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On the effects of calcination conditions on the surface and catalytic properties of γ-Al_2O_3-supported CoMo hydrodesulfurization catalysts

Y.S. Al-Zeghayer [a], B.Y. Jibril [b,*]

[a] *Chemical Engineering Department, College of Engineering, King Saud University, P.O. Box 800, Riyadh 11421, Saudi Arabia*
[b] *Petroleum and Chemical Engineering Department, Sultan Qaboos University,*
P.O. Box 33, AlKhod, PC 123, Muscat, Oman

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Abstract

A series of alumina-supported cobalt-molybdenum catalysts were prepared by the incipient-wetness method. Different calcination temperatures (673–873 K) and durations (2–96 h) were used to obtain the catalysts. Samples of the catalysts were characterized by X-ray photoelectron spectroscopy (XPS). Depending on the calcination condition, two forms of molybdenum (Mo^{4+} and Mo^{6+}) and sulfur (S_1 and S_2) were identified. The ratio of Mo^{4+}/Mo^{6+} appeared to be affected more by the duration than by the calcination temperature. However, increase in the calcination temperature (673–873 K) led to an increase in the amount of cobalt interacting with the alumina support, with a corresponding decrease in Co-Mo-S ensembles. The catalysts were tested in hydrodesulfurization of dibenzothiophene (DBT). The catalyst with 24 h calcination time exhibited the highest DBT conversion. For the catalyst at a conversion of 38.8%, biphenyl (BP) and cyclohexylbenzene (CHB) were produced with selectivities of 82.8 and 17.2%, respectively. When either the calcination temperature or duration was increased, a smaller amount of CHB was observed. This has been associated with changes in the catalysts' surface properties.

Keywords: Hydrodesulfurization; Dibenzothiophene; CoMo/Al_2O_3; Calcination Biphenyl; Cyclohexylbenzene; X-ray photoelectron spectroscopy

1. Introduction

The present and likely future further restrictions on environmental pollution have spurred the research activities in catalytic hydrodesulfurization (HDS) of petroleum feedstock. The HDS is used in petroleum refining and processing to remove sulfur; which is one of the sources of air pollution. It also prolongs catalysts' life and decreases corrosion of the process equipment. Sulfided transition metal catalysts have been widely researched and shown to be effective for the reaction [1–5]. By far the most exhaustively investigated catalyst for the reaction is Co-Mo/Al_2O_3. It has been suggested that the active metal center occurs at coordinatively unsaturated species in the structure of MoS_2 lamellae [6]. In addition, for alumina support, several levels of chemical interaction have been shown to exist between amorphous alumina and the transition metal oxides [7,8]. Depending on the consequence of the interactions, some of the species formed only transiently, some are moderately stable and some are so highly stable as to resist complete sulfidation. This has led to different degree of activities or promotion of the catalysts.

The activities of CoMo-based catalysts have been shown to be improved by the appropriate choice of the catalyst preparation conditions [9–17]. The manner of impregnating the active components [12–14] and the calcination conditions [12,15–17] were found to be important variables for optimizing the activities. In view of this, we considered it of interest to explore the influence

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* Corresponding author. Tel.: +968 24413333x2582; fax: +968 24413416.
E-mail address: baba@squ.edu.om (B.Y. Jibril).

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of calcination conditions on the performances of γ-alumina-supported CoMo catalysts. In this report, we present results of a study on the effects of calcination time and temperature on the physicochemical and catalytic properties of the catalyst for hydrodesulfurization of dibenzothiophene.

2. Experimental

2.1. Catalysts preparation

The catalyst support was γ-alumina supplied by Norton/Hydronyl (UK). Its chemical composition was: $Al_2O_3 > 99.85$, $SiO_2 < 0.09$, $Na_2O < 0.015$ and $Fe_2O_3 < 0.06$. Its physical properties were: apparent porosity = 65–75%, bulk (particle density) = 1.0–1.2 g/cm^3, apparent specific gravity = 3.3–3.5, surface area = 200–240 m^2/g and total pore volume = 0.57–0.67 cm^3 Hg/g. The support was grinded and sieved to give a size range of 36–72 mesh. The chemicals used in the catalyst preparation were ammonium molybdate (VI) tetrahydrate, $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ and cobalt (II) nitrate hexahydrate, $Co(NO_3)_2\cdot 6H_2O$. The materials used in the catalyst testing were dibenzothiophene, tetralin, decalin and dimethyldisulfide $(CH_3)_2S_2$. Table 1 gives typical properties of the materials. All chemicals were of analytical grade quality as supplied by Aldrich Chemical Company.

A series of sulfided cobalt molybdate catalysts was prepared by co-impregnation of γ-Al_2O_3 with solutions containing appropriate amounts of cobalt nitrate and ammonium molybdate. Amounts of salts enough to wet the support (2.2 ml) were dissolved in distilled water. The concentration of the solution was adjusted to give sample containing 15.4 wt% of MoO_3 and an amount of cobalt to obtain Co/Mo ratio of 0.4. The support was dried at 373 K for 2 h. It was then co-impregnated with a solution for 30 h. The samples were dried in air (at 323 or 393 K) and calcined at different temperatures (673 or 873 K) and for different durations (2, 8, 24 or 96 h). But in all cases the calcination temperature was reached at a slow rate of 1 K/min. The calcination decomposes the precursor salts to non-active oxidic form. The oxide form was sulfided to catalytically active form using a solution of dimethyldisulfide (2 wt% sulfur equivalent) in decalin solvent at 323 K and atmospheric pressure until H_2S breakthrough was observed. Hereafter, the catalysts are represented based on their respective calcination temperatures and durations. For instance, that the catalyst is represented as C673/24 indicates that it was calcined at 673 K for 24 h. In this report, four catalysts are considered. They are: (i) C673/24, (ii) C873/24, (iii) C673/96 and (iv) C673/2. The first two were dried at 393 K while the other two were dried at 323 K prior to calcination.

Table 1
Properties of some of the compounds used

Compound/properties	Tetralin	Decalin	DBT	DMDS
Molecular weight	132.21	138.25	184.27	94.20
Melting point (K)	242.00	231.00 (*cis*) 238.00 (*trans*)	372.00	188.30
Boiling point (K)	479.00	466.3 (*cis*) 458.3 (*trans*)	605.00	382.7
Density (g/cm^3)	0.973	0.8963	–	1.06
Flash point (K)	350.00	331.00	–	280.00
Auto ignition temperature (K)	657.00	523.00	–	–
Vapor density	4.55	4.76	–	3.24
Explosion range (%)	0.8–5	0.7–4.9	–	–

2.2. Catalysts characterization

The XPS spectra of the samples were measured and recorded on a VG Escalab 200-C spectrometer using Mg Kα radiation (1253.6 eV). The base pressure in the analysis chamber was kept in the range 5×10^{-10}–1×10^{-9} mbar. Energy scales were referred to the C 1s peak, which was assumed to have a binding energy of 285.0 eV. The sample treatments were all carried out in a high-pressure gas cell directly connected to an ultra high vacuum system. The samples were pretreated in synthetic air (1.1 bar, 773 K) in order to obtain comparable and reproducible surface conditions. All reduction treatments were carried out with 20% H_2 in N_2 (1.1 bar, 773 K).

2.3. Catalysts testing

The catalyst evaluation was carried out by passing solutions containing dibenzothiophene at a concentration of 1 or 2 wt% in the hydrogen donor solvent (tetralin) through a fixed bed containing 1 g of the catalyst particles. The use of a hydrogen donor solvent ensured that an ample supply of hydrogen was readily available for the reaction without any need for adding gas phase hydrogen. The reaction was conducted over the temperature range of 590–633 K at a pressure of 10 MPa; the flowrates required to give measurable conversions were between 0.5 and 2 g/min. The catalyst was initially sulfided before testing. When sulfiding was completed, flow was switched to the solution containing dibenzothiophene in tetralin that was pumped from a storage tank using a pulse free HPLC pump. The mixture was then preheated to the required temperature before passing to a temperature-controlled reactor; a stainless steel tube 15 cm in length and 4.5 mm in internal diameter containing sieved catalyst particles. Quenching then took place before pressure reduction and analysis. The analysis was done using a Pye 104 model gas chromatography (GC) fitted with a capillary column (0.25 mm internal diameter × 0.319 mm outside diameter); a flame ionization detector (hydrogen at 45 ml/min and air at 800 ml/min). Helium (230 ml/min) was used as a carrier.