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Effects of boron in Co–Mo/B–Al_2O_3 hydrotreatment catalysts

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Abstract

Several mild hydrocracking 3 wt.-% Co–10 wt.-% Mo/B–Al_2O_3 catalysts have been prepared by adding H_3BO_3 into a boehmite dough during kneading + extrusion, drying and calcination prior to impregnation. HDS, HDN and cracking were monitored in the hydrotreatment of a VGO feedstock and the optimum B content was estimated around 3 wt.-%. The effects of boron on these catalysts will be discussed here with a particular focus on the effect of boron during impregnation. Using a simple hydrothermal treatment method by soxhlet, B can be extracted, with hot water, from catalysts and from supports. Simultaneously, on supports calcined at 600°C, the formation of a boehmite phase was detected after extraction.

Keywords: Co–Mo/B–Al_2O_3 catalysts; Boron, effect of

1. Experimental

0, 1, 2, 3 and 5 wt.-% B, 10 wt.-% Mo and 3 wt.-% Co catalysts were prepared by impregnation of the B-containing alumina supports described previously [1,2], with ammonium heptamolybdate (AHM), dried at 130°C, then impregnated with $Co(NO_3)_2 \cdot 6H_2O$, dried again, and finally calcined at 500°C, in a rotary kiln, under dry air (8 l/min).

Soxhlet extraction with ion-exchanged water was typically done with a 3 g sample. The temperature of water during an extraction cycle slightly decreased, but remained between 100 and 93°C. After extraction, samples were dried at 130°C.

Catalytic activity tests were carried out in a downflow microreactor (10 ml) using a vacuum gas oil (VGO) of Middle-East origin (properties in Table 1). HDS and HDN activities at 360, 380 and 400°C, LHSV = 2, 80 kg/cm^2, and cracking (of the 360°C$^+$ fraction) at 400 and 420°C, LHSV = 1, were measured. Catalytic activities are expressed by the rate constant assuming reaction orders of 1.5, 1 and 2 for HDS, HDN and cracking, respectively. These reaction orders had been determined by previous kinetic studies carried out in this laboratory [3].

2. Results and discussion

2.1. Effect of boron on HDS, HDN and cracking, Figs. 1–3

2 sets of catalysts were prepared in this study: in the first series — open symbols — B-containing catalysts were macroporous (average macropore diameter: 1.5 μm) and the macro-

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Table 1
Properties of the vacuum gas oil

Density	0.9263 g/cm^3	UOP (K)	11.9
Sulfur content	2.451 wt.-%	Nitrogen content	1110 ppm

ASTM distillation: D-86 and D-1160		*GC Simulated distillation*	
IBP-360°C	7.1 vol.-%	IBP-360°C	8.9 wt.-%
360–500°C	56.6 vol.-%	360–500°C	71.6 wt.-%
500-FBP = 535°C	36.3 vol.-%	500°C-FBP	19.5 wt.-%

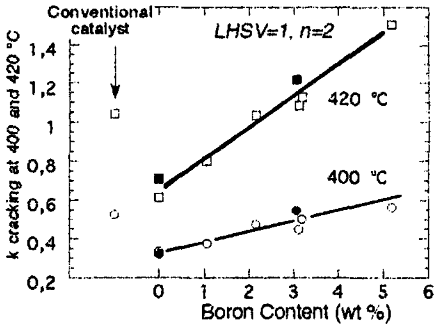

Fig. 3. Cracking rate constants.

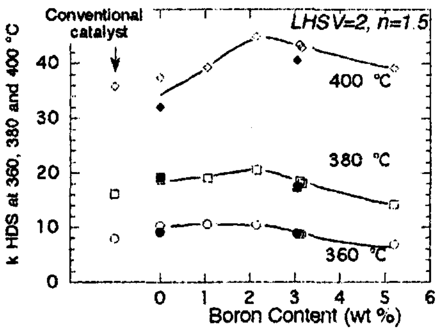

Fig. 1. HDS rate constants.

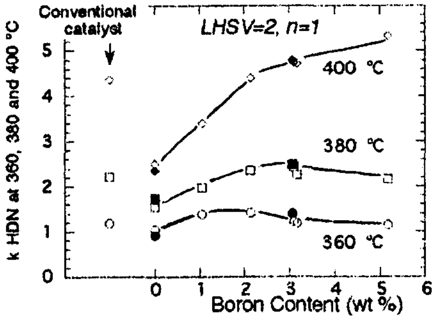

Fig. 2. HDN rate constants.

pore volume increased with the boron content; however, the second series — closed symbols — was made macropore-free. Macropores are well known to decrease the mechanical properties of the extrudates, however they improve the diffusion. Both types should be considered in the development of mild hydrocracking catalysts. Several catalysts have been tested and characterized, results on only a few of them are reported here, Table 2. A conventional 'mild hydrocracking' catalyst was also used for comparison. B-containing catalysts have already been studied [4–6], however, little is known on them, especially when the support is prepared by kneading.

The cracking activity increased with the boron content, as expected from the well known effect of boron on the acidity of alumina [7–9]. Optimum boron content for HDS and HDN reactions depends on the reaction temperature; it shifts from between 1% and 2% B at 360°C to between 2 and 3 wt.-% B at 380–400°C. The

Table 2
Data on B-containing catalysts. 2 Series with and without macropores

	Series with macropores						Macropore-free	
B content (wt.-%)	0.0	1.1	2.2	3.1	3.2	5.2	0.0	3.1
Surface area [a] (m^2/g)	221	254	216	230	229	208	218	229
Pore Volume [a] (ml/g)	0.50	0.47	0.41	0.40	0.39	0.34	0.52	0.41
d_{50} [a,b] (Å)	84	76	71	75	73	84	89	80
Macropore vol. [c] (μl/g)	9	24	25	49	40	54	10	10

[a] BET method with N_2 ± 10 m^2/g.

[b] Average pore diameter.

[c] Pores larger than 500 Å.

Table 3
XPS analysis on a macropore-free 3 wt.-% B-containing catalyst

Relative Al/B atomic ratio	Support	Catalyst
Crushed	94	106
Pellet surface	96	218

Base = 100: average for crushed samples, precision: ±20%.

optimum fall in the claimed range of most patents where B is used as an additive [6].

2.2. *Effect of boron during impregnation*

In macropore-free B-catalysts metal distribution was uniform in the pellets except for a slight metal enrichment of the surface. However, the surface area of B-containing supports decreased more after impregnation than for B-free catalysts, probably due to pore plugging. An other positive effect of boron addition is the improvement of the Side Crushing Strength in macropore-free catalysts [1].

On both, 3.7% B-containing support (macropore-free) and on the derived 3 wt.-% Co–10 wt.-% Mo catalyst, the Al/B atomic ratio was measured on the surface of the pellets and on the crushed pellets by XPS analysis. The boron content on the pellet surface decreased after impregnation, Table 3. Occelli and Debies reported, for a B + zeolite-based catalyst prepared similarly, that the extrudates surface was richer in boron than the interior [4]. They assigned this effect to migration of B_2O_3 during calcination of the support, although no data are reported.

Nevertheless, McArthur, in a US patent [9] and Izumi et al. [7], reported that in alumina-boria catalysts, boron can be easily extracted with hot water. This is confirmed in this study. Boria is also easily dissolved in hot water, but the compounds 9 Al_2O_3–2 B_2O_3 and 2 Al_2O_3–B_2O_3 appear to be hydrothermally stable up to at least 1950 and 1035°C, respectively [9].

An other explanation to the results obtained by Occelli and Debies, that would account also for our observations, is that the surface was washed out during impregnation and that boron was removed from the pellet surface [2]. The B-containing catalyst prepared by Occelli and Debies was macroporous (with 50% of the pore volume in pores bigger than 1000 Å) and it is well known that if the evaporation takes place in the mesopores which are constantly replenished by the solution contained in the macropores, in case of an impregnation without interactions, it may lead to a surface enrichment, as in Occelli and Debies' case [10]. This is especially the case when there is occluded macroporosity. However, in our case, in absence of macropores or with our very large macropores, the pellet surface was depleted. Boron migration during calcination, due to hydrothermal conditions, seems unlikely, as it would also appear during the support calcination.

Soxhlet extraction was carried out on supports before and after calcination. After 16 h of extraction, nearly all the boron has been removed from a 3.7% B support calcined at 600°C. The extraction is even easier for uncalcined supports, indicating that a strong bond with alumina has not been formed yet. By increasing the calcination temperature up to 900°C, the amount of boron retained after 2 h of extraction is increased, due to the formation of the aluminum borate phase 9 Al_2O_3–2 B_2O_3. After extraction, the dried supports were analyzed by XRD and SEM. The XRD analysis have shown the formation of a boehmite phase, the amount of which increases with the extraction time, Fig. 4. SEM pictures taken on the extrudates after extraction show the formation of a 'chestnut' type structure [11,12]. This structure is preserved after calcination at 550°C, Fig. 5. A similar type of 'chestnut structure' was also observed after extraction of a B-free support for 16 h. Such a structure was only visible at the periphery of the extrudates. As large crystallites are thermodynamically more stable, they tend to form where space is available.

The formation of a boehmite phase by hydrothermal treatment of an alumina sample has already been reported [2,11–13] and, as in the present case, represented about 20 wt.-% of the

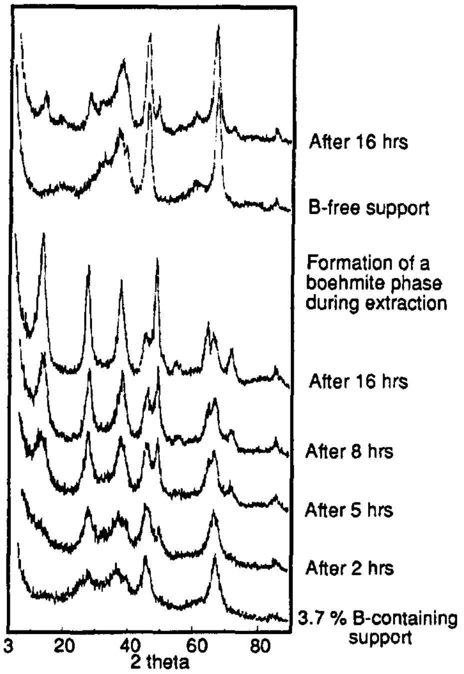

Fig. 4. XRD spectra of supports before and after soxlet extraction in hot water.

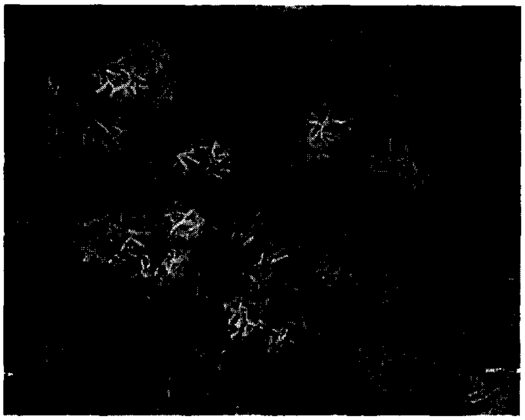

Fig. 5. SEM micrograph of a B-containing support after 8 h of extraction, calcined 1 h at 550°C.

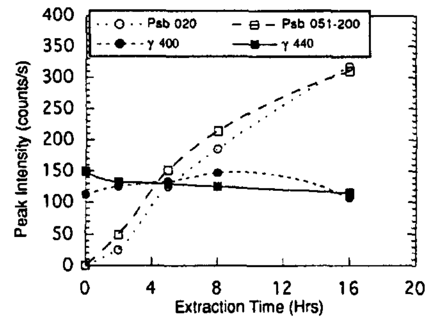

Fig. 6. XRD peak intensity after extracting pseudoboehmite (Psb) and gamma Alumina (hkl).

alumina [2,13]. In addition, the amount of boehmite phase formed from a 3.7 wt.-% B-containing support is much higher, about 70 wt.-%, than from a B-free support. As the XRD peak intensities of the γ-Al_2O_3 phase did not change with the extraction time (Fig. 6), it is believed that the boehmite phase was formed from the amorphous phase, the latter being probably a B-substituted pseudoboehmite-like phase. In B-free supports an amorphous phase is probably also present, which leads to the boehmite phase in smaller quantities.

After calcination at 550°C, for 1 h, in a muffle furnace, the surface area, pore volume and SCS were once again measured. The data reported in Table 4 indicate that the SCS remained high after extraction and is probably due to the chestnut structure. These data also indicate a deep reconstruction of the support: the surface area and the pore volume also remained high, however the average pore diameter, d_{50}, decreased and the pore size distribution became monomodal, see Ref. [1] for details on the support.

Table 4
Effect of the B extraction on supports after calcination

Extraction time (h)	B-content (wt.-%)	Boehmite content (wt.-%) [a]	SCS (kg) ± 0.5 kg	Surface area (m^2/g) ± 10 m^2/g	Pore volume (ml/g)	d_{50} (Å)
0	3.7	0	4.9	291	0.60	82
2	1.66	10	3.9	322	0.55	53
8	0.47	50	5.1	307	0.56	59

[a] Determined before calcination.

It was also observed that the amount of boron that can be extracted, in 2 h, from catalysts is slightly higher than for supports. This indicates that during the impregnation-drying-calcination steps, some boron was already removed from the alumina surface and made easier to extract.

3. Conclusion

Addition of 3 wt.-% B in alumina supported Co–Mo catalysts had little effect on HDS, however HDN and cracking activities were sharply improved.

The results presented here indicate that boron is likely to be extracted during the impregnation of a B-containing support, although it will remain in the pellets. A B-containing support impregnated with water only, did not form a boehmite phase detectable by XRD or SEM, however TG/DTA analysis indicated the presence of strongly adsorbed water.

The supports that can be made by B-extraction might prove interesting for the treatment of low boiling point cuts, or for exhaust gas treatment for example, due to their high surface area, pore volume and SCS for a low average pore diameter. Chestnut-like supports have already been proposed for deNO$_x$ [11], as well as for HDM catalysts [11,12].

As reported here, the main drawback of B-containing catalysts is the weakness for water. The amount of water formed during hydrotreatment is rather small, so life tests of these catalysts would be especially interesting.

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