Development of a hydroprocessing catalyst containing Boron and Nano-boron compounds

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ABSTRACT

Hydroprocessing is a refinery process of catalytic cracking and hydrogenation to break down low value heavy hydrocarbons and to remove sulphur, nitrogen, oxygen and metals to the specified limits at high temperature and pressure using hydrogen in order to produce primarily valuable middle distillates (jet fuel and diesel). Recently, catalyst with boron complexes has been an interesting topic to the catalyst community. In literature, the studies are composed of micron-sized boron particles and the addition of boron to the catalyst has been giving benefits to the hydroprocessing reactions. In this study, aside from the studies in the literature, nano-sized boron complexes were added to the catalyst and synthesized catalyst was studied in hydroprocessing reactions. Boron complexes are amongst the natural resources of Turkey and due to its great material characteristics improve the high activity and selectivity of catalyst. This study is a part of R&D project supported by TUBITAK (ARDEB 1003 with project number 213M194). In this project, catalysts with boron are synthesized and characterized by using international standards. The characterization results give feedback to the synthesis procedure and play an important role optimizing the final recipe catalyst synthesis. With the completion of the project, potential application of boron complexes in catalyst will be studied and this will lead to projects involving large-scale studies. The obtained know-how from this project will enable us to develop new R&D projects with catalyst manufacturers. Moreover, it will help us to develop new synthesis route for the production of a catalyst that is intended just for Tüpraş's production needs.

Keywords: Nanotechnology, boron, hydroprocessing

1 INTRODUCTION

Today, hydroprocessing applications has an important role in refinery technologies. Besides, a great deal of research in the field of heterogeneous catalysis used in hydroprocessing reactions is being devoted for the production of ultra clean gas oil. Hydroprocessing catalysts are required to address environmental restrictions imposed on the content of fuels which leads research into more selective catalyst recipes [1]. For many years, bimetals (cobalt–molybdenum and nickel–molybdenum) supported onto Al_2O_3 has been used as hydrotreating catalysts. Recently, in order to enhance the catalyst performance, silica-alumina materials is also used as support material [2]. Developing catalyst with high activity and stability plays an important role in petroleum refining industry. By changing the support properties (surface area, pore volume, acidity), the activity and the selectivity of a catalyst can be controlled. In literature, it has been shown that addition of additives such as boron to $CoMo/Al_2O_3$ and $NiMo/Al_2O_3$ catalysts improves the performance of the catalyst in hydrotreating reactions. The main idea behind the incorporation of additives (boron) to the support is that boron constrains the interaction between metal phase and support, therefore hardly sulfidable $CoAl_2O_4$ and $Al_2(MoO_4)_3$ cannot be formed. Moreover, boron addition seems to have positive effect on the acidic sites, hydrogenation activities, metal dispersion and surface properties of the catalysts [3-6]. In addition to above mentioned properties, boric acid has been shown to react with Al-OH groups to form a boria over layer which stabilizes the structure and creates Al-O-B bridge, leading to a formation of surface B-OH groups [7]. In this study, to enhance the catalyst properties the effect of boron as well as the effect of nano-alumina has been studied. The preparation method and conditions were optimized to obtain a support with high surface area using sol-gel method. The conditions that were optimized were boric acid concentration, hydrolysis ratio, nitric acid and metal alkoxide concentration. The synthesized catalysts were characterized by XRD, TEM, BET, BJH adsorption/desorption and FT-IR techniques.

2 EXPERIMENTAL

The commercial alumina (Siralox 1.5/100) used in this study was obtained from SASOL. Aluminum isopropoxide (Sigma-Aldrich), 1-propanol (Merck), nitric acid (Merck), cobalt(II)nitrate hexahydrate (Merck) and ammonium heptamolybdate tetrahydrate(Merck) were used as obtained.

2.1 Catalyst Preparation

The catalysts used in this study were prepared by sol-gel and impregnation methods. A sol-gel process was developed to prepare mesoporous nano alumina supports with high BET surface area. The sol-gel precursors for Al_2O_3 were aluminum isopropoxide (AIP) which was dissolved in 1-propanol. Deionized water was added to the solution so that hydrolysis ratio was 21 and the temperature was adjusted to 85 ºC. Following that, nitric acid was used as a catalyst and the solution were aged. To be able to obtain mesoporous Xerogel, the solution was dried and calcined. The details of the synthesis procedure can be seen in Figure 1. Boria-alumina supports were prepared by impregnation of boric acid solutions at different concentrations onto alumina. Cobalt and molybdenum metals were impregnated onto the boria-alumina support by using cobalt(II)nitrate hexahydrate and ammonium heptamolybdate tetrahydrate as precursors.

2.2 Catalyst Characterization

The specific surface area, pore volume, and porosity distribution of alumina (micro and nano) supports were obtained from nitrogen adsorption–desorption isotherms, determined at 77K with an ASAP 2020 (Micromeritics) apparatus. Surface areas were calculated by the Brunauer–Emmett–Teller (BET) method, and the pore size distribution and total pore volume were determined by the Barrett–Joyner–Halenda (BJH) method. Prior to adsorption, the samples were outgassed at 200 ºC for 1h. The measurements were done using international standards namely ASTM D4365-95, D4641-12, D4222-03.

X-ray diffraction measurement was performed to investigate boron-modified alumina supports using Rigaku Miniflex II instrument. The measurements were done using

international standards namely ASTM D4926-06, D5758-01, D5357-03, D3942-03, D396-03.

The infrared spectra of $B_2O_3(x)–Al_2O_3$ carriers were collected using PerkinElmer® Spectrum™ 100 FT-IR spectrometer. Transmission Electron Microscopy measurements were performed on JEOL JEM 2100 HRTEM operating at 200 kV (LaB6filament) with Oxford Instruments X-Sight 6498 EDS system.

3 RESULTS AND DISCUSSION

Commercial alumina (Al_2O_3*) has a surface area of 108.3 m^2/g. Addition of 1-5 % boric acid dissolved in ethanol solution did not result a significant decrease in the surface area of the alumina. It can be said that boron loading did not clog the pores of the alumina. After the impregnation of CoMo onto the boron modified commercial alumina support, surface area decreased but not significantly. This can be attributed to the filling of the pores of alumina support by molybdenum oxide and cobalt oxide agglomerated species. Results can be seen in Table 1.

XRD patterns of all B_2O_3-Al_2O_3 supports regardless of the boron concentration exhibit only diffraction peaks characteristic of γ-alumina, which indicate that no large bulk crystalline phases other than the parent γ-alumina carrier are present (not shown here).

Table 1: BET results of B_2O_3-Al_2O_3* and CoMo/B_2O_3-Al_2O_3*. The values in parentheses indicates the weight percentage of B_2O_3

Catalyst	BET Surface Area (m²/g)	BJH Desorption cumulative volume of pores (cm³/g)	BJH Desorption average pore width (nm)
Al2O3*	108.3	0.39	9.6
B₂O₃(1)-Al₂O₃*	112.8	0.39	9.1
B₂O₃(2)-Al₂O₃*	111.3	0.38	9.2
B₂O₃(3)-Al₂O₃*	111.6	0.37	8.8
B₂O₃(4)-Al₂O₃*	111.6	0.37	9.0
B₂O₃(5)-Al₂O₃*	111.1	0.37	8.9
CoMo/B₂O₃(1)-Al₂O₃*	88.6	0.29	8.9
CoMo/B₂O₃(2)-Al₂O₃*	88.4	0.28	8.9
CoMo/B₂O₃(3)-Al₂O₃*	86.3	0.28	9.2
CoMo/B₂O₃(4)-Al₂O₃*	85.5	0.28	9.1
CoMo/B₂O₃(5)-Al₂O₃*	84.4	0.27	9.0

*Commercial Alumina
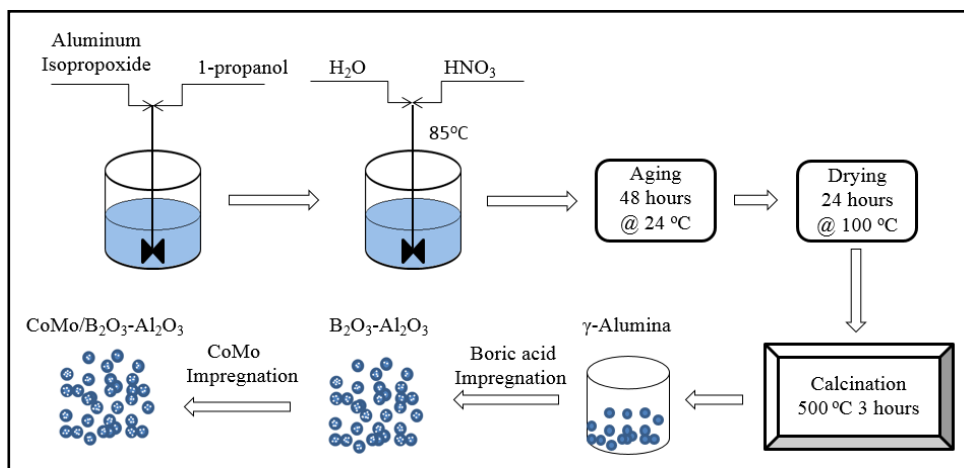
Figure 1: Synthesis procedure of CoMo/B_2O_3-Al_2O_3

XRD patterns of CoMo/B$_2$O$_3$-Al$_2$O$_3$* is shown in Figure 2. Besides the XRD peaks of support material, the XRD patterns of CoMo/Al$_2$O$_3$* and CoMo/B$_2$O$_3$(x)-Al$_2$O$_3$* catalysts exhibit presence of additional XRD features, with main peaks detected at 23º, 26º, and 27º. The peaks at 23º and 27º are ascribed to the presence of crystalline MoO$_3$, while the peak at 26º belong to the crystalline CoMoO$_4$. Increase in boria loading from 0 to 5% leads to an increase in the intensity of crystalline MoO$_3$ peaks. It can be said that, addition of boron to the support material leads to a change in the interaction degree between the support materials and the metal oxides, which results in change in the dispersion of metal oxides on the support surface. In a further study, the sequence of impregnation (CoMo first, followed by boria) should be studied to understand the effect of boria on the interaction between the support material and metal phase.

Figure 3 shows the effect of boria addition onto the Al$_2$O$_3$*. Boria free support does not show any bands in region 1000-1750 cm^{-1}. Increase in boria concentration in CoMo/B$_2$O$_3$(x)-Al$_2$O$_3$* catalyst shows an increase in the intensity of peaks at 1050 and 1380 cm^{-1}. These bands are likely due to asymmetric B-O stretching of borates on the alumina surface [8].

Nano alumina (Al$_2$O$_3$) synthesized following the recipe shown in Figure 1. The synthesis recipe was optimized to get a high surface area which is 406.2 m²/g. The comparison of commercial alumina and the synthesized alumina is shown in Table 2. It can be seen that the synthesızed alumina has a much larger surface area than commercial alumina.
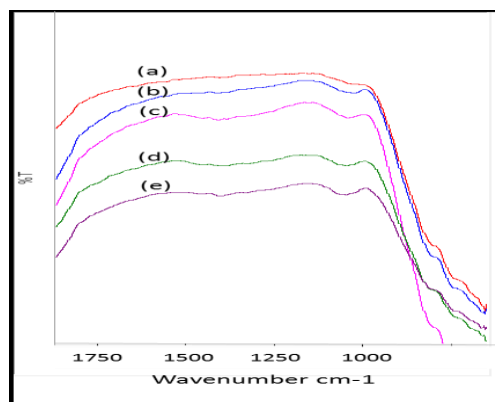

Figure 3: FT-IR spectra of of Al$_2$O$_3$* (red-a), CoMo/B$_2$O$_3$(1)-Al$_2$O$_3$*(blue-b), CoMo/B$_2$O$_3$(3)-Al$_2$O$_3$* (pink-c), CoMo/B$_2$O$_3$(4)-Al$_2$O$_3$* (green-d), CoMo/B$_2$O$_3$(5)-Al$_2$O$_3$* (purple-e)

Table 2: BET results of Al$_2$O$_3$* and the synthesized alumina with boria and CoMo impregnation

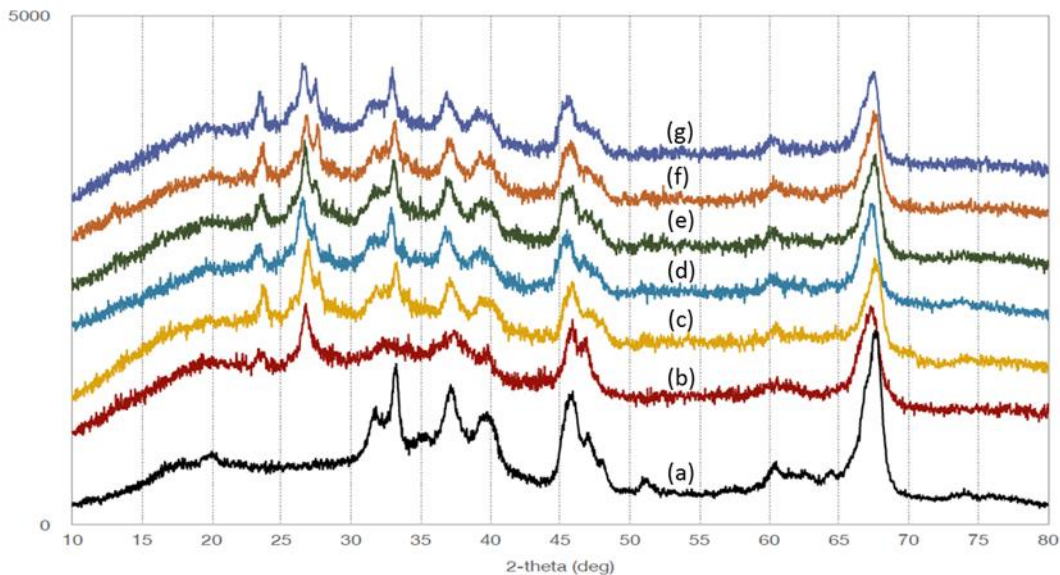|	Al$_2$O$_3$*	Al$_2$O$_3$	B$_2$O$_3$(3)-Al$_2$O$_3$	CoMo/B$_2$O$_3$(3)-Al$_2$O$_3$
BET Surface area (m²/g)	108.3	406.2	392.7	356.8
BJH Desorption cumulative volume of pores (cm³/g)	0.39	0.99	0.97	0.66
BJH Desorption average pore diameter (nm)	9.6	5.2	5.4	4.8

Figure 2: XRD patterns of Al$_2$O$_3$* (black-a), CoMo/Al$_2$O$_3$* (red-b), CoMo/B$_2$O$_3$(1)-Al$_2$O$_3$*(yellow-c), CoMo/B$_2$O$_3$(2)-Al$_2$O$_3$* (blue-d), CoMo/B$_2$O$_3$(3)-Al$_2$O$_3$* (green-e), CoMo/B$_2$O$_3$(4)-Al$_2$O$_3$* (orange-f), CoMo/B$_2$O$_3$(5)-Al$_2$O$_3$* (purple-g)

The XRD patterns of Al_2O_3, $B_2O_3(3)-Al_2O_3$, $CoMo/B_2O_3(3)-Al_2O_3$ is presented in Figure 4. The results show that the support used in this study is γ-alumina. The only observed peaks are γ-alumina peaks, due to metals being in amorphous phase rather than crystalline phase. The broadness of the diffraction means that the alumina crystallites would have a small size or low crystallinity as said before. It can be concluded that metals are well-dispersed into the alumina support. No peaks assignable to B_2O_3 were observed. Moreover, the intensity of alumina peaks slightly decrease due to support-metal interaction decreasing alumina crystalline size.

In a future study, catalytic activity of boron modified-alumina catalysts will be studied in a tubular packed bed reactor at high pressure and high temperature conditions. The gas and liquid product will be analyzed in terms of sulphur and nitrogen content. The evaluation will be done by comparing the reference catalyst and the synthesized catalysts in terms of hydrotreating activity using both distillates and VGO as feedstock. This will also be an indication of catalyst activity at different types of feedstock.

Figure 4: XRD patterns of Al_2O_3 (blue-a), $B_2O_3(3)-Al_2O_3$ (red-b), $CoMo/B_2O_3(3)-Al_2O_3$ (green-c).

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[8] Jorge Ramirez, Perla Castillo, Luis Cedefio, Rogelio Cuevas, Marco Castillo , Jose Maria Palacios, Antonio Lopez-Agudo, Applied Ca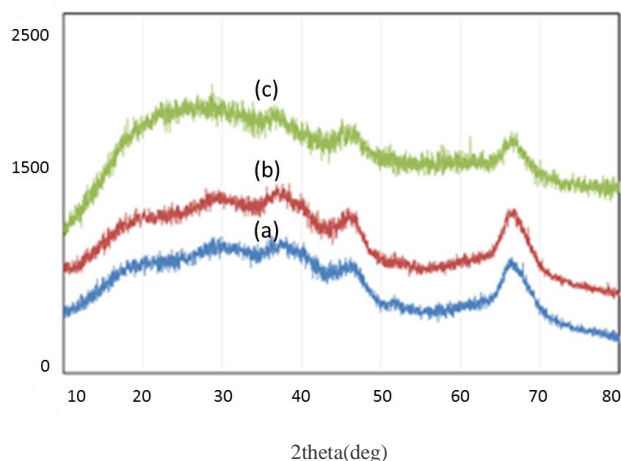talysis A: General 132, 317-334, 1995