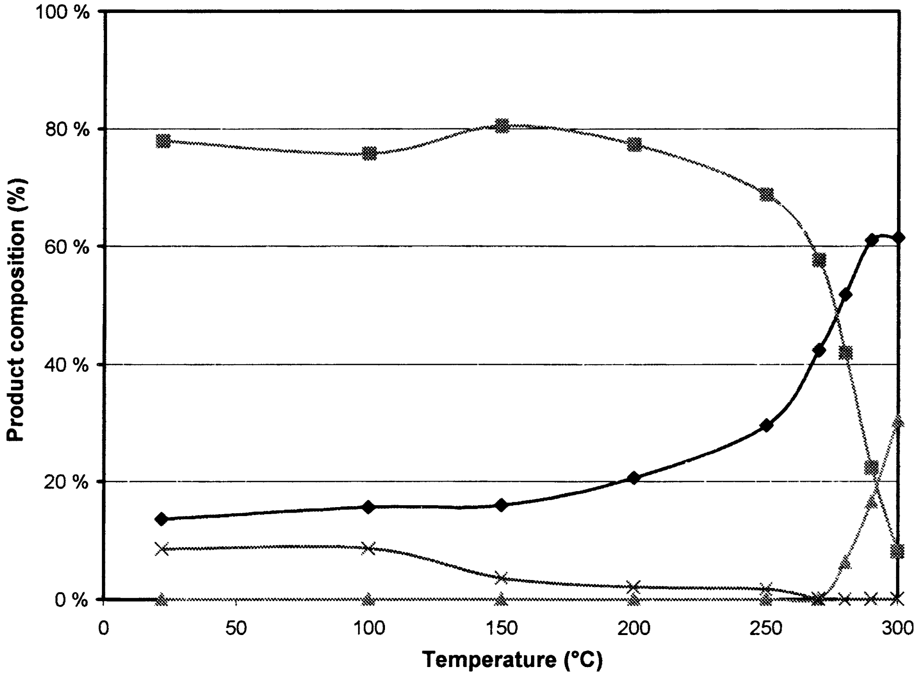


Figure 1. Thermal decomposition of diborane under 1.4 bar in an empty reactor after 4 min time-on-stream.: (◆) borane, (■) diborane, (▲) triborane and (*x*) tetraborane.

59 in the product mixture it could be observed that these ratios varied with increasing temperature (figure 2). The 11/24 ratio increased whereas the 48/59 ratio decreased with increasing temperature. These ratios were compared to the corresponding *m*/*z*-ratios of diborane and pentaborane, respectively (figure 3, table 1). The 11/24 *m*/*z*-ratio for diborane is 0.316 and it was increasing from diborane to pentaborane [16], whereas opposite trend for 48/59 *m*/*z*-ratio was observed for tetraborane and pentaborane (table 1). When the mass spectrum of pentaborane was subtracted from the mass spectrum of the thermal decomposition of diborane the ratio 11/24 *m*/*z*-ratio was increasing at higher temperatures. Moreover the 11/24 *m*/*z*-ratio of the product mixture was at 200 °C 0.28. Based on these facts the peak 1 in the gas chromatogram of the product mixture could thus be interpreted to be borane and analogously peak 4 to be tetraborane. The peak 3 between diborane and

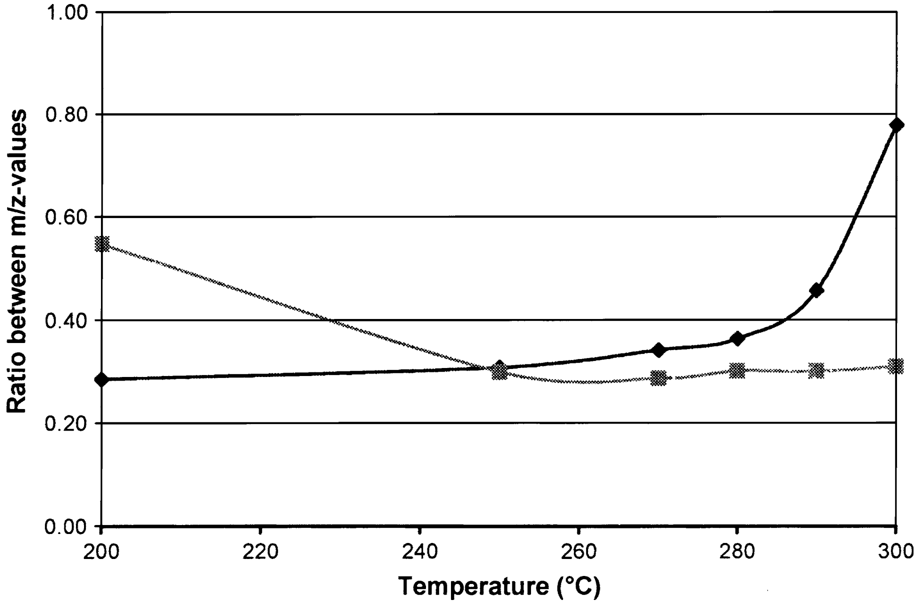


Figure 2. (a) Area units of different compounds and (b) the ratio between *m*/*z*-values in the identification of boron hydrides in the thermal decomposition of diborane under 1.4 bar. Symbols: The ratio between *m*/*z*-values of 11/24 (◆) and 48/59 (■).

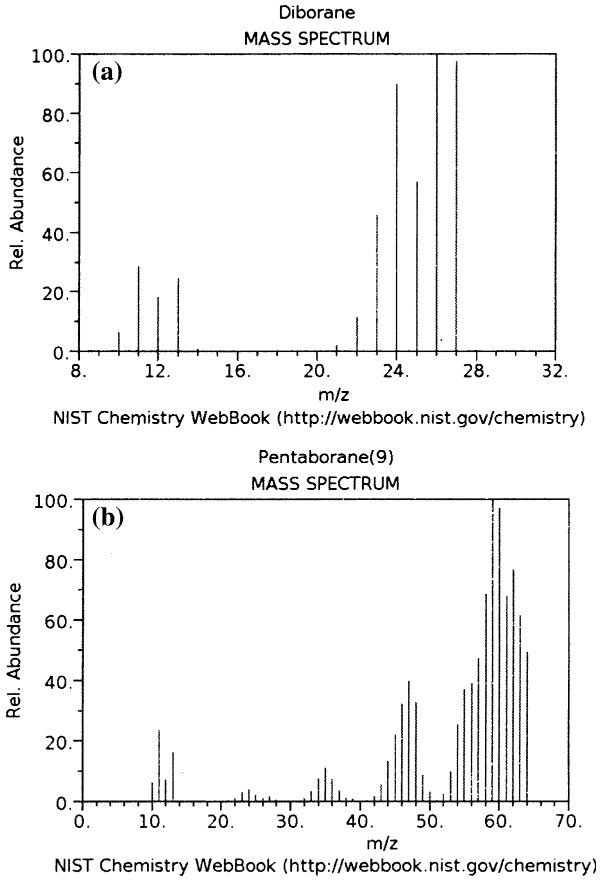


Figure 3. NIST reference mass spectrum for (a) diborane and (b) pentaborane.

Table 1

Reaction mechanisms in thermal decomposition of diborane (entries 1–14) and pyrolysis of heavier boron hydrides (entries 15–24)

Entry	Reaction
1	$2\ B_2H_6 \rightleftharpoons BH_3 + B_3H_9$
2	$BH_3 + B_2H_6 \rightleftharpoons B_3H_9$
3	$B_3H_9 \rightleftharpoons B_3H_7 + H_2$
4	$2\ B_3H_9 \rightarrow 3\ B_2H_6$
5	$BH_3 + B_3H_7 \rightleftharpoons B_4H_{10}$
6	$B_2H_6 + B_3H_7 \rightarrow BH_3 + B_4H_{10}$
7	$BH_3 + B_4H_{10} \rightleftharpoons B_5H_{11} + H_2$
8	$B_3H_9 + B_3H_7 \rightarrow B_2H_6 + B_4H_{10}$
9	$2\ B_3H_7 \rightarrow B_2H_6 + B_4H_8$
10	$B_3H_9 + B_4H_{10} \rightarrow B_2H_6 + B_5H_{11} + H_2$
11	$B_3H_7 + B_4H_{10} \rightarrow B_2H_6 + B_5H_{11}$
12	$H_2 + B_4H_8 \rightarrow B_4H_{10}$
13	$BH_3 + B_4H_8 \rightleftharpoons B_5H_{11}$
14	$B_3H_9 + B_4H_8 \rightarrow B_2H_6 + B_5\ H_{11}$
15	$2\ B_3H_7 \rightarrow B_6H_{12} + H_2$
16	$B_3H_7 + B_4H_8 \rightarrow B_2H_6 + B_5H_9$
17	$2\ B_4H_8 \rightarrow B_3H_7 + B_5H_9$
18	$B_3H_7 + B_5H_9 \rightarrow B_2H_6 + B_6H_{10}$
19	$2\ B_4H_8 \rightarrow B_2H_6 + B_6H_{10}$
20	$B_4H_8 + B_5H_9 \rightarrow B_3H_7 + B_6H_{10}$
21	$B_6H_{12} \rightarrow BH_3 + B_5H_9$
22	$B_3H_7 + B_6H_{12} \rightarrow B_4H_8 + B_5H_{11}$
23	$B_4H_8 + B_6H_{12} \rightarrow B_5H_9 + B_5H_{11}$
24	$B_4H_8 + B_6H_{10} \rightarrow 2\ B_5H_9$

tetraborane could thus be triborane, either B_3H_7 or B_3H_9. Additionally traces of pentaborane and hexaborane could be observed by mass spectrometry (figures 4 and 5). Furthermore, even solid products were formed in the reactor. One of these could have been decaborane, which was also suggested in thermal decomposition by Bragg *et al.* [18] and Fehlner *et al.* [19].

The thermal decomposition of diborane was relatively slow at temperatures below 200 °C, whereas at higher temperatures the decomposition proceeded with a higher rate. In the work of Klein *et al.* [20] the thermal decomposition of diborane was observed to occur above 80 °C. The formation of borane increased with increasing temperature. Below 250 °C tetraborane was formed, whereas above this temperature it was not observed in the product mixture. This result is in accordance with [21], where formation of tetraborane below 250 °C in the pyrolysis of diborane was reported. Triborane was the second prominent product above 280 °C and its formation was favored at higher temperatures. From the mechanistic point of view it was stated in the literature [22] that the rate determining step in the diborane decomposition would be the formation of triborane. Very complex reaction mechanism for the thermal decomposition of diborane has been proposed by Long *et al.* [23] (table 2, entries 1–14). These proposed products correspond well with the product distribution obtained in the current study. If the mechanism is extended to contain also the pyrolysis of heavier boron hydrides, the formation of hexaborane can be explained (table 2, entries 15–24).

According to literature the main product from the pyrolysis of diborane at 180 °C is pentaborane B_5H_{11}, whereas at higher temperatures, i.e. at 250–300 °C, the main product is pentaborane B_5H_9. Additionally it has been confirmed that when pentaborane B_5H_{11} is pyrolyzed at 100 °C, in the presence of diborane and tetraborane, the major part of the formed pentaborane B_5H_9 originates from pentaborane B_5H_{11} [23]. The first step in the thermal decomposition of diborane could be [24]:

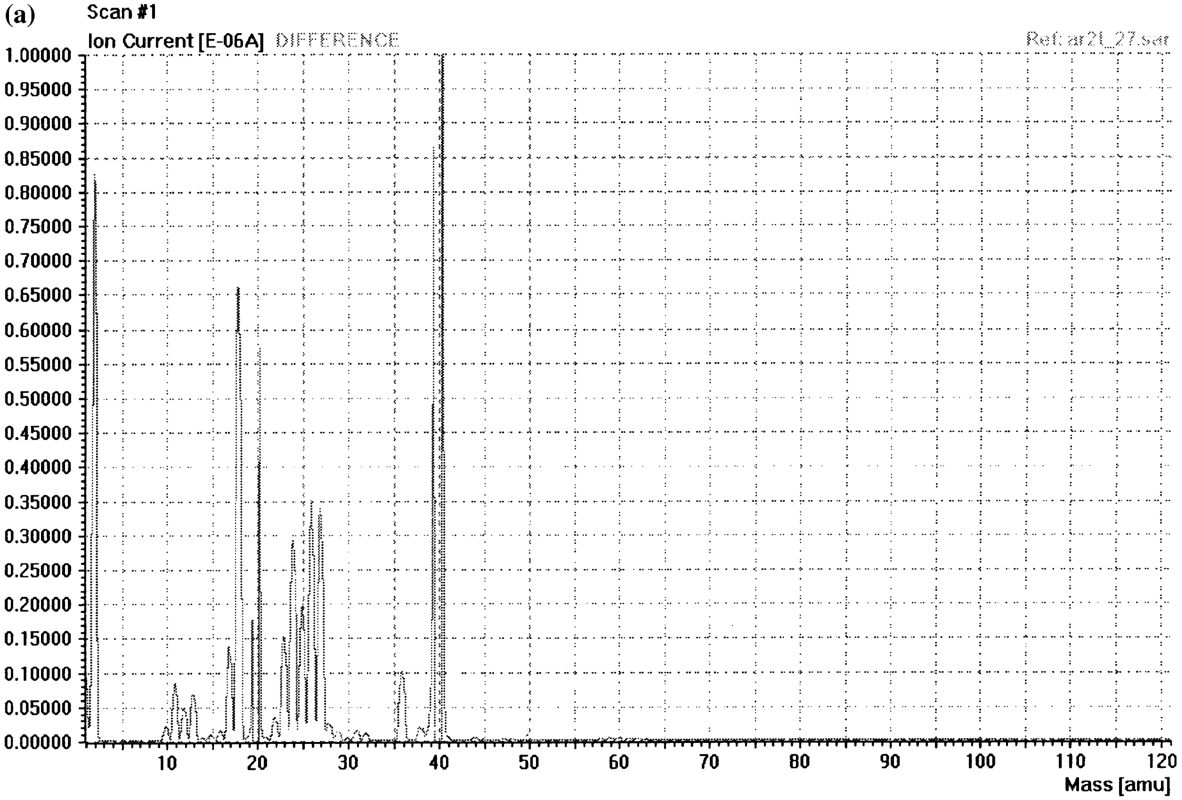
$$B_2H_6 \rightleftharpoons 2\ BH_3 \tag{8}$$

Additionally the possibility of the formation of BH_5 was discussed [25]. This could occur in the presence of hydrogen, when hydrogen is released from reaction (3) (table 2). Stanton *et al.* [26] have additionally shown that high partial pressure of hydrogen decreased the decomposition rate of diborane.

3.2. *Catalytic decomposition of diborane*

3.2.1. *Decomposition of diborane over Al_2O_3*

The same Al_2O_3 catalyst was investigated in diborane decomposition in consecutive experiments shown in table 3, where also diborane conversions and selectivities to borane in gas-phase are given. The same method in the



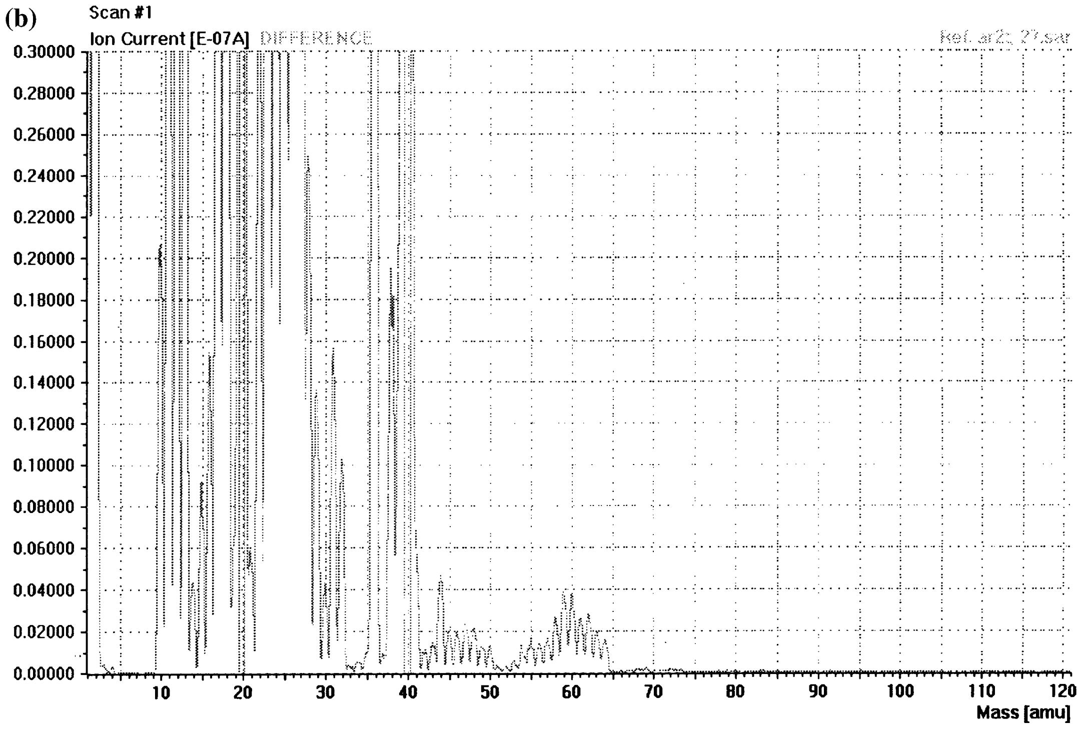


Figure 4. (a) The mass spectrum from the thermal decomposition of diborane at 200 °C and (b) the same mass spectrum in a larger scale.

peak identification as described in section 3.1 was used in the interpretation of the catalytic decomposition of diborane. A gas chromatogram of the product distribution in diborane decomposition over Al_2O_3 at 200 °C under 5 bar is shown in figure 6 and the time-on-stream behavior of diborane conversion based on gas-phase products over Al_2O_3 at different temperatures is presented in figure 7. The conversion of diborane increased with increasing temperature under 1.8 bar total pressure. Furthermore catalyst deactivation was

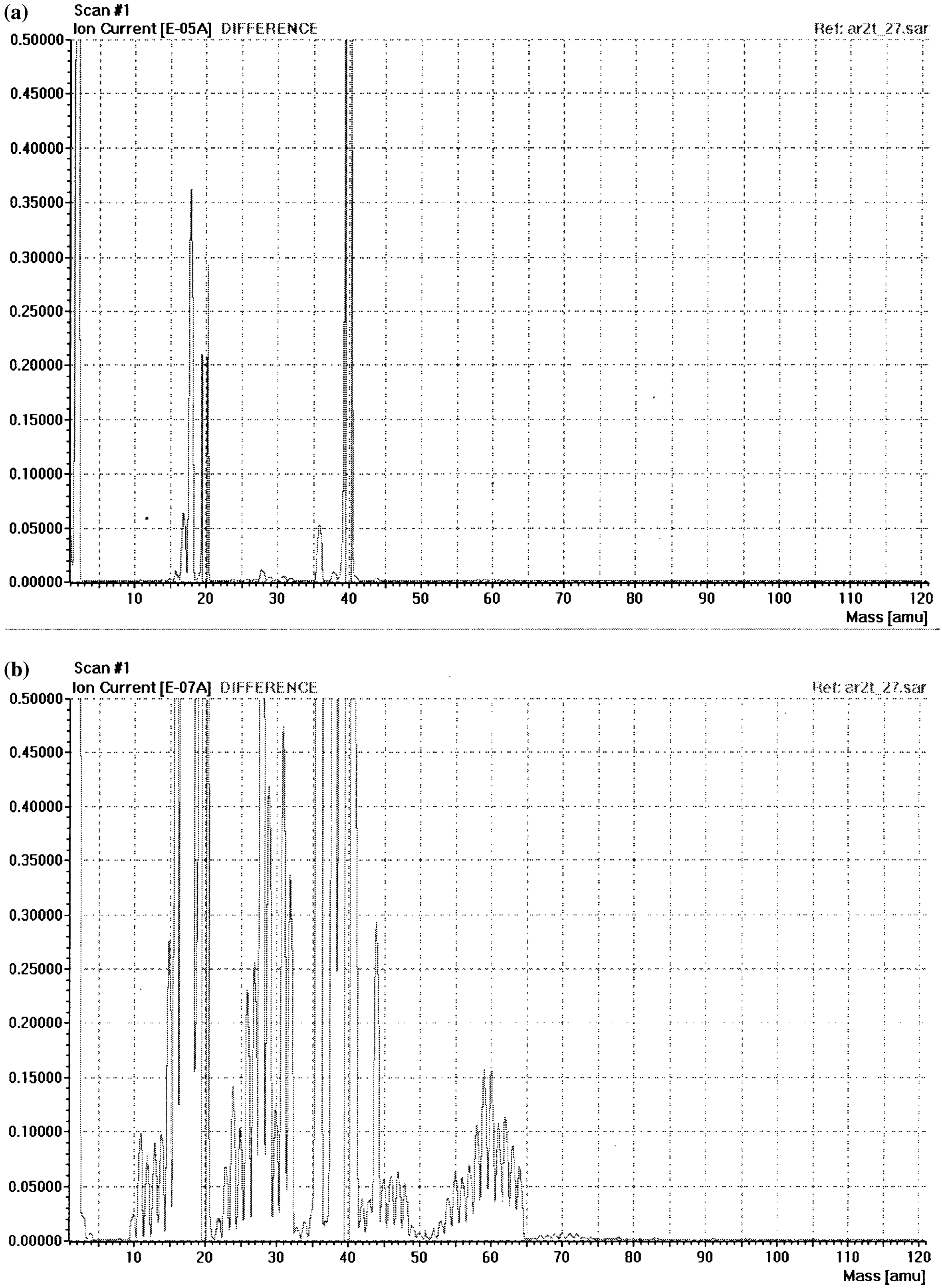


Figure 5. (a) The mass spectrum from the thermal decomposition of diborane 300 °C and (b) the same mass spectrum in a larger scale.

very prominent at 100 °C. It can, however, be noticed that the pressure gradually increased upstream the catalyst bed indicating some catalyst plugging via formation of solid products (table 3). When the reaction temperature was decreased and the pressure level was 6.5 bar, nearly complete conversion of diborane was observed under all other conditions, but not at 100 °C (table 3).

Table 2
The m/z-ratio of 11/24 and 48/59 obtained in the thermal decomposition of diborane compared with the NIST library

m/z ratio	B_2H_6 decomposition at 200 °C	B_2H_6 decomposition at 300 °C	B_2H_6 [16]	B_4H_{10} [16]	B_5H_9 [16]
11/24	0.28	0.78	0.316	2.9	6.3
48/59	0.56	0.3	–	large	0.326

Three different products were obtained in diborane decomposition (figure 8). Two of the products were the same as observed in the thermal decomposition of diborane, namely borane and triborane B_3H_9 and the peak between diborane and triborane B_3H_9 was tentatively assigned to be triborane B_3H_7. The formation of borane increased with increasing temperature, whereas only traces of triborane could be observed above 150 °C. The selectivities to borane as a function of time-on-stream at a given temperature and pressure are given in parenthesis in table 3 at the given conversion level. The selectivities to borane were very low at 100 °C under 1.8 bar (experiment 1 in table 3), whereas at higher temperatures the corresponding values were close to 100%. Additionally the selectivity to borane decreased with time on stream in experiment 1 in table 3, i.e. with decreasing conversion of diborane at 100 °C and 12.8 bar. It could, however, be seen that some selectivity decrease was observed at 250 °C and under 2 bar after 12 min time on stream at 100% (experiment 4 in table 3). Under 6.5 bar total pressure the conversions of diborane were 100% or close to that and the selectivities to borane increased with decreasing temperature (experiments 6–8, table 3). This result cannot be interpreted in a straightforward way, since under lower total pressure (1.8 bar) the selectivity underwent through a maximum with increasing temperature. It should, however, been kept in mind that the same Al_2O_3 catalyst was used in all the experiments and the formation of solid products had occurred already at higher temperatures under 2 bar. Thus these results show a cumulative behavior of the catalyst under 6.5 bar and the high selectivity obtained in experiment 9 (table 3) could be due to the catalyst deactivation occurred already in the first experiment.

The present results indicated that the selectivity to borane increased with increasing temperature, whereas oligomerization of boron decreased with increasing temperature. There are two reports in the literature, where catalytic reactions of diborane were investigated over Al_2O_3 [13,14]. In [13] the diborane reactions were investigated over alumina, which was pretreated at several temperatures in vacuum and the analysis was carried out by FTIR. This method gave information

Table 3
Conversion of diborane and selectivity to borane (in parenthesis) as a function of time on streams at different temperatures and pressures over Al_2O_3

Entry	Temperature (°C)	Pressure upstream the catalyst bed (bar)	Conversion (%) (selectivity, (%)) after 4 min	Conversion (%) (selectivity, (%)) after 8 min	Conversion (%) (selectivity, (%)) after 12 min
1	100	1.8	94 (11)	–	29 (6)
2	150	1.8	84 (96)	84 (98)	85 (98)
3	200	1.9	99 (98)	98 (98)	98 (97)
4	250	2.0	100 (95)	100 (95)	100 (91)
5	300	2.3	100 (97)	–	–
6	250	6.5	100 (85)	–	100 (86)
7	200	6.4	100 (82)	100 (89)	100 (87)
8	150	6.7	100 (95)	100 (98)	98 (96)
9	100	6.0	74 (100)	54 (100)	43 (100)

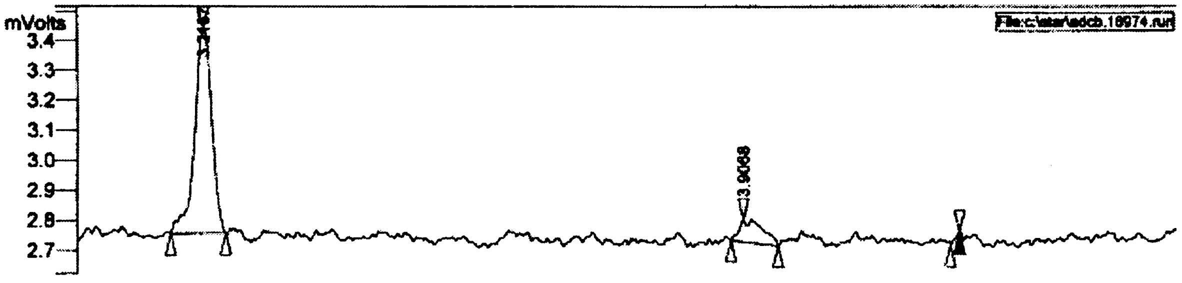


Figure 6. The gas chromatogram from the products formed in the decomposition of diborane over Al_2O_3 at 200 °C under 5 bar. Borane with retention time 3.21 min is the main product, whereas the product with a retention time of 3.91 min could be B_3H_9.

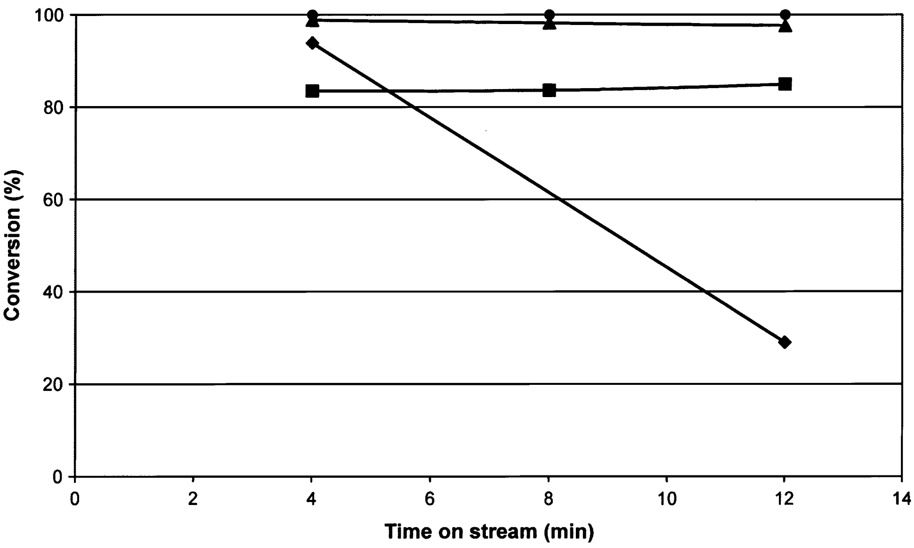


Figure 7. Conversion of diborane over Al_2O_3 as a function of time on stream at (◆) 100 °C, (■) 150 °C, (▲) 200 °C and (●) 250 °C under 1.5 bar.

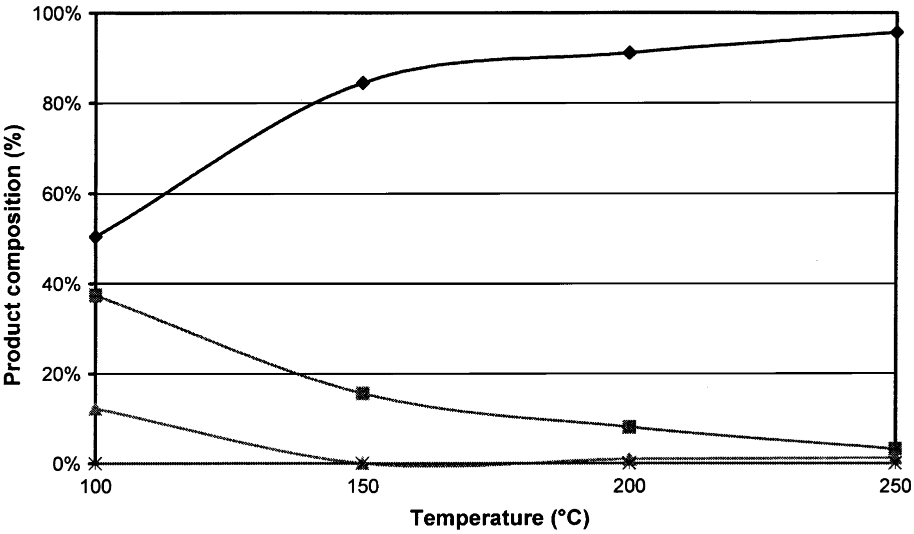


Figure 8. Decomposition of diborane over Al_2O_3 under 10 bar. Products calculated as average values from different time-on-streams at different temperatures in (%) of the total area: (◆) borane, (■) diborane, (▲) triborane B_3H_7 and (x) triborane B_3H_9.

about the chemisorbed surface species of boron containing molecules. The boron containing surface species on alumina confirmed by [13] were bridged structures of B_xH_y, with vibration frequencies close to $Al(BH_4)_3$. Such species are formed in a reaction of diborane with surface –OH groups resulting in hydrogen evolution and depending on reaction conditions also in formation of borane and/or oligomers. In [14] two differently pretreated Al_2O_3, i.e. at 800 °C and at 200 °C, were used as catalysts and the gas phase products from diborane decomposition over alumina were investigated by FTIR at 60 °C. Over the former material the formation of tetra- and pentaborane and hydrogen was confirmed, whereas over the latter catalyst no reaction was occurring [14]. It was suggested in [14] that diborane can adsorb and dissociate over Al_2O_3 surface pretreated at 800 °C. Additionally the oligomerization of diborane at 60 °C was confirmed by formation of new peaks in the spectrogram. According to [14] two molecules of hydrogen were eliminated during the formation of B–B bond and the oligomer exhibited either terminal BH_2 or BH_3 groups. This result is in accordance with the data in the present study.

Reaction mechanism for diborane decomposition over alumina was proposed by [13] according to which diborane can either split to two borane molecules or react with surface hydroxyl groups of alumina. The following surface reactions can occur:

$$-OH + B_2H_6 \rightarrow -O-BH_2 + H_2 + BH_3 \qquad (9)$$

$$-OH + BH_3 \rightarrow -O-BH_2 + H_2 \qquad (10)$$

The former reaction would suggest borane formation, whereas the latter reaction is a consecutive reaction of borane leading to formation of oligomerization products. The current data suggest additionally that the oligomerization of diborane is more favorable at lower temperatures, which is in accordance with [14].

3.2.2. Decomposition of diborane over Pt/Al_2O_3

The conversion of diborane increased with increasing temperature over Pt/Al_2O_3 catalyst (figure 9), analogously to Al_2O_3 catalyst. Furthermore catalyst deactivation was observed at 100 °C under 9.9 bar over Pt/Al_2O_3 catalyst and the pressure increase was noticed (table 4) indicating the formation of solid boron hydrides inside the reactor.

The main product in diborane decomposition over Pt/Al_2O_3 catalyst was borane (table 4) being the only product in the first experiment at 100 °C under 9.9 bar (table 4, experiment 1). Another product was observed in the second experiment at 150 °C under 9.9 bar. In the chromatogram borane had a retention time of 3.24 min and the unidentified product eluated with a retention time of 3.43 min, i.e. before diborane eluation at 3.5 min. Borane was the main product (79%) under 10 bar and 250 °C over Pt/Al_2O_3 at 100% conversion of diborane. Additionally it was observed that in the experiments above 250 °C solid products, which plugged the reactor, were formed. In the later experiments (experiments 5 and 6 in table 4) the complete conversion of diborane were observed and the only gaseous product was borane. This result is analogous to the results obtained over Al_2O_3 catalyst indicating that during catalyst deactivation the selectivity to borane was enhanced.

4. Comparison between the thermal and the catalytic decomposition of diborane

The catalytic decomposition of diborane was faster than the thermal decomposition (figure 10a) independently of the catalyst used. The thermal decomposition of diborane started at 100 °C. However the complete conversion of diborane could not be obtained in the

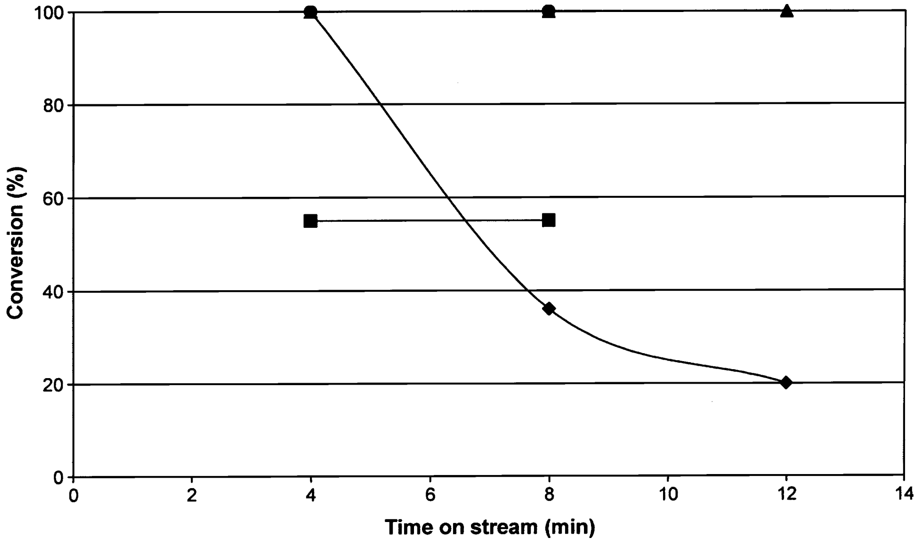


Figure 9. Conversion of diborane over Pt/Al_2O_3 catalyst as a function of time on stream at (◆) 100 °C, (■) 150 °C, (▲) 200 °C and (●) 250 °C under 9.9 bar.

Table 4

Conversion of diborane and selectivity to borane (in parenthesis) as a function of time on streams at different temperatures and pressures over Pt/Al_2O_3

Entry	Temperature (°C)	Pressure upstream the catalyst bed (bar)	Conversion (%) (selectivity, (%)) after 4 min	Conversion (%) (selectivity, (%)) after 8 min	Conversion (%) (selectivity, (%)) after 12 min
1	100	9.9	100 (100)	36 (100)	20 (100)
2	150	9.9	55 (84)	55 (76)	–
3	200	9.9	100 (71)	100 (55)	100 (75)
4	250	10.9	100 (74)	100 (83)	–
5	250	8.1	100 (100)	100 (100)	100 (100)
6	200	11.5	100 (100)	100 (100)	100 (100)

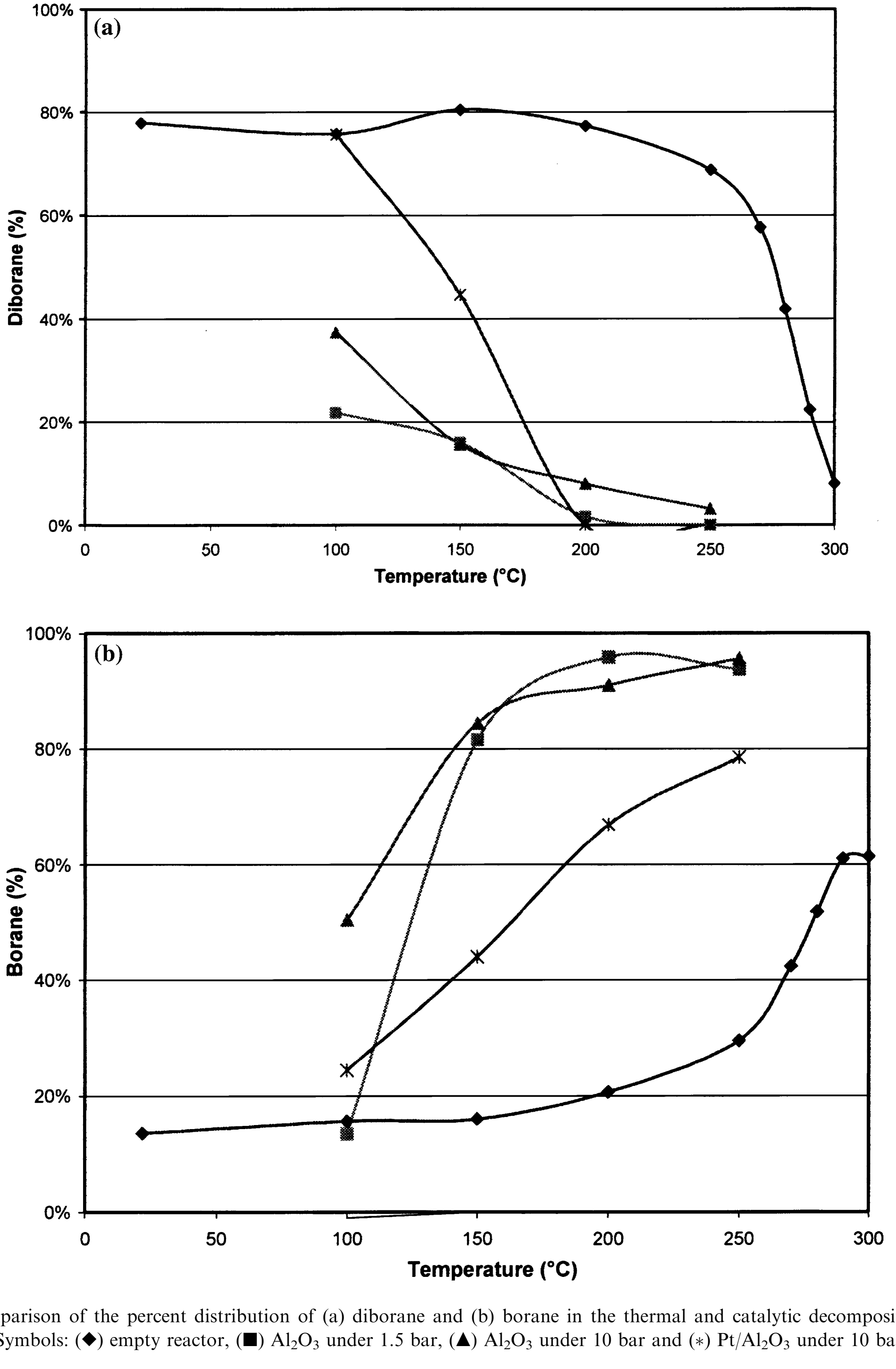


Figure 10. Comparison of the percent distribution of (a) diborane and (b) borane in the thermal and catalytic decomposition of diborane. Symbols: (◆) empty reactor, (■) Al_2O_3 under 1.5 bar, (▲) Al_2O_3 under 10 bar and (∗) Pt/Al_2O_3 under 10 bar.

thermal decomposition even at 300 °C, whereas nearly complete or complete conversion of diborane was achieved over Al_2O_3 under 1.5 bar (figure 10a). The main product in the decomposition of diborane on Al_2O_3 was borane (over 80%) above 200 °C (figure 10b) as well as over Pt/Al_2O_3. The conversion of diborane was higher over Al_2O_3 than over Pt/Al_2O_3 catalyst below 150 °C (table 5), whereas at higher temperatures complete conversion of diborane was achieved over the latter catalyst. A direct comparison of the product distribution at different temperatures over the two catalysts is not feasible, since the conversion levels are different. Over Al_2O_3 catalyst twice as much borane (50.4%) was formed than over Pt/Al_2O_3 (24.4%) at 100 °C under 10 bar, but the conversion level over the former catalyst was 2.6 times higher than that for Pt/Al_2O_3 (table 5).

Table 5
Comparison of the side products in catalytic decomposition of diborane over Al_2O_3 and Pt/Al_2O_3 catalysts at different temperatures under 10 bar. The conversion level is given in parenthesis

Product	Catalyst	(%) at 100 °C (conversion (%))	(%) at 150°C (conversion (%))	(%) at 200 °C (conversion (%))	(%) at 250 °C (conversion (%))
B_3H_7	Al_2O_3	12.2 (62.6)	0 (84.4)	0.9 (92.0)	1.2 (96.8)
unidentified[a]	Pt/Al_2O_3	0 (24.4)	11.4 (55.4)	33.2 (100)	21.4 (100)

[a] Retention time 3.43 min.

Noteworthy is however the fact the products were not the same over these catalysts (table 5) indicating that the catalytic sites act in a different way depending the nature of the catalyst. Over both catalysts used in this work solid products were formed in the decomposition of diborane. These products were most probably the boron hydrides containing more than 10 boron atoms. The solid material exhibited polymer type consistence and caused plugging of the reactor. Analogously to these results Beckman *et al.* [12] have reported the formation of solid boron hydrides in the catalytic decomposition of diborane. The formation of polymer type material could additionally be explained by thermolysis of diborane. In the thermolysis of B_4H_{10} or B_5H_{11} 40% and 50% of non-volatile solid boron hydrides, respectively, were formed [27]. Furthermore rubber like powder was formed in the decomposition of B_5H_{11} above 100 °C [28]. The decomposition of heavier boron hydrides, i.e. decaborane, was reported to occur above 200 °C [29,30].

5. Conclusions

Both thermal and catalytic decomposition of diborane was investigated in a fixed bed reactor in pressure and temperature ranges of 2–15 bar and 100–300 °C. The products were identified by comparing the *m*/*z*-ratios of the mass spectrometric data in thermal decomposition of diborane with the library data. In the thermal decomposition of diborane the main products were triborane, tetraborane, pentaborane and hexaborane. Additionally solid products, heavier boron hydrides were formed. The thermal decomposition of diborane, was, however, quite slow below 200 °C, above which the reaction proceeded much faster. Tetraborane was formed only under 250 °C, whereas triborane formation occurred above 280 °C and was more prominent at higher temperatures.

Reported in this study values of diborane conversion and product selectivities are based on the gas phase analysis. At the same time solid boron hydrides were formed plugging the reactor in the presence of catalysts after prolonged time on streams. The catalytic decomposition of diborane was significantly faster than the thermal decomposition of diborane, for both Al_2O_3 and, Pt/Al_2O_3 catalysts. Significant catalyst deactivation was observed over Al_2O_3 resulting in 100% selectivity to borane.

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