

Characterization of Fresh Oil Hydro Treating Catalysts

Jamal M.Amous

Chemical Engineering Department, College of Engineering, University of Hail, Saudi Arabia

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Abstract Catalysts are of great importance in catalytic processes. Key features of oil hydrotreating catalysts are highlighted. These catalysts play a significant role in removing impurities, as sulfur and other hetero-atoms existing in these oil fractions. These catalysts are composed of mainly, molybdenum salts spread in the porous structure of the carrier, mainly γ -Alumina (γ -Al₂O₃). Other metal salts supporting the action of the catalytic activity of Molybdenum, as Cobalt, Nickel, are added. The first step in the process of catalyst production is the drying of the wet salts mixture to remove moisture. The oxidic precursor is produced by the calcination of the dried mixture. The choice of the appropriate catalyst is based on its ability to maintain a high level of activity for long periods before re-activation. This ability depends on the chemical composition and on the porous structure of the carrier, which ensures the appropriate properties such as the density of active centers, particle strength, and porous structure parameters. Also, the catalyst resistance to chemical poisons destroying active centers in particular, is considered as a limiting factor in selecting the catalyst.

Keywords Co-Mo Catalysts, Hydro treatment, Porous structure, Promoter, Surface Chemistry, Activity

1. Introduction

The hydrotreatment of oil fractions is accomplished by the catalytic reaction of hydrogen with hetero-atoms present in petroleum fractions. Sulfur is the main harmful hetero atom present in these fractions. Other heteroatoms present are N, O, Ni, V. These atoms are removed by the catalytic hydrotreatment producing compounds of these hetero atoms bonded with hydrogen. For this purpose, huge amounts of catalysts are consumed annually in the widespread hydrotreatment units all over the world [1]. Hydrotreatment for refined products is accomplished efficiently under high temperature and pressure in the presence of hydrogen and a suitable catalyst having enhanced and controlled cracking activity [2].

From a commercial point of view it is necessary to consider the compositions of the cobalt –molybdenum and nickel- molybdenum carried on γ -Alumina support. The

Ni-Mo combination became increasingly important in situations where hydrogenation is desired. The nature of the chemical compounds present on the specific surface of the catalyst, determine both the selectivity and activity mode of the catalyst itself. Occelli and Rennard [3] showed that a supported Ni–Mo catalyst is active for hydrogenation-hydrocracking of vacuum gas oil feed stocks. In previous works, Merida et.al [4] described the method of preparation and the surface properties of fluorinated alumina-zirconium phosphate materials, as well as their use as supports for preparing Ni-Mo catalysts. These catalysts proved to be highly active for the hydrogenation reactions [5].

Investigating the hydrotreating catalysts, M. de Jong et al., performed surface XPS analysis on catalyst samples made by impregnating thin films of Silica (SiO₂) and γ -Alumina carriers, with complexes of Cobalt and Molybdenum, found out that, MoS₂ formation precedes the formation of cobalt sulfides at specified temperatures and that the performance of the tested catalysts is as those for catalysts with similar high specific surface areas [6].

Chemical properties depend on the active material's nature, concentration and dispersion on the carrier. The Molybdenum (Mo) sulfide acting as the catalyst and cobalt (Co) acting as promoter and stabilizer for the catalytic activity of Mo sulfide catalyst [7]. The preparation procedure and the conditions applied during the calcination have an important role on the determination of the final porous structure and on the nature of the different chemical species present. These processes have a direct and significant impact on the behavior of the final catalyst. The reduction and presulfidation processes are not less important than the calcination process. Reduction and presulfidation operations are usually carried in situ.

2. Chemical Composition of Hydro-treating Catalysts

Oil hydrotreating catalysts contain 2.5 to 5.0 wt% of the promoter which is usually Cobalt or Nickel oxides, while the mass ratio of the basic constituent, the Molybdenum oxide, is in the range between 10 to 15 %. It must be mentioned that Tungsten can replace Molybdenum, but the high cost of Tungsten is the main factor that prevents the wide

application of Tungsten in these catalysts.

The mass fraction of the carrier which is usually γ - Al_2O_3 is in the range between 80-86.5 wt%. Ahuja et al. [8] concluded that chemical composition of the catalyst affects strongly the chemical activity during the hydro desulfurization of Thiophene dissolved in Toluene. Also, they observed the dual Mo-Ni is effective in the cases where hydrogenation is desired and that the most suitable duals for hydro-desulfurization is that containing Mo and Co compounds.

Thermodynamic phase equilibrium curves support that under the applied operating conditions in Hydrodesulfurization (HDS) processes, the MoS_2 and Co_9S_8 are the most stable constituents, where little amounts of Hydrogen Sulfide are sufficient to convert all the Mo and Co oxides to the corresponding sulfides.

Richardson [9] studied the magnetic properties of various catalysts with cobalt and molybdenum compounds and concluded that unsulfided catalysts can be considered as mixtures of Al_2O_3 , CoAl_2O_4 , CoO , MoO_3 , CoMoO_4 , and a "complex Co-Mo oxide". The active components of this mixture are those in which cobalt exists in an octahedral arrangement of oxide ions, e.g., CoO , CoMoO_4 and the Co-Mo complex. Tetrahedral cobalt, as in CoAl_2O_4 , is presumed inactive. Ashley and Mitchell [10] concluded that Co-Mo catalysts contain cobalt (II) in about equal amounts of tetrahedral and octahedral configurations. Ashley and Mitchell detected no evidence of the existence of well-defined compounds in the catalyst. Richardson [9] and Ashley and Mitchell [10] reconciled between these two views, first by considering the catalyst as a mixture of compounds in a formal sense, second, in the hierarchy of activity of octahedral Co., Richardson [9] considered the CoO and CoMoO_4 to be only moderately active, while the unspecified Co-Mo complex is stated to be the true catalyst. The fraction of this active complex was determined by magnetic measurements [11].

The chemical constituents of HDS catalysts were determined by Richardson [9] referring to their drying and calcination procedures. Richardson found out that at lower calcination temperatures, the Co forms are CoO and CoAl_2O_4 . As the temperature of heat treatment increases, the concentration of tetrahedral CoAl_2O_4 increases at the expense of CoO , and the magnetic moment falls. At about 650°C , CoMoO_4 begins to be formed competing favorably with CoAl_2O_4 , and the magnetic moment increases again. Similar variations in the magnetic behavior of cobalt-alumina preparations were noted by Ashley and Mitchell [10] and by Greenwald [12] at somewhat higher temperatures. Greenwald [12] found his cobalt-alumina preparations, treated at 1500°C , to be mixtures of tetrahedral and octahedral Co, while Ashley and Mitchell [10], who had calcined their cobalt aluminate at 1000°C , deduced from magnetic measurements that the calcined cobalt aluminate is 100% tetrahedral cobalt. Richardson found that the concentration of active Co and Mo compounds is dependent on the initial Co-Mo ratio, as well as on the

calcination-treatment temperatures.

The partial discrepancies between the results of the experimental surface investigations and theoretical thermodynamic data of the hydrotreating catalysts may be attributed to the probability that part of the Cobalt is bonded permanently to the surface of the carrier making the sulfidation of the cobalt atoms more difficult. Also, conducting the processes of reduction under unfavorable conditions may lead to the formation of Co-Mo compounds which are difficult to convert to sulfides. It must be mentioned also, that the high sensitivity of the sulfides to air Oxygen, may convert sulfides into the corresponding Co-Mo oxides upon taking the catalyst out of the reactor for surface analysis and examination.

Thus, the difficulty in obtaining reliable results concerning the chemical composition of the active phase of the catalyst led the researchers to refer back to basics supporting that the Molybdenum and Cobalt sulfides are the most stable compounds and these sulfides are the heart of the active phase of the catalyst. This conclusion is supported by the observed full similarity between the action of promoted catalyst carried on a porous carrier (γ - Al_2O_3) and the unsupported catalysts MoS_2 and Co_9S_8 .

3. Catalyst Preparation and Generation of the Catalytic Activity

A solution of Ammonium Paramolybdate salt is used to impregnate the γ -Alumina with the Molybdenum salt. The mixture is subjected to a drying process, and then the Cobalt Nitrate solution is added to impregnate the mixture with the Cobalt salt. Calcinations at moderate (650 - 800°C) temperatures process is then necessary to convert the solid mixture to the oxidic precursor of the catalyst.

The oxidic precursor is placed in the reactor for the reduction process which is to be carried under certain conditions of partial hydrogen pressure, H_2 flow rate and temperature. Then the reduced catalyst is sulfided in situ by the hydrogen sulfide or the organic sulfur compound or carbon sulfide [13].

Hamid A. Al-Mergen testing different HDS catalysts prepared by different methods arrived to the conclusion that applying the organic matrix combustion (OMXC) methods lead to catalysts which are more active up to approximately 60% as compared with the corresponding catalysts prepared by mechanical and conventional impregnation methods [14].

Usually, chemical materials are added to the catalyst, such as citric acid, silicon, sodium, boron and fluorine, to the impregnated carrier with Molybdenum and Cobalt for improving the performance of the catalyst [15-17]. Ammus [18] studied the deactivation phenomena associated with the application of Co-Mo / γ - Al_2O_3 catalysts and concluded that catalyst deactivation depends upon the porous structure parameters and the rate of coke and metals deposition on the catalyst particles. Deactivation due to Coke deposition is reversible and can be recovered, while metals deposition causes irreversible loss in catalyst activity [19].

Table 1. Physical and chemical features of CoO –MoO₃ catalysts with different supports [20]

No.	support	Composition*Wt%		color	Surface area m ² /g	Atomic ratio S _{total} /Mo**
		MoO ₃	CoO			
1	γ-Al ₂ O ₃	4	-	white	160	1.41***
2	γ-Al ₂ O ₃	8	-	white	159	1.81
3	γ-Al ₂ O ₃	12	-	white	152	2.00
4	γ-Al ₂ O ₃	6	4	gray	150	-
5	γ-Al ₂ O ₃	8	4	Blue gray	147	-
6	γ-Al ₂ O ₃	12	4	blue	144	2.38
7	SiO ₂	4	-	Pale yellow	272	1.82
8	SiO ₂	8	-	Pale Yellow green	247	1.95
9	SiO ₂	12	4	Violet gray	223	2.4
10	SiO ₂	12	6	Dark gray	217	2.61

*: balance is γ-Al₂O₃

** :analyzed after sulfidation : 50 cm³/min,
(NTP H₂S/H₂), volume ratio 1/6, 400 °C,
duration 2h.

***: MoO₃ /γ-Al₂O₃ : samples used for
analysis were supported on ketjen fluid powder
γ-Al₂O₃ grade B.

Typical physical and chemical features of some oil hydrotreating catalysts are shown in Table 1.

In Table 2, L. Coulier et.al, [21, 22], found out that HDS catalytic activity of promoted catalysts are higher than that for un promoted catalysts, while the hydrogenation selectivity is lower for the promoted catalysts compared with that for the un promoted samples. Also they observed that for supported and unpromoted catalysts, activity increases in the direction SiO₂ < Al₂O₃ < TiO₂.

Table 2. Thiophene HDS activity (%) and (HYD) selectivity of Al₂O₃ supported catalysts

Catalyst	HDS activity%	HYD(Butne/products)
Mo/Al ₂ O ₃	0.37	0.04
CoMo/Al ₂ O ₃	0.72	0.01
NiMo/Al ₂ O ₃	2.84	0.02

In Table 3, De Beer et.al, [23] testing promoted and un promoted Mo/Al₂O₃ catalysts on thiophene hydro-desulfurization found out that catalytic activity increases, by increasing the MoO₃ percentage and that promoted Mo catalysts showed higher activities than the un promoted catalysts.

Table 3. Effect of promoter and MoO₃wt% on catalyst activity in thiophene desulfurization

MoO ₃ , wt%,	4	6	10	12
Conversion %, MoO ₃ /Al ₂ O ₃ *	3.8	8	21	23
Conversion %, CoO-MoO ₃ /Al ₂ O ₃ *	4.2	13.9	23	28

*: 180 mg catalyst, pre-reduced at 400°C, 50 cm³/min, NTP H₂ with 6 vol % Thiophene, run duration 1.5 h at 400°C.

4. Conclusions

Oil hydrotreating catalysts play important role in the chemical industry of oil fractions hydrotreatment. Fractions contain impurities as sulfur, hetero-atoms, metals, the removal of these impurities is essential. These catalysts must have specifications that ensure catalysts long life, high activity and maintaining their activity for long periods. Pore size distribution, pore mean diameter, pore void fraction, specific surface area, particle mechanical strength, chemistry of pore walls with the active centers and dispersed chemical compounds are the main parameters affecting catalysts performance. Unsupported catalysts MoO₃ show activities strongly dependent on the calcination temperature. Its activity drops as the calcinations temperature increases. Supported catalysts showed activities at higher levels depending on their high specific surface area. The promoting effect of cobalt can be clearly seen from the high Sulfur/molybdenum contents and from the higher desulfurization reaction rates accompanying the action of the promoted and supported Molybdenum catalysts against the unsupported catalysts.

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