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Sulfur Removal in Gasoil Feedstocks by Hydrotreating Process: A Comparative Study

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Abstract

This study focuses on the hydrodesulfurization process of two different types of feedstocks: low and high-sulfur-content gasoil. The objective is to remove sulfur using a commercial $Co-Mo/\gamma$ -Al2O³ catalyst obtained from the Daura refinery. The catalyst underwent various characterization tests, including BET surface area, crush strength, and composition tests using atomic absorption. Similarly, the feedstocks were also characterized before the evaluation process. The study explored the impact of temperature, LHSV (Liquid Hourly Space Velocity), and pressure as operating conditions for gasoil hydrodesulfurization (HDS) using the commercial catalyst Co-Mo/ γ -Al₂O₃ in a pilot hydrotreating unit located at the petroleum research & development centre. The findings indicated that decreasing LHSV led to an increase in sulfur removal. Furthermore, increasing the temperature showed a general trend of increased sulfur removal for both high and low sulfur gasoil feedstocks. These trends were observed within the optimal operating conditions of LHSV 1 hr⁻¹, 375^oC temperature, 35 bar pressure, and a ratio of 200 cm³ of hydrogen gas to 200 cm³ of hydrocarbon. These results shed new light on the potential of this catalyst for effectively treating heavier fuels containing complex sulfur compounds.

Keywords: HDS, Co-Mo, sulfur removal, gasoil, operating conditions.

إزالة الكبريت من زيت الغاز باستخدام عملية المعاملة بالهيدروجين : دراسة مقارنة

الخالصة:

تركز هذه الدراسة على عملية إزالة الكبريت بالهيدروجين لنوعين مختلفين من المواد المغذية: زيت الغاز ذو المحتوى المنخفض والعالي من الكبريت. الهدف هو إزالة الكبريت باستخدام عامل مساعد تجاري 3O2Al-γ/Mo-Co تم الحصول عليه من مصفى الدورة. خضع العامل المساعد الختبارات تحديد الخصائص المختلفة، بما في ذلك المساحة السطحية باستخدام تقنية BET ، قوة مقاومة السحق، واختبارات تركيب المكونات باستخدام الامتصاص الذري. وبالمثل، تم أيضًا تحديد خصائص المواد الخام قبل عملية التقييم. استكشفت الدراسة تأثير درجة الحرارة، السرعة الفراغية لكل ساعة(LHSV (، والضغط كظروف تشغيل لعملية إزالة الكبريت بالهيدروجين لزيت الغاز باستخدام العامل المساعد التجاري 3O2Al-γ/Mo -Co في وحدة ريادية التجريبية الموجودة في مركز البحث والتطوير النفطي. أظهرت النتائج أن تقليل LHSV أدى إلى زيادة في نسبة إزالة الكبريت. علاوة على ذلك، أظهرت زيادة درجة الحرارة اتجاهًا عامًا لزيادة نسبة إزالة الكبريت لكلا النوعين من زيت

الغاز (الذي يحتوي على كبريت منخفض وعالي). تم ملاحظة هذه الاتجاهات ضمن ظروف التشغيل المثلى التي تشمل 1 LHSVساعة،1- درجة حرارة 375 درجة مئوية، ضغط 35 بار، ونسبة 200 سم³ من غاز الهيدروجين إلى 200 سم³ من الهيدروكربونات. تسلط هذه النتائج الضوء على إمكانيات هذا العامل المساعد في معالجة الوقود األثقل التي تحتوي على مركبات الكبريت المعقدة بشكل فعال.

1. Introduction:

Elevated levels of sulfur have been found to cause catalyst deactivation, that plays pivotal role in refinery processes, which in turn leads to the release of harmful sulfur compounds into the atmosphere during many refining processes [1], [2]. To reduce the emissions of SO_2 , NO_X , aromatics compounds, vapor, and soot particulates from the refineries and their products after the combustion process, global environmental legislation has been put in place [3]. There are several techniques for desulfurization, including Biodesulfurization (BDS), Hydro-desulfurization (HDS), extractive desulfurization, and Oxidative Desulfurization (ODS). These techniques are being studied worldwide to produce ultraclean petroleum fuels with low levels of sulfur compounds to comply with environmental legislation. HDS is the most widely used technique for removing sulfur from heavy and light fuels in refineries. This process typically involves treatment by a catalyst and hydrogen to convert sulfur (S) compounds to hydrogen sulfide (H_2S) [3],[4]. Hydrotreating catalysts are commonly used to increase the conversion rate of heavy feedstocks and to enhance the purity of final products. They also play a crucial role in pretreating streams for chemical processes such as gasoline production catalytic reforming process, Fluid Catalytic Cracking (FCC), and hydrocracking. The Sulfided forms of Co and Ni promoted Mo on γ -Al₂O₃ catalysts are vital for HDS due to their remarkable properties as catalyst support [5],[6]. Typical catalyst systems incorporate mixed sulfide catalysts of CoMo and NiMo loaded on γ -Al₂O₃. CoMo and NiMo are commonly used for large HDS duty and hydrodenitrogenation (HDN) operations respectively, γ -Al₂O₃ is a popular support material in heterogeneous catalysis due to its high surface area, thermal stability, and ability to disperse active phases[7], γ -Al₂O₃ can be produced using various methods such as sol-gel, hydrothermal processing, and controlled precipitation. The other methods of producing γ -Al₂O₃ involve inorganic aluminum salts, alkoxides, metallic powders, waste alumina, and kaolin [8]. Typically, the traditional method for creating a promoted M_0S_2/A_2O_3 catalyst involves the use of either simultaneous or successive impregnation of molybdenum and promoter salts onto alumina, supported by calcination (producing oxides), and performing the necessary sulfidation before being used [9].

Molybdenum sulfide is the preferred active component for catalysts, although tungstencontaining catalysts are also used, but only for specific applications such as lube oil treatment. Cobalt (CoMo) and nickel (NiMo) are also used as promoters for molybdenum catalysts. Any catalyst promoter has the effect of significantly increasing the activity of active metal sulfide.^[10]

Researchers in the catalysis field continue to face challenges in developing a supported catalyst based on molybdenum that possesses a greater concentration of active metals on its external surface while also achieving a high dispersion [11]. Certain researchers have explored methods for managing HDS catalysts that contain a significant load of metal oxides in order to obtain the active sulfide phase at a lower temperature for pre-sulfiding. This approach aims to prevent the sintering of the catalyst, which occurs at higher temperatures [12].

In a study on hydrodesulfurization (HDS) of heavy gas oil with a sulfur concentration of 4000 ppm, reference [13], tested Co-Mo/Al₂O₃ and Co/Al₂O₃ catalysts in a fixed bed reactor at 300 ^oC and pressure 30 MPa. The objective was to investigate the influence of catalysts in removing dibenzothiophene from heavy gas oil. The results indicated that HDS% was 50% and 80% respectively, and showed an increase in HDS% with increasing temperature.

reference [14], examined the hydrodesulfurization (HDS) of gas oil using CoMo and NiMo catalysts supported in alumina-silica and alumina-zeolite through a two-stage or layer catalyst bed at 340°C and 25 MPa with HDS (90%). In another study, reference [15], explored the effects of H² purity, pressure, gas/oil ratio, temperature, and LHSV on HDS activities of heavy gas oil in a micro-trickle bed reactor using a commercial NiMo/Al₂O₃ catalyst."The author studied the effect of space velocity in the range of $(0.65-2 h^{-1})$ and temperature of $(360 - 400)$ °C in a separate set of experiments. The findings revealed that the HDS percentage amounted to a staggering 96.6%, and it became evident that the efficacy of the HDS process remained unaffected by the purity of H_2 , the pressure, or the ratio of H_2 to HC. Interestingly, as the space velocity increased, the efficiency of hydrodesulfurization diminished, while an elevation in temperature resulted in an augmentation of hydrodesulfurization. The highest point of activity was reached at approximately 360°C. The effectiveness of a catalyst, measured by its capacity for desulfurization, activity, and selectivity, hinges on a variety of factors. These include the specific attributes of the catalyst, the concentration of the active elements, the properties of the support medium, and the method of synthesis. Furthermore, the reaction conditions, the procedure of sulfiding, the temperature, and the partial pressure of hydrogen and H2S also play a

part. The concentration and type of sulfur compounds present in the feedstock stream, along with the design of the reactor and the overall process, also influence the catalyst's performance [7],[16]. This work includes studying the HDS activity of CoMo\ γ -Al₂O₃ catalyst which is normally used for naphtha and kerosene sulfur removal in Daura refinery; therefore, two types of Iraqi gas oil feedstocks would be introduced: high and low sulfur as feedstock for investigating the best removal percentage ,then demonstrating and comparing results related to the effects of operating conditions such as LHSV, temperature, and pressure on the degree of sulfur removal, as well as different parameters that could affect the catalyst activity, like surface area and active metal loading, and finally to discover the capability of that catalyst to treat the complex sulfur compounds existed in gas oil.

2. Experimental work:

2.1 Materials:

A commercial catalyst in extruded form was supplied by refineries which was then characterized as it would be shown later in Table (3).

2.1.1 Feedstocks:

Two types of gasoil were used as the feedstock for hydrodesulfurization evaluation, were brought from Daura refinery, Table (1) shows the feedstock specifications.

Characteristics	Low sulfur gasoil	High sulfur gasoil
Sulfur content, ppm	1967	10432
Sp. Gravity @ 15.6 $°C$	0.8233	0.8401
Viscosity (a) 40 °C	2.9115	3.64
Flash point °C	75	80
Pour point	-15	-15
Ash wt%	nil	0.0039
Carbon residue wt%	0.01	0.05

Table (1): Properties of the Gasoil feedstock

2.1.2 Equipment:

A hydrotreating pilot unit manufactured by Vinci- technologies company- France was used as a rig for performing experimental procedure.

2.2 Hydrodesulfurization Experiments Procedure:

The hydrotreating process for gasoil feedstocks was conducted within a temperature range of 300 to 375 °C, LHSV range of 1 to 4 hr⁻¹, under a steady hydrogen pressure of 35 bars, and a hydrogen to hydrocarbon ratio of 200 cm³/cm³. These parameters were applied to two types of gasoil feedstocks obtained from Daura refinery, aiming to evaluate the efficiency of the catalyst in minimizing sulfur content in the feed. After a stabilization period of 1.5 hours necessary for reaching a steady state, the final product was gathered for sulfur content analysis. The specifics of the hydrotreating experiment's operation conditions are outlined in Table (2).

2.3 Catalyst Evaluation in Reactor System:

The catalytic process was conducted using a continuous hydrotreatment evaluation reactor system, located in the refining department of the petroleum research and development center. This unit comprises four key areas: the feed section, reactor section, control section, and the cooling, condensation, and collecting section. For this operation, 40 grams of the commercial catalyst was charged into the fixed bed reactor of the pilot unit, with a catalyst layer length of 23 cm. The reactor's top and bottom parts were filled with an inert ceramic balls material, each having a layer of 3 cm length. To purge the system from oxygen, the unit was flushed with nitrogen. Initial tests showed a moisture content of 340 ppm in the nitrogen, which was reduced to 270 ppm by heating the system to between 150 and 200 degrees Celsius for a duration of 90 minutes. This process was conducted at a pressure of 10 bars and a flow rate of 300 Normal liters per minute.

After five runs, each lasting 1.5 hours and under the same conditions, the final moisture content was reduced to 11 ppm. The schematic diagram of the unit and a section of the reactor are depicted in Figures (1) and (2), respectively.

2.4 Catalyst HDS Operation:

The performance of the Co-Mo/ γ -Al₂O₃ catalyst was evaluated for the Hydrodesulfurization (HDS) process using two kinds of feedstocks, namely high sulfur gasoil and low sulfur gasoil with sulfur content of 10432 ppm and 1967 ppm, respectively. The catalyst was positioned in the reactor and its effectiveness for sulfur elimination was analyzed through a continuous series of tests, which spanned a specific range of temperatures and the liquid space velocities. The effect of temperature and the LHSV on Co-Mo catalyst HDS capabilities at temperatures of 300°C and

375 \degree C, and LHSV of 1 and 4 hr⁻¹, was assessed. Other factors like reaction pressure and H₂/HC ratio remained constant at 35 bars and 200 cm^3/cm^3 , respectively for both types of feedstocks. All the studied parameters are presented and elaborated in excel graphs; The hydrodesulfurization activity of the catalyst was calculated using the following equation:

 $S\% = (ST_{feed} - ST_{product}) / ST_{feed}$, where;

HDS% is hydrodesulfurization activity. STfeed is the total sulfur content (ppm) of the feed and STproduct is the total sulfur content (ppm) of the product.

Fig. (1): Hydrotreating pilot

Fig. (2): reactor section of the unit

1. Feedstock tank, 2. Dosing pump, 3. Hydrogen gas, 4. Reactor, 5. controlpanel, 6. Cooling and condensation section, 7. Separation flask, 8. furnace jacket.

Table (2): Operation conditions of hydrodesulfurization process experiments

2.5 Test methods and evaluation equipment:

Catalyst evaluation equipment that was used for characterization of catalyst which are indicated below, where different instruments procedures were utilized according to ASTM standard, Table (3) lists all physical and chemical specifications of the catalyst.

2.5.1 BET Surface Area and Texture Properties:

The activity of the catalyst support is greatly influenced by the internal surface area and pore volume it comprises. A higher surface area leads to more active sites, which in turn increases the activity of the catalyst. The BET surface area and total pore volume of $CoMo\gamma-Al₂O₃$ catalyst were 203 m²/g and 0.4026 g/cm³ respectively. The N₂ adsorption/desorption isotherm obtained was assigned to type IV shape according to IUPAC classification [17],[18]. The measurements were conducted using nitrogen adsorption with micromeritics ASAP2020. The samples were analyzed using nitrogen as the adsorbate at liquid nitrogen temperature. The instrument automatically calculated the BET surface area and pore volume of the samples using N_2 isotherm, and the results were recorded on the computer attached to the instrument. Prior to the measurements, the samples were degassed under vacuum at 200-250°C for 4-8 hours.

2.5.2 Bulk density:

Powdered, granular, or flaky materials tapped density is greatly influenced by the way the particles are packed together. As the particles are tapped, they gradually pack more efficiently, leading to a decrease in powder volume and an increase in tapped density. The tested bulk density of this type of catalyst was found to be $0.756 \text{ cm}^3/\text{g}$. The test was conducted using an auto tap density analyzer from Quantachrome Instruments, USA, the test method adheres to the ASTM B527, D4164, and D4781 standards, which are located in the refining department at the Petroleum Research and Development Center.

2.5.3 Crush Strength Resistance:

The test on the grain crushing strength for commercial catalyst Co-Mo/ γ -Al₂O₃ using the Crush SP – Crush Strength testing device from MATEC materials technologies, USA. which is compliant with ASTM D4197 and ASTM D6175 standards,the average crush strength of about 40 pellets tested was 12.5 N/mm.

2.5.4 Loss on ignition:

The catalyst was tested for one hour at 650°C to lose weight. The tests are used in inorganic analytical chemistry, especially in mineral analysis. It involves a severe heat raising (igniting) of a sample of material at a certain temperature, enabling the volatile substance to escape, until its mass stops to change. The last loss of combustion was 1.8wt% with the Carbolite 1500°C furnace.

2.5.5 Metallic Composition:

The active metals composition was tested by handling atomic absorption technique located in analytical laboratories of petroleum research and development center, for the catalyst were 2.95 wt% of CoO according to ASTM D-72600-20, while 7.65wt% of MoO₃ these metals were conducted using vogel 575, IMOA method ,0.19% of Na₂O was tested according to ASTM D-5863.

2.5.6 Sulfur content:

The sulfur content of gasoil feedstock and hydrotreated products were determined by the Sindie OTG sulfur analyzer which is in Refining Department, PRDC; which provides tests for ULSD and gasoline and other types of fuels and crude oil. a Monochromatic WD XRF per ASTM D7039 is used for analyzer and is compliant with ISO 20884. The sulfur content results for the two feeds were 10432 & 19067 ppm respectively.

Characteristics	units	value
Bulk Density	gm/cm3	0.756
Crushing Strength	N/mm	12.5
BET surface area	$m2\$ gm	203
Pore volume	$cm3\$	0.4026
Ignition Loss	@650°C - 1 hr wt%	1.8
MoO ₃	$wt\%$	7.65
CoO	$wt\%$	2.95
Na2O	$wt\%$	0.19

Table (3): characterization of CoMo/ γ -Al2O³ catalyst

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3. Results and Discussions:

3.1 Effect of Temperature:

3.1.1 High sulfur gasoil:

HDS activity was studied through the effect of temperature as demonstrated in Figure (3). High sulfur gasoil content is 10432 ppm as sulfur removal is increased from 4565.22 to 3478.26 ppm (56.24 % to 66.66 %) with increasing temperature from 300° C to 375° C respectively at liquid hourly space velocity (LHSV) of 1 hr^{-1} and constant pressure of 35 bar. In the same trend, the sulfur removal was increased from 8316.45 to 7120.12 ppm (20.28 % to 31.75%) at liquid hourly space velocity (LHSV) of 4 hr^{-1} and at the same range of temperature.

3.1.2 Low sulfur gasoil:

HDS activity for sulfur removal from low sulfur gasoil feedstock having 1967 ppm sulfur content was also tested using the same catalyst and at the same operating conditions. It can be observed from Figure (4) that the sulfur removal increased from 832.12 to 309.44 ppm (57.71 % to 84.27 %) with increasing temperature from 300° C to 375° C respectively at liquid hourly space velocity of 1 hr^{-1} and constant pressure of 35 bar. In the same trend, the sulfur removal was increased from 1516.13 to 1128.56 ppm (22.95 % to 42.65%) at liquid hourly space velocity of 4 hr^{-1} at the same range of temperature.

Table (4) indicates the sulfur removal values. The implications of these results are discussed herein, in general; the percentage of sulfur removal in wt.% is increased with increasing the temperature of reaction from 300 to 375 °C at constant LHSV for the Co-Mo/ γ -Al₂O₃ catalyst, this may be attributed to the increase of active sites.

Reference [19], found that the rate of reaction to remove complex sulfur compounds increases with temperature due to the increase in active internal molecular motions.

This suggests that hard conditions are not necessary for the reaction to occur with hydrogen. "Reference [20], [21], discovered that surpassing 300° C in temperature can cause the hydrocarbon component to dissociate, which leads to a reduction in the synergistic effect of the solid catalyst. This, in turn, results in a significant improvement in the reaction's efficiency and a decrease in sulfur component conversion[22].

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Fig. (3): Effect of Temperature on sulfur Fig. (4): Effect of Temperature on sulfur **removal for high sulfur gasoil removal for low sulfur gasoil**

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Table (4): Sulfur removal results

3.2 Effect of liquid hourly space velocity:

Effect of LHSV on sulfur removal percentage was studied using $1, 4 \text{ hr}^{-1}$ at temperature range 300 and 375^oC with 35 bar pressure and 200/200 cm3/cm3 H₂/HC ratio. Figures (5) & (6) show that as a general trend, the optimal percentage of sulfur removal increases when the LHSV is reduced to 1 hr⁻¹, at 375°C, the percentage of sulfur removal is 66.66% and 84.27% for high sulfur gasoil and low sulfur gasoil feedstocks, respectively. The Liquid Hourly Space Velocity (LHSV) is a ratio that compares the hourly volume of liquid feed to the volume of catalyst in a packed bed reactor[23]. As LHSV increases, the residence time of reactants in the reactor decreases, which means that there is less time for the reaction to occur. This can lead to lower sulfur removal efficiency, especially for high sulfur gasoil, as observed at LHSV of 4 hr⁻¹

compared to 1 hr⁻¹ at different temperatures. When the Liquid Hourly Space Velocity (LHSV) decreases, the amount of feed contacting the same quantity of catalyst per unit time is reduced. Conversely, when LHSV increases, a greater amount of feed passes through the reaction per unit time. These observations agree with the results of Steiner and Blekkan[24]. Sulfur compounds can competitively reduce catalytic active sites and poison the catalyst, leading to a reduction in hydrogenation activity [25],[26].

Fig. (5): Effect of LHSV on sulfur removal Fig. (6): Effect of Temperature on sulfur for high sulfur gasoil removal for low sulfur gasoil

3.3 Effect of Pressure:

In this part, we will illustrate the effect of pressure that was studied at only 35 bar because of the lack of time allocated to run extra experiments so, we decided to not investigate on other different values of pressure.

It is notable that 35 bar pressure is considered the optimal value for sulfur removal in the hydrotreating process. As per Syed T. Hussain et al.'s observations [27], increasing pressure leads to more sulfur removal by increasing the hydrogenolysis of sulfur compounds. Additionally, Debajyoti Bose[28], found that increasing pressure decreases coke formation. The findings revealed by the effect of pressure are worth discussing, as this phenomenon can be explained by Henry's Law (C=kP), where c represents the concentration of dissolved gas. According to k, gas dissolution is directly proportional to its partial pressure above the liquid. Raising the H_2 partial pressure increases the concentration of H_2 in the liquid phase, which enhances hydro-treating activities. The pressure is intended to break down the bonds between

sulfur compounds and hydrocarbon molecules. Conversely, if the H_2 partial pressure falls below the design level, catalyst deactivation can occur due to coke formation [29].

3.4 Effect of Active Metal and Promoter:

The tested percentage of active metals is demonstrated in Table (3) for the commercial catalyst were 7.65 $\&$ 2.95 wt% for MoO₃ and CoO respectively, while it is usually should be within the range of 12 and 4 wt% for MoO₃ and CoO respectively. The relatively low wt% of the active metal and promoter in this catalyst might be the reason to reduce the HDS activity, especially for the high sulfur gasoil feedstock.

Active metals such as Mo, Co, and Ni have been identified as effective catalysts for removing sulfur compounds. Molybdenum disulfide $(MoS₂)$ is a required component of the catalyst system,since it can dissociate hydrogen molecules, adsorb reactant molecules, and release sulfur as hydrogen sulfide reversibly, it is highly effective [30]. Molybdenum is highly resistant to sulfur poisoning and has been shown to participate in selective oxidation [31].

The layer structure of $MoS₂$ is responsible for its catalytic activity. Catalytic sites are situated at the edges of the slab, where sulfur derivatives adsorb near an edge site and react with hydrogen atoms to produce hydrocarbon and hydrogen sulfide [32]. The catalyst is likely to undergo a phase transition, leading to different kinetic parameters. It is concluded that a robust interaction between the metal sulfide and sulfur component is crucial for high HDS activity [33]. It is interesting to note that maximum sulfur removal achieved were 66.66 % and 84.27% in both high and low sulfur gasoil feedstocks respectively, at optimal conditions (LHSV 1 hr⁻¹, Temp. 375 & 35 bar pressure), that used within the aforementioned active metal percentages.

3.5 Effect of Catalyst Support Surface Area:

High surface area (203 m²/g) of the tested catalyst contributed in the increase of the efficiency of HDS% as superior results were seen in comparison with catalysts that has lower surface area. As previously mentioned, high surface area promotes selective edge-bonding of the catalyst and favors a high metal-edge/S-edge ratio, which enhances the sulfur removal process. A comparable pattern of results was observed by [34] Laurenti et al, [35] Abdul Razak, demonstrated unique behavior (intrinsic activity in HDS and selectivity) for various catalysts with high surface area, which is related to a higher dispersion of the active phase in catalyst interactions.

4. Conclusions:

The overall behavior of the HDS process of gasoil feedstock showed an increase in sulfur removal with increasing temperature from 300 to 375° C and decreasing LHSV from 4 hr⁻¹ to 1 hr⁻¹, other effects of liquid hourly space velocity (LHSV), pressure, active metal and promoter, and catalyst support surface area on the sulfur removal efficiency in hydrotreating processes were also investigated and compared, the findings indicate that increasing temperature and decreasing LHSV lead to higher sulfur removal percentages. Additionally, increasing pressure enhances hydrogenolysis of sulfur compounds and reduces coke formation. The presence of active metals such as Mo and Co, as well as a high catalyst support surface area, also contribute to improved sulfur removal efficiency. Overall, optimizing these factors can significantly enhance the hydrotreating process for sulfur removal in gasoil feedstocks. This study have verified that using this catalyst produces good results and proved that it could serve to reduce sulfur compounds in gasoil although it was designed to process sulfur in kerosene hydrotreating units.

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Abbreviations

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