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Catalysis Today 71 (2002) 403–410

CATALYSIS TODAY

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# Effect of boron source on the catalyst reducibility and Fischer–Tropsch synthesis activity of Co/$TiO_2$ catalysts

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## Abstract

A series of Co/B/$TiO_2$ (B = ammonium borate, boric acid, *o*-carborane, 0.01–1.5 wt.% B) catalysts were synthesized. The addition of boron decreased the reducibility of the Co as determined from temperature-programmed reduction studies and $H_2$ reduction/$O_2$back titration studies. This in turn decreased the FT activity but not the turnover frequency of the Co catalyst.

*Keywords:* Fischer–Tropsch; Cobalt; Boron; TOF; Reduction

## 1. Introduction

The interaction between a support and a metal oxide (catalyst) precursor is an important factor in determining the dispersion of a metal catalyst and hence the behaviour of a catalyst. A method used to control the surface properties of a support is by addition of inorganic chemical additives, such as boron, to the support.

The effect of boron addition to an alumina supported cracking catalyst [1], as well as toluene disproportionation and xylene isomerization catalysts [2] has been reported. The alumina surface modification [1,3–5], via formation of Al–O–B–O–Al bonds [2] resulted in modified catalytic activity. Studies on the effect of boron on NiMo/$Al_2O_3$ hydrotreating catalysts suggested that boron *diminished* the interaction of the metal with the alumina support, thus increasing the activity of the catalyst [6]. However, in a characterization study of cobalt oxide supported on boron modified alumina, Houalla and Delmon [7] concluded that boron addition *promoted* the interaction of cobalt with alumina. Stranick et al. [8] in a more detailed study on Co/$Al_2O_3$ catalysts showed that the effect of boron on cobalt dispersion was strongly dependent on the cobalt loading. More recently the effect of low loadings of $B_2O_3$ on $Al_2O_3$ revealed that $B_2O_3$ modified the acidic nature of the support [9].

In an earlier study on the effect of boron (as boric acid) on titania supported cobalt catalysts, we found that the addition of boron resulted in an increase in the interaction of cobalt oxides with titania [10]. We now wish to report on the effect of the boron source on titania supported cobalt Fischer–Tropsch catalysts. Boric acid, ammonium borate and *o*-carborane were used to modify the titania support (Fig. 1). Boric acid is a weak inorganic acid ($pK_a = 9.14$) with a trigonal planar structure, while ammonium borate is a neutral salt with a tetrahedral structure. Both these boron sources have been extensively used in the preparation of catalysts. *o*-Carborane, however, is not normally used in catalytic studies [11]. Carboranes (also known as

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PII: S0920-5861(01)00467-9

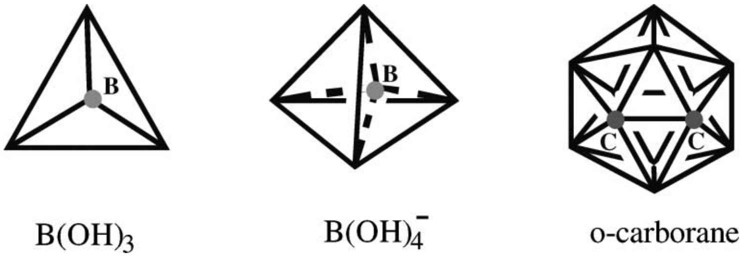

Fig. 1. Structures of boron complexes added to $Co/TiO_2$.

heteroboranes or carbaboranes) are clusters that contain both boron and carbon atoms. The hydrogen atoms attached to the carbon atoms are very mildly acidic.

We have thus used three extreme types of boron sources to evaluate the effect of boron on $Co/TiO_2$ catalysts.

## 2. Experimental

Three series of boron modified titania supports (0.02–1.5 wt.% boron) were prepared by pore volume impregnation of titania with aqueous solutions of boric acid [10], ammonium borate and methanol solutions of *o*-carborane (obtained as a gift from Professor E.W. Neuse, Chemistry Department, University of the Witwatersrand). Samples were dried at 120 °C for 16 h and then calcined at 400 °C in air for 6 h. Cobalt (10 wt.%) was deposited on the boron modified titania by pore volume impregnation with cobalt nitrate solutions. Samples were re-dried at 120 °C for 16 h. All catalysts are represented as $Co(10)/B(x)/TiO_2$ in which $x$ is the percentage loading of boron. Atomic absorption spectroscopy (AAS) was employed to determine the cobalt and boron loading after calcination at 400 °C. The results were very close to the expected values, indicating that boron is not lost in the calcination reaction.

Information regarding the catalyst morphology, reduction and dispersion was obtained using various techniques, including BET surface area, XRD, TPR, $O_2$ titration and $H_2$ chemisorption. The methods were described in detail in [10].

Prior to Fischer–Tropsch reaction, catalysts were calcined at 300 °C for 24 h and activated under flowing hydrogen at 300 °C for 24 h. Fischer–Tropsch synthesis was then performed at 250 °C and 8 bar pressure, using a $CO:H_2$ ratio of 1:2 and a GHSV of $350\,h^{-1}$ [10]. All catalysts were monitored over an induction period of 3 days, followed by a 4 day mass balance. Gaseous and liquid product fractions were analysed by on-line gas chromatograph, while separation of the wax products was achieved using an off-line capillary-column gas chromatograph.

## 3. Results and discussion

### 3.1. Characterization studies

A loss in BET surface area is observed for the ammonium borate modified catalysts as the boron loading is increased viz. from $44.8\,m^2/g$ at 0.02 wt.% boron loading to $34.7\,m^2/g$ at 1.5 wt.% boron loading. A bigger loss in BET surface area occurs in the *o*-carborane modified system when the boron loading is increased viz. from $45.1\,m^2/g$ at 0.02 wt.% boron loading to $27.5\,m^2/g$ for 1.5 wt.% boron loading. *o*-Carborane with a polyhedral structure (and bigger molecular diameter) blocks the pores of the support more severely than boric acid [10] and ammonium borate.

### 3.2. X-ray diffraction (XRD) studies

Powder XRD studies on $B(1.5)/TiO_2$ supports modified by boric acid, ammonium borate and carborane revealed that no crystalline boron compound could be detected in these boron modified titania samples. All of the XRD patterns of $Co(10)/B(x)/TiO_2$ catalysts exhibited diffraction lines characteristic of $Co_3O_4$ in addition to those of the titania. The line broadening

Table 1
$Co_3O_4$ crystallite size in Co(10)/B($x$)/$TiO_2$ catalysts[a] modified by different boron sources

| Boron loading (wt.%) | $Co_3O_4$ crystallite size (nm) | | |
|---|---|---|---|
| | Boric acid | Ammonium borate | Carborane |
| 0.00 | 25.9 | 25.9 | 25.9 |
| 0.02 | 24.0 | 25.6 | 28.0 |
| 0.05 | 21.4 | 25.3 | 24.2 |
| 0.10 | 19.0 | 21.5 | 25.0 |
| 0.50 | 19.4 | 20.9 | 24.3 |
| 1.00 | 16.5 | 17.8 | 23.0 |
| 1.50 | 14.4 | 15.1 | 21.4 |

[a] Catalysts were calcined at 300 °C for 6 h.

of the (3 1 1) diffraction line of $Co_3O_4$ was used to estimate the $Co_3O_4$ crystallite size using the Scherrer equation [12]. The results are shown in Table 1. It is clear that for all three series of Co(10)/B($x$)/$TiO_2$ catalysts $Co_3O_4$ crystallite size decreases with increasing boron loading. The order of effect of boron source on the $Co_3O_4$ crystallite size is boric acid $\sim$ ammonium borate $>$ carborane.

### 3.3. Temperature-programmed reduction (TPR)

TPR data were recorded for Co(10)/B($x$)/$TiO_2$ catalysts calcined at different temperatures (200–400 °C). Three reduction peaks were generally observed and are attributed to the reduction of the $NO_x$ group (first peak) and the two stage reduction of the $Co_3O_4$ supported on the titania (second and third peaks), respectively. The shapes of the TPR profiles of all the catalysts are similar; only the position of the peaks associated with the $Co_3O_4$ reduction is different. The data for the second and third reduction peaks are listed in Tables 2 and 3. The following trends are apparent from the TPR study: (i) for all three series of catalysts the two reduction peaks shift to higher temperatures as the boron loading is increased; (ii) for all three series of catalysts, both reduction peaks shift to higher temperatures with an increase in catalyst calcination temperature; (iii) boric acid has the largest effect on the reduction peak position of Co/$TiO_2$ and carborane the least. For example, for the boric acid modified catalysts, calcined at 200 °C, the second peak is shifted from 280 to 450 °C when the boron loading was

Table 2
The second reduction peak position of the Co/B/$TiO_2$ catalysts

| Boron loading (wt.%) | Calcination temperature, $T_c$ (°C) | Peak position (°C) | | |
|---|---|---|---|---|
| | | Carborane | Ammonium borate | Boric acid |
| 0.00 | 200 | 280 | 280 | 280 |
| 0.02 | 200 | 290 | 285 | 280 |
| 0.05 | 200 | 292 | 310 | 315 |
| 0.10 | 200 | 290 | 320 | 335 |
| 0.50 | 200 | 315 | 330 | 352 |
| 1.00 | 200 | 310 | 420 | 450 |
| 1.50 | 200 | 315 | – | – |
| 0.00 | 300 | 290 | 290 | 290 |
| 0.02 | 300 | 290 | 310 | 290 |
| 0.05 | 300 | 300 | 335 | 335 |
| 0.10 | 300 | 315 | 365 | 360 |
| 0.50 | 300 | 315 | 415 | 410 |
| 1.00 | 300 | 320 | 440 | 450 |
| 1.50 | 300 | 320 | – | 463 |
| 0.00 | 400 | 300 | 300 | 300 |
| 0.02 | 400 | 310 | 310 | 300 |
| 0.05 | 400 | 325 | 350 | 350 |
| 0.10 | 400 | 325 | 370 | 380 |
| 0.50 | 400 | 330 | 450 | 430 |
| 1.00 | 400 | 330 | 470 | 470 |
| 1.50 | 400 | 340 | – | – |

Table 3
The third reduction peak position of the $Co/B/TiO_2$ catalysts

| Boron loading (wt.%) | Calcination temperature, $T_c$ (°C) | Peak position (°C) | | |
|---|---|---|---|---|
| | | Carborane | Ammonium borate | Boric acid |
| 0.00 | 200 | 410 | 410 | 410 |
| 0.02 | 200 | 420 | 420 | 415 |
| 0.05 | 200 | 422 | 450 | 450 |
| 0.10 | 200 | 420 | 470 | 470 |
| 0.50 | 200 | 450 | 507 | 520 |
| 1.00 | 200 | 450 | 520 | 530 |
| 1.5 | 200 | 460 | – | – |
| 0.00 | 300 | 425 | 425 | 425 |
| 0.02 | 300 | 415 | 450 | 430 |
| 0.05 | 300 | 420 | 470 | 475 |
| 0.10 | 300 | 430 | 485 | 490 |
| 0.50 | 300 | 460 | 520 | 520 |
| 1.00 | 300 | 460 | 550 | 570 |
| 1.50 | 300 | 465 | – | 591 |
| 0.00 | 400 | 420 | 420 | 420 |
| 0.02 | 400 | 430 | 450 | 425 |
| 0.05 | 400 | 435 | 480 | 485 |
| 0.10 | 400 | 445 | 510 | 510 |
| 0.50 | 400 | 465 | 550 | 550 |
| 1.00 | 400 | 470 | 565 | 590 |
| 1.50 | 400 | 495 | – | – |

increased from 0.02 to 1.0 wt.%. However, for the carborane modified system, the second peak is only shifted from 290 to 310 °C when the boron loading is increased from 0.02 to 1.0 wt.%. The same trend was observed for the third peak position as well.

### 3.4. $O_2$ titration and $H_2$ chemisorption

All catalysts were reduced at 300 °C for 16 h. The percentage reduction was determined using $O_2$ titration, assuming that the cobalt metal is oxidized to $Co_3O_4$ [13]. The following trends were observed: (i) for the three series of catalysts, at low boron loadings (B wt.% $<0.05$), the extent of reduction of the catalysts is unaffected by the addition of boron. At higher boron loadings (B wt.% $>0.1$), the extent of reduction of the catalysts decreases with increasing boron loading; (ii) the effect of boric acid on the extent of reduction of the $Co(10)/TiO_2$ catalyst is similar to that of ammonium borate. Carborane has less effect on the extent of reduction of $Co/TiO_2$ catalyst, viz. the percentage reduction was decreased from 52.3 to 43.7 when the boron loading was increased from 0.1 to 1.5 wt.%. The effect of boron source on the reducibility of catalysts follows the order: boric acid $\sim$ ammonium borate $>$ carborane.

The percentage dispersions of the reduced catalysts (Table 4) were calculated from $H_2$ chemisorption measurements assuming a H/metal ratio of 1 [10].

### 3.5. Fischer–Tropsch synthesis

The activities and selectivities of the boric acid modified $Co/TiO_2$ catalysts for Fischer–Tropsch synthesis have been reported previously [10]. Thus only data for the ammonium borate and carborane modified $Co/TiO_2$ catalysts are given here.

#### 3.5.1. Ammonium borate modified $Co/TiO_2$ catalysts

Table 5 displays the effect of boron loading on the catalytic properties of the ammonium borate modified $Co(10)/TiO_2$ catalysts for Fischer–Tropsch synthesis. In order to compare the data with boric acid modified catalysts, all conditions used were the same as those

Table 4
Effect of boron loading on % dispersion and % reduction of Co/$TiO_2$ catalysts[a]

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| *Boric acid* | | | | | | | |
| Boron loading (wt.%) | 0.00 | 0.02 | 0.05 | 0.10 | 0.50 | 1.00 | 1.50 |
| % Reduction[b] | 59.8 | 58.6 | 51.3 | 42.5 | 31.6 | 34.5 | 29.0 |
| $H_2$ uptake[c] (ml/g cat.) | 0.35 | 0.34 | 0.41 | 0.32 | 0.29 | 0.27 | 0.17 |
| % Dispersion | 1.90 | 1.82 | 2.20 | 1.71 | 1.59 | 1.46 | 0.92 |
| *Ammonium borate* | | | | | | | |
| Boron loading (wt.%) | 0.00 | 0.02 | 0.05 | 0.10 | 0.50 | 1.00 | 1.50 |
| % Reduction | 59.8 | 60.2 | 50.6 | 47.5 | 33.2 | 27.5 | 25.1 |
| $H_2$ uptake (ml/g cat.) | 0.35 | 0.33 | 0.31 | 0.29 | 0.26 | 0.20 | 0.19 |
| % Dispersion | 1.90 | 1.79 | 1.68 | 1.46 | 1.40 | 1.11 | 0.98 |
| *Carborane* | | | | | | | |
| Boron loading (wt.%) | 0.00 | 0.02 | 0.05 | 0.10 | 0.50 | 1.00 | 1.50 |
| % Reduction | 59.8 | 61 | 54.7 | 52.3 | 53.1 | 45.6 | 43.5 |
| $H_2$ uptake (ml/g cat.) | 0.35 | 0.34 | 0.38 | 0.33 | 0.33 | 0.34 | 0.30 |
| % Dispersion | 1.90 | 1.82 | 2.10 | 1.79 | 1.80 | 1.84 | 1.65 |

[a] All catalysts were calcined at 300 °C for 6 h and reduced at 300 °C for 16 h.

[b] % Reduction was measured by $O_2$ titration at 300 °C.

[c] $H_2$ chemisorption was measured at 100 °C after catalysts were reduced at 300 °C for 16 h.

reported previously [10]. At low boron loadings (B wt.% <0.05), CO conversion and reaction rate do not change; at higher boron loadings (B wt.% >0.1), CO conversion and reaction rate decrease with increasing boron loading. This trend is similar to the effect of boron loading on the extent of reduction of the catalysts. Fig. 2 shows the variation of CO conversion and reaction rate with the percentage reduction of catalysts. Linear relations are observed, showing an increase in CO conversion and reaction rate with an increase in the extent of reduction of the catalysts. This indicates that the reaction rate is dependent on the amount of reduced cobalt metal [14].

The selectivity data also falls into two groupings. For B loadings <0.05% no significant trends are discernible. For B > 0.05%, the selectivity to higher hydrocarbons increases as the activity of the catalyst decreases.

Methane selectivity for all catalysts containing boron is lower than that of the boron-free catalyst. It

Table 5
Effect of boron loading on Fischer–Tropsch synthesis of the ammonium borate modified

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| Co/$TiO_2$ catalysts | | | | | | | |
| Boron loading (wt.%) | 0.00 | 0.02 | 0.05 | 0.10 | 0.50 | 1.00 | 1.50 |
| CO conversion (%) | 48.6 | 48.0 | 47.6 | 42.2 | 40.0 | 35.0 | 28.3 |
| Reaction rate (μmol/g cat./s) | 0.76 | 0.75 | 0.73 | 0.66 | 0.62 | 0.52 | 0.44 |
| Selectivity (%, by mass) | | | | | | | |
| $C_1$ | 21.5 | 19.3 | 19.5 | 14.2 | 12.2 | 15.2 | 16.4 |
| $C_2$–$C_4$ | 13.1 | 9.5 | 10.2 | 12.1 | 14.6 | 14.3 | 15.2 |
| $C_5$–$C_{11}$ | 47.0 | 49.0 | 53.0 | 52.0 | 43.0 | 36.5 | 35.0 |
| $C_{12}$–$C_{18}$ | 11.1 | 11.3 | 9.6 | 14.0 | 17.5 | 17.0 | 13.2 |
| $C_{18+}$ | 7.3 | 10.9 | 7.8 | 8.7 | 12.7 | 16.4 | 20.0 |
| Paraffin (%) | 92.7 | 93.1 | 91.2 | 89.5 | 88.6 | 92.6 | 94.5 |
| Olefin (%) | 6.5 | 5.9 | 7.0 | 8.1 | 9.0 | 6.2 | 4.5 |
| Oxygenates (%) | 0.6 | 0.7 | 0.9 | 1.6 | 1.8 | 1.2 | 0.8 |
| ASF value ($\alpha$) | 0.63 | 0.73 | 0.68 | 0.72 | 0.77 | 0.79 | 0.82 |

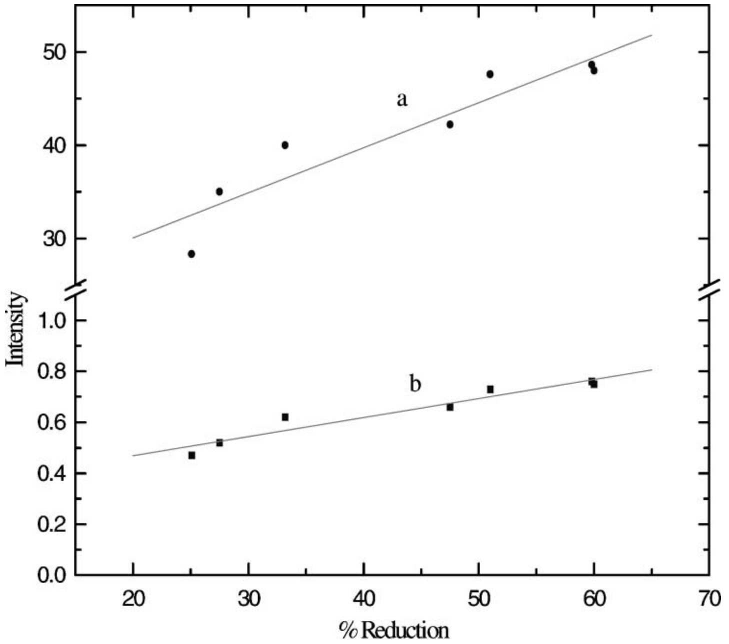

Fig. 2. Variation of the % reduction of ammonium borate modified Co/$TiO_2$ catalyst with (a) % CO conversion and (b) reaction rate (μmol/g cat./s).

is also clear from Table 5 that for all the catalysts, the $C_5$–$C_{11}$ fraction is the predominant product. The second most abundant product is dependent on the boron loading. For the low boron loading catalysts, more light petroleum gases ($C_2$–$C_4$) are produced; for the higher boron loading catalysts, more heavy hydrocarbons are produced. The ASF chain growth parameter ($\alpha$-value) increases with increasing boron loading.

A change in selectivity is expected with conversion, possibly related to diffusional/readsorption issues [15–17], as the Co particle size and Co–B interaction varies with boron loading. Further, catalysts containing boric acid as B source [10] showed a decrease of long chain products with increasing B content. The source of B thus has an effect on the product distribution but this effect is not related to the degree of reducibility (Table 4) nor particle size (Table 2) as both B sources yield similar physical parameters. It is possible that this effect relates to the acidic nature of the B source—the more acidic the source, the shorter the average carbon chain length.

### *3.5.2. Carborane modified Co/$TiO_2$ catalysts*

Table 6 shows that boron loading only has a marginal effect on the catalytic properties of the carborane modified Co/$TiO_2$ catalysts for Fischer–Tropsch synthesis. The following trends are apparent: (i) at low boron loadings (B wt.% $<0.05$), CO conversion and reaction rate do not vary with increasing boron loading; at higher boron loadings (B wt.% $>0.1$), CO conversion and reaction rate decrease slightly with increasing boron loading; (ii) the effect of boron loading on CO conversion and reaction rate of the catalysts is not dramatic; the reaction rate decreases from 0.76 for boron-free catalyst to 0.67 μmol/g cat./s for the 1.5 wt.% boron catalyst; (iii) $C_{18+}$ selectivities increase with increasing boron loading. This tendency is reflected in the ASF chain growth parameters, which gradually increase from 0.63 for the boron-free catalyst to 0.73 for the 1.50 wt.% boron catalyst.

It is thus apparent that the more minor trends in selectivity and activity detected for the carborane loaded catalyst are in the same direction as that detected for the ammonium borate loaded catalysts.

Table 6
Effect of boron loading on Fischer–Tropsch synthesis of the carborane modified Co/TiO$_2$

| Boron loading (wt.%) | 0.00 | 0.02 | 0.05 | 0.10 | 0.50 | 1.00 | 1.50 |
|---|---|---|---|---|---|---|---|
| CO conversion (%) | 48.6 | 47.2 | 49.3 | 45.9 | 45.5 | 42.1 | 44.2 |
| Reaction rate (μmol/g cat./s) | 0.76 | 0.72 | 0.79 | 0.71 | 0.70 | 0.65 | 0.67 |
| Selectivity (%, by mass) | | | | | | | |
| $C_1$ | 21.5 | 19.6 | 21.1 | 15.5 | 17.6 | 18.3 | 23.2 |
| $C_2$–$C_4$ | 13.1 | 12.8 | 11.5 | 14.5 | 13.3 | 14.1 | 11.2 |
| $C_5$–$C_{11}$ | 47.0 | 53.0 | 49.0 | 49.9 | 50.5 | 44.0 | 39.6 |
| $C_{12}$–$C_{18}$ | 11.1 | 10.2 | 12.0 | 12.2 | 9.5 | 13.0 | 12.5 |
| $C_{18+}$ | 7.3 | 5.3 | 8.5 | 8.2 | 8.8 | 11.1 | 12.7 |
| Paraffin (%) | 92.7 | 93.5 | 91.5 | 86.0 | 89.0 | 90.6 | 93.4 |
| Olefin (%) | 6.4 | 6.1 | 6.7 | 9.1 | 7.4 | 6.5 | 5.5 |
| Oxygenates (%) | 0.6 | 0.7 | 0.9 | 0.4 | 0.6 | 0.3 | 0.3 |
| ASF value ($\alpha$) | 0.63 | 0.66 | 0.71 | 0.72 | 0.75 | 0.78 | 0.73 |

### *3.6. Comparison of the Co(10)/B(x)/TiO$_2$ catalysts modified by boric acid, ammonium borate and carborane*

#### *3.6.1. Effect of boron source on reducibility and dispersion of Co/TiO$_2$ catalysts*

In a previous publication [10], we concluded that the decrease in the reducibility of Co/TiO$_2$ catalysts caused by boric acid could be due to two effects: firstly, boron could increase the interaction between $Co_3O_4$ and $TiO_2$; secondly the addition of boron may result in the formation of a surface cobalt–boron compound which is more difficult to reduce. Thus the reducibility of Co/TiO$_2$ directly reflects the interaction between $Co_3O_4$ and the B sources. TPR and $O_2$ titration measurements indicated that the carborane

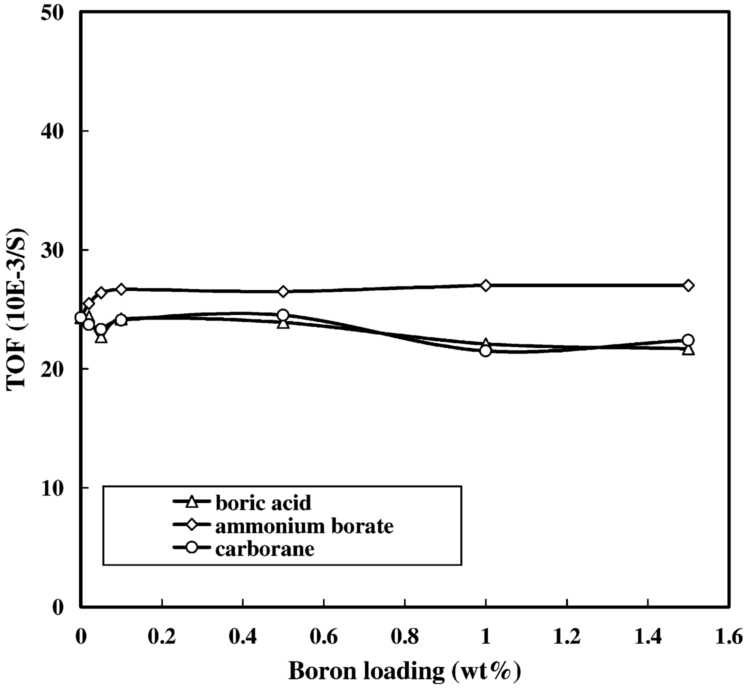

Fig. 3. Effect of boron loading on the TOF of the Co/TiO$_2$ catalysts.

modified Co/$TiO_2$ catalysts were reduced more easily than those modified by boric acid and ammonium borate. This is consistent with the effect of the boron source on the $Co_3O_4$ crystallite size, indicating that the small crystallite sized, well-dispersed cobalt oxides, which display the stronger interaction with the support, are the most difficult to reduce.

### *3.6.2. Effect of boron source on the Fischer–Tropsch reaction rate and TOF of Co/$TiO_2$ catalysts*

For all three series of catalysts, at low boron loadings (B wt.% $<0.05$), reaction rate increases with increasing boron loading; at higher boron loadings (B wt.% $>0.1$), there is a decrease in reaction rate. Compared to the boric acid and ammonium borate modified catalysts, the carborane modified catalysts always displays the higher reaction rate. The level of reduction and dispersion of the three series of catalysts can explain this finding.

Fig. 3 shows the effect of boron source on the FT turnover frequency (TOF) of Co/$TiO_2$ catalysts. It is clear that TOF remained almost invariant and does not depend on the boron loading and boron source. The ammonium borate modified catalysts displays a slightly higher TOF.

This is a remarkable finding since three quite different sources of B have been used in the study. This further supports the suggestion that the Fischer–Tropsch reaction is only dependent on the amount of reducible Co available for the reaction.

## 4. Conclusion

The 10 wt.% Co/$TiO_2$ catalysts modified by different amounts of boron from boric acid, ammonium borate and carborane were characterized by various techniques and investigated by a reactor study for Fischer–Tropsch synthesis. The boron source was found to have a profound influence on both the catalyst reducibility and the FT reaction. TPR and $O_2$ titration measurements indicated that the carborane modified catalysts were reduced more easily than those modified by boric acid and ammonium borate.

The addition of boron to Co/$TiO_2$ catalysts decreased the activity substantially, although the effect varied for the different boron sources. The greatest effect was found to be on the boric acid modified catalysts. The order of the effect was found to be boric acid $>$ ammonium borate $>$ carborane. This order is the same as that of increasing reducibility and increasing metal dispersion. Indeed the effect leads to a TOF that remained constant and is unaffected by the addition of boron for all the catalysts studied.

The FT product selectivity was influenced by the identity of the boron source and was dependent on the boron loading.

## Acknowledgements

We wish to thank THRIP, SASTECH, the NRF and the University for financial support.

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