Barium as a secondary promoter for Ni–Mo catalyst supported on alumina

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The addition of barium, as a secondary promoter, to alumina-supported Ni–Mo (nickel oxide–molybdenum oxide) catalyst was investigated. The results of thiophene hydrodesulfurization experiments carried out on the catalysts show that the addition of small amounts of barium (<0.7 wt%) leads to a significant improvement in their thiophene hydrodesulfurization. Experiments carried out in an autoclave also show that the presence of barium leads to improvement in the properties of the products obtained after gas oil processing. These results may help in developing catalysts with improved activities, as only a small amount of barium secondary promoter is required.

Keywords: active species, barium, alumina, hydrodesulfurization (HDS), secondary promoter, hydrocracking, cumene, thiophene, gas oil, nickel oxide–molybdenum oxide catalyst system

1. Introduction

It has been shown that the addition of a secondary promoter to a Ni–Mo supported catalyst has led, in some cases, to an enhancement of catalytic activity [1,2]. For example, the addition of fluoride has led to a significant increase in cumene cracking activity for the catalysts supported on alumina [3,4]. Since barium has not been extensively investigated as a secondary promoter, it was decided that it should be investigated. Barium was chosen for investigation because it was reported in a patent that the addition of a low loading of barium to γ-alumina leads to an increase of hydrodenitrogenation (HDN) activity for a gas oil feed [5]. Since this is an isolated report, and since the active species for HDN and hydrodesulfurization (HDS) have been shown to be the same [6], the addition of small loadings of barium to the catalyst should lead to an increase in HDS activity. It was therefore decided that the activity of the Ni–Mo supported catalyst for hydrocracking and HDS reactions with and without this promoter should be investigated. Real feed stock studies (using gas oil) were also carried out on the catalysts using an autoclave, and the improvement in the characteristics of the oil after reaction is investigated.

Different loadings of barium were added to the support by the incipient wetness method, either by adding the barium first and later adding the active species (Mo) and primary promoter (Ni) to give the BNM series, or by adding barium after the addition of the other components (NMB series). It has been shown previously, for fluoride, that the order of secondary promoter addition may affect the activity of the catalyst system [7].

2. Experimental

The γ-alumina used as support for the barium-promoted Ni–Mo catalysts was prepared by mixing 100 g of boehmite (AlOOH) with 30 ml of distilled water and mulling the mixture for about 5 min. Two further 10 ml additions of distilled water were made and the mixture was mulled again for 5 min after each addition. The mixture (powder) was then left to dry in air overnight and in the oven at 120 °C for another night. The powder was then calcined by drawing air through it at 500 °C for 4 h.

The metals (Ni, Mo) were added to the supports by the incipient wetness method. The required amount of $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ salt (to give 15% MoO_3 loading) was dissolved in 0.85 ml of distilled water and added to 2 g of the support and the mixture then was mulled together for about 2 min. $NiNO_3\cdot 6H_2O$ (to give 3% NiO loading) was also dissolved in 0.15 ml of distilled water and added to the above mixture. The mixture was mulled again for 3 min and then left to dry in air for 6 h after which it was transferred to an oven and dried overnight at 110 °C. The dried catalyst was then heated at 4 °C per minute from 25 to 500 °C, and then calcined at 500 °C for 4 h.

Barium was added to the Ni–Mo/γ-alumina catalysts also by the incipient wetness method using $BaCl_2$. The required quantity of $BaCl_2$ (to give the desired barium loading) was dissolved in 1 ml of distilled water and added to 2 g of the catalyst and the mixture was mulled for about 3 min. The same drying and calcination procedure was carried out as described above for the alumina support. For the BNM series of catalysts, the barium was impregnated before the metals, while for the NMB series, the metals were impregnated first.

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2.1. Cumene hydrocracking

The cumene hydrocracking studies were carried out in a fixed-bed, stainless-steel, continuous-flow microreactor. A mass of 0.150 g of catalyst (80–100 mesh) was sandwiched between layers of quartz wool in the reactor (15 mm i.d.), and was activated by passing either helium gas (for oxidic experiments) or 10% H_2S in H_2 (sulfided experiments) over it for 90 min while the reactor temperature was held at 500 °C. The temperature of the reactor was then reduced to 400 °C and cumene was passed over the catalyst from a presaturator held at $\sim$15 °C in a stream of hydrogen. The products were analyzed by an on-line HP 5890 gas chromatograph equipped with a TCD detector. Samples were taken and analyzed by the GC automatically every 20 min and the reaction was stopped after the feed had passed over the catalyst for 4 h.

The corrected areas for each of the products were obtained by deducting the amount of impurities (area) of each product present when cumene is injected into the GC prior to the start of the experiment from the total area for the particular product. The relative response factor (RRF) was determined by injecting known quantities of the product into the GC (under the same conditions as that used for the catalytic reactions) and then determining the absolute response factor (ARF) which is given by

$$\mathrm{ARF} = \frac{W_i}{A_i}, \tag{1}$$

where W_i is the amount of component i in moles, and A_i is the measured area of the peak of component i in the gas chromatograph obtained under the same conditions as during the catalysts testing runs. The relative response factor is obtained by dividing the response factor of the product by that of cumene.

2.2. Hydrodesulfurization (HDS)

HDS reactions were carried out over the metal-loaded, sulfided catalysts with the same reactor and detection system used for the cumene hydrocracking reaction. The only difference is that the bubbler was replaced by one containing thiophene. The same types of gases were used for activation and reaction as for hydrocracking. Samples were taken and analyzed by the GC automatically every 15 min. The usual products here are C_4 hydrocarbons (n-butane, 1-butene, *cis*- and *trans*-2-butene) which all have the same retention time. Their response factors are approximately the same and so the percentage thiophene conversion was calculated as

$$100 - \%\ \text{thiophene in the product} = \%\ \mathrm{C}_4\ \text{in product.}$$

2.3. Hydroprocessing

Gas oil hydroprocessing was carried out using an Autoclave Engineers 300 ml capacity Hastalloy C batch reactor. The experiment was carried out in three stages: sulfidation of catalyst, removal of excess sulfur, and the hydroprocessing procedure.

During sulfidation, 2 ml of carbon disulfide is added to 1 g of the catalyst in the reactor. The sulfidation was then carried out by using a hydrogen pressure of 1000 psi and a temperature of 440 °C. The sulfidation was allowed to proceed for 3 h under these conditions. The reactor was then allowed to cool to room temperature and the pressure released and all gases vented. After this, the excess sulfur was removed by re-pressurizing the reactor to 1000 psi with hydrogen and heating to 440 °C. The reaction was allowed to run for 3 h again, then cooled down to room temperature and the gases vented.

To initiate the hydroprocessing reaction, approximately 22 g of gas oil was added to the sulfided catalyst under an argon atmosphere (to prevent the oxidation of the catalyst by air). The catalyst and gas oil were then mixed together and the reactor pressurized to 1000 psi; the temperature then was raised to approximately 410 °C. The reaction was allowed to run for 3 h during which time the mixture was stirred continuously. After 3 h, the experiment was stopped and the reactor was allowed to cool down to room temperature. All gases are then vented off and the liquid product was separated from the solid (catalyst) by using a Pasteur pipette. The liquid sample was then analyzed by the methods described below to learn the extent of the improvement in the quality of the gas oil by the use of the particular catalyst.

2.4. Analysis of products

Carbon, hydrogen and nitrogen (C, H, N) analyses were carried out on the liquid sample using a CEC 440 Elemental Analyzer. The sulfur content was determined using an ANTEK 7000 analyzer and density was determined using a PAAR DMA 40 density-meter at 15 °C.

A Bruker ACE-200 NMR instrument was used to determine the amount of carbon present in the sample. The percentage of aromatic carbon in the sample is then taken as an indication of the aromaticity. An inverse gated decoupling pulse sequence with a delay time of 1 s was utilized. Samples were made by diluting the product with deuterated chloroform to give 40% v/v solutions. About 1 ml of 0.05 M of $\mathrm{Cr(acac)_3}$ was then added to act as a relaxation agent. 2000 scans are collected for each sample, so the analysis is always done overnight to allow for complete data collection. Using the deuterated chloroform triplet chemical shift at 77 ppm as a reference, the percentage aromatic content is estimated from the integrated area for aromatic carbon (160–110 ppm) and aliphatic carbon (60–5 ppm) regions.

3. Results and discussion

3.1. Surface area

The surface area of the NMB and the BNM samples is shown in table 1. It can be seen that the surface area decreases with increasing barium loading for both series. This may indicate that barium is blocking the pores of the catalysts.

3.2. Cumene hydrocracking reaction

The result of hydrocracking experiments, with the catalysts sulfided by passing a stream of H_2S/H_2 gas, and with the oxidic catalysts in helium is presented in tables 2 and 3. The first thing that should be noted is that the conversion is very small in all cases and, therefore, barium does not seem to affect the hydrocracking activity as much as fluoride, phosphorus, or other secondary promoters [8–12]. The insignificant improvement in activity, at least for this reaction, would not therefore justify the additional time and resources put into the extra preparation step involved in the addition of barium to the catalysts.

Table 1
Surface area for the barium-promoted catalysts.

Barium (wt%)	Surface area (m^2/g) NMB[a]	BNM[b]
0.0	159	159
0.1	149	155
0.3	148	152
0.5	144	148
0.7	129	139
1.0	128	134

[a] Catalysts prepared by impregnating Ni and Mo before Ba.
[b] Catalysts prepared by impregnating barium before Ni and Mo.

The results for the sulfided and oxidic BNM catalysts are presented in table 2. The first observation for the sulfided BNM catalysts is that the addition of barium (up to 1.5% loading) leads to a small enhancement in activity, compared to catalysts without barium. This increase in conversion is due to the increase in the amount of both α-MeS and benzene produced.

However, as the barium loading is increased above 0.1 wt%, conversion remains constant at 2.80 until 0.7 wt% barium has been added. Further increase in the loading of barium leads to a decrease in percent conversion. The reduction in conversion is due to the lower yield of benzene. This reduction in benzene yield may be explained as due to the reduction in the acid strength of the support in the presence of barium. Barium is less electronegative than aluminum (0.9 compared to 1.5 for aluminum) and so electron density will favor aluminum which will therefore make hydroxyl groups attached to aluminum less acidic and, thus, more difficult to release to the feed to form carbocation. The result shows that the presence of barium does not possibly lead to increased acidity but to increased dehydrogenation activity, as the amount of α-MeS produced in the presence of barium is more than that produced in its absence.

For the experiment carried out under oxidic condition, all the BNM catalysts show an improved activity over pure

Table 2
Cumene hydrocracking conversion and product distribution for BNM catalysts.

Catalyst designation	Cumene hydrocracking (oxidic)					Cumene hydrocracking (sulfided)				
	Conv. (%)	Product distribution[a]				Conv. (%)	Product distribution[a]			
		Benz	Et-Benz	α-MeS	others		Benz	Et-Benz	α-MeS	others
0	2.25	1.01	0.11	0.96	0.17	2.48	0.90	0	1.59	0
0.1BNM	4.35	1.40	0.22	1.66	1.08	3.36	1.25	0.27	1.84	0
0.3BNM	4.72	1.45	0.32	1.95	1.00	2.82	0.78	0.06	1.98	0
0.5BNM	6.12	1.14	0.20	2.82	1.96	2.84	0.40	0.16	2.27	0
0.7BNM	3.94	1.41	0.11	1.76	0.66	2.78	0.62	0.11	2.05	0
1.0BNM	3.43	0.91	0.12	1.86	0.53	2.70	0.58	0.12	2.00	0
1.5BNM	2.97	0.98	0.02	1.93	0.04	2.57	0.71	0	1.86	0
2.0BNM	2.81	0.89	0.20	1.72	0	2.23	0.39	0.13	1.71	0
2.5BNM	2.79	0.76	0.13	1.91	0	2.18	0.33	0.04	1.82	0

[a] Benz = benzene; Et-Benz = ethylbenzene; α-MeS = α-methylstyrene; others = mainly n-propylbenzene.

Table 3
Cumene hydrocracking conversion and product distribution for NMB catalysts.

Catalyst designation	Cumene hydrocracking (oxidic)					Cumene hydrocracking (sulfided)				
	Conv. (%)	Product distribution[a]				Conv. (%)	Product distribution[a]			
		Benz	Et-Benz	α-MeS	others		Benz	Et-Benz	α-MeS	others
0	2.25	1.01	0.11	0.96	0.17	2.48	0.90	0.00	1.59	0
0.1NMB	3.40	0.84	0.06	2.05	0.45	4.70	1.22	0.41	2.07	1.01
0.3NMB	2.77	0.62	0.04	1.79	0.32	3.52	1.29	0.09	2.05	0.08
0.5NMB	3.06	0.84	0.12	1.80	0.30	2.97	0.77	0.17	2.04	0.00
0.7NMB	2.35	0.69	0.04	1.61	0.01	2.60	0.52	0.00	2.08	0.00
1.0NMB	2.61	0.50	0.10	2.02	0.00	2.85	0.68	0.02	2.09	0.06

[a] Benz = benzene; Et-Benz = ethylbenzene; α-MeS = α-methylstyrene; others = mainly n-propylbenzene.

alumina. There is also an initial increase in conversion until 0.5 wt% barium has been added after which there was a decrease. Again, the main difference is in the amount of α-MeS produced, as the amount of benzene remains almost constant after the initial increase over the amount produced by catalysts containing no barium.

One interesting observation is that the conversion for the oxidic sample, in every case, is slightly higher than that of the sulfided sample. This is unusual, as previous work in our laboratory [4,13] has shown that hydrocracking experiments under oxidic conditions show lower conversion than under sulphiding conditions.

The result for the NMB catalysts is presented in table 3. The same trend is observed here as for the BNM series of catalysts – an initial increase in conversion over that observed for Ni–Mo/γ-alumina and as barium loading is increased further (above 0.1 wt%) conversion goes down. All the catalysts investigated have a higher conversion than the one without barium.

Compared to the BNM catalysts, conversion is higher for the NMB catalysts with the same barium loading. This may be due to the covering of some of the active species by barium in the catalyst with barium added after Ni and Mo. In addition, the higher activity may be due to lower deactivation of the catalyst.

For the oxidic NMB catalysts, the conversion ranges from 3.40 to 2.35% with no clear trend. However, the catalyst containing 0.1 wt% barium still has the maximum conversion. As explained above, the reduction in activity, with increased barium loading, may be due to the low electronegativity of barium compared to that of aluminum or it may be a surface area effect (see above). The blockage of the pores may lead to less area accessible to the feed and, therefore, reduced activity.

3.3. Thiophene HDS activity

The thiophene HDS activity of a series of catalysts containing different loading of barium oxide was carried out and the result is presented in figure 1. The result shows that the HDS activity is significantly increased by the addition of barium up to 0.3 wt% loading. As the loading is increased beyond 0.3 wt% the HDS activity then decreases. However, the activity is still higher than that of the catalyst without barium, at loadings up to 0.7 wt% barium. It should be noted that the increase in activity occurs even when the surface area is decreasing. This therefore shows that the increase in activity is not a surface area effect.

No explanation was given for the observed improvement in HDN activity by the addition of barium to Ni–Mo supported on γ-alumina in the only paper that reported the use of barium as a secondary promoter [5]. A plausible explanation is that the presence of low loadings of barium may have improved the dispersion of the catalyst on the surface. It is also possible that the orientation or the electronic structure of the active species is affected so that more active area is exposed to the feed. One other possible explanation is that the Ba may have helped in the formation of the active Ni–Mo–O species. The mode of action may be similar to that of fluoride on γ-alumina, which was shown to increase the HDS activity up to 1.7% loading after which there was a decrease [14]. The reason for the observed decrease in activity after 0.7 wt% loading is not clear, but it is possible that the presence of barium at higher loadings prevents the precursor to the active species "Ni–Mo–O" from being formed.

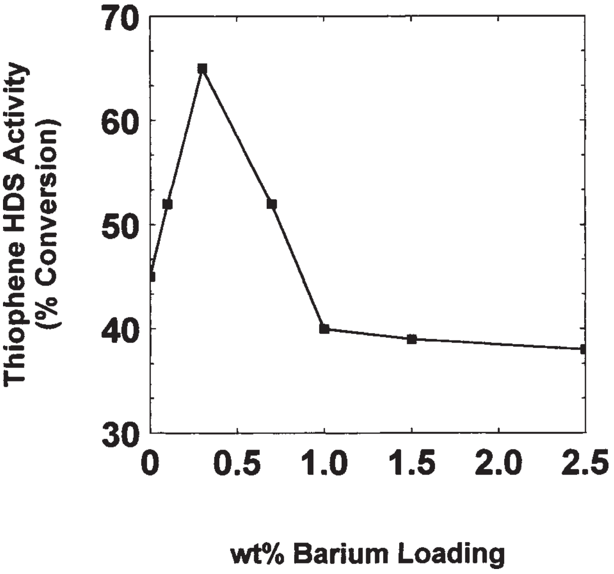

Figure 1. Thiophene HDS activity for Ni–Mo and Ba-promoted Ni–Mo catalysts supported on γ-alumina.

3.4. Hydroprocessing

Real feeds are far more complex than the model compounds used in the studies of the activity of catalysts. This is because they contain many compounds and the possibility of reactions or competition between the different compounds for the same active sites is very high. It is therefore necessary to do real feed stock studies to complement the model compound studies. This will help in gaining a better understanding of the processes going on during reaction.

The characteristics that are usually monitored are hydrogen to carbon ratio, % aromatic carbon, wt% sulfur, and the density of the feed. All these give an indication of the improvement that has taken place on the feed. The H : C ratio and % aromatic carbon provide an indication of the extent of hydrogenation of the feed, and density provides an indication of either hydrogenation or hydrocracking activity of the catalyst, or both. The % sulfur gives an extent of sulfur removal in the feed and will give an indication of the HDS capability of the catalyst. The higher the H : C ratio and the density, and the lower the % aromatics and wt% sulfur in the product, the better the catalyst.

The result for the BNM series of catalysts is presented in table 4. The first noticeable observation is that the density of the product from the catalysts promoted with barium is consistently lower than that of the unpromoted

Table 4
Properties of liquid products from hydroprocessing gas oil over the BNM catalysts.

Catalyst	Density (g/cm^3)	H : C	S (wt%)	Aromatic C (%)
Feed[a]	0.9921	1.44	4.48	40.0
0.0BNM[b]	0.9105	1.56	0.42	29.0
0.1BNM	0.9033	1.64	0.63	27.6
0.3BNM	0.9025	1.68	0.45	33.8
0.5BNM	0.9019	1.69	0.66	29.8
0.7BNM	0.9027	1.67	0.66	31.0
1.0BNM	0.9000	1.69	0.65	27.2
1.5BNM	0.9042	1.67	0.63	28.4
2.0BNM	0.8998	1.67	0.63	30.0
2.5BNM	0.9057	1.67	0.71	32.9

[a] Unreacted gas oil.
[b] 0.0BNM is Ni–Mo/Al$_2$O$_3$, 0.1 etc., is the wt% barium loading.

catalyst. This shows that the BNM series of catalyst are better hydrogenation/hydrocracking catalysts. The fact that they are better hydrogenation catalysts can be seen in the third column of table 4, where the H : C ratio for the promoted catalysts is approximately 1.65 for all barium loadings, and much higher than that of the unpromoted catalyst which is 1.56. This shows a very good improvement in H : C ratio when compared to the unreacted feed (1.44). The fact that the H : C ratio of the product for all loadings of barium is almost constant at 1.65 may explain why only low loading of barium is required for improved activity.

The sulfur removal capability of the promoted catalyst is good when one looks at the fact that it is reduced from 4.48% for the unreacted feed to approximately 0.65% for the promoted catalysts. However, the sulfur removal capability is lower than that of the unpromoted catalyst, except for the catalyst with 0.3 wt% barium, which shows comparable sulfur removal activity. It should be noted that the catalyst with 0.3 wt% barium is the most active catalyst for HDS (see above). The result of the sulfur removal activity is different from that in the presence of thiophene. Clearly, thiophene HDS is not a good model compound reaction to predict how barium promotes sulfur removal from real feedstock. It may also be possible that the barium HDS promotion is affected by carbonaceous residues. In this batch reactor, where products are not removed from the catalyst, this could be a problem.

The percentage aromatic carbon is lower for the product obtained using the promoted catalyst than for the original feed. However, the values vary from 27.2 to 33.8 for the promoted catalysts, while it is only 29.0 for unpromoted catalysts. The percentage aromatic carbon may give a good indication of the improvement on the feed, but it is still possible to have a high aromatic carbon content and have a good catalyst if the aromatics are found in the diesel fraction of the synthetic oil. This is because a high aromatic content is needed to have a high cetane number, which is needed for diesel oils.

Table 5
Properties of liquid products from hydroprocessing gas oil over the NMB catalysts.

Catalyst	Density (g/cm^3)	H : C	S (wt%)	Aromatic C (%)
Feed[a]	0.9921	1.44	4.48	40.0
0.0NMB[b]	0.9105	1.56	0.42	29.0
0.1NMB	0.8940	1.60	0.68	27.8
0.3NMB	0.9058	1.61	0.56	28.5
0.5NMB	0.9043	1.65	0.44	30.5
0.7NMB	0.9003	1.67	0.54	28.6
1.0NMB	0.9056	1.63	0.58	27.9

[a] Unreacted gas oil.
[b] 0.0NMB is Ni–Mo/Al$_2$O$_3$, 0.1 etc., is the wt% barium loading.

The result for the NMB series of catalysts is presented in table 5, and the results are almost identical to those of the BNM catalysts. There is an improvement in the density of the product obtained from the catalysts with barium over that of the catalyst containing no barium. The H : C ratio is also much higher for the barium-promoted catalysts than for the Ni–Mo/alumina catalysts. The wt% sulfur is higher than that from unpromoted catalysts, but much lower than that of the BNM series of catalysts. The NMB catalysts may therefore be better HDS catalysts than the BNM catalysts. Unfortunately, the thiophene HDS activity of these catalysts was not determined. The aromatic carbon content is also comparable to that of the unpromoted catalyst. Apart from the catalyst promoted with 0.5 wt% barium, the aromatic carbon content of the product is much lower than that from the product obtained over Ni–Mo/alumina.

4. Conclusion

Barium was used as a secondary promoter for Ni–Mo/γ-alumina catalysts. Even though the presence of barium does not show any significant improvement in the cumene hydrocracking activity of the catalysts, its presence leads to a significant improvement in the thiophene HDS activity.

Real feed stock studies, using gas oil, show that the presence of a small loading of barium on Ni–Mo alumina catalysts leads to an improvement in the properties of the product (H : C ratio, density, and percent aromatic carbon) after processing. However, for sulfur removal, only the catalyst loaded with 3 wt% (BNM) or 5 wt% (NMB) was as effective as the catalyst without barium.

The sequence of impregnating the barium onto the support also seems to be very important to the catalytic activity of the catalysts. The catalysts with barium impregnated first before Ni and Mo are less active than the one in which the barium is impregnated after Ni and Mo.

More work is currently being done to understand the reason(s) for the significant improvement in the HDS activity of Ni–Mo catalysts on the addition of barium. Laser raman spectroscopy (LRS), temperature-programmed reduction (TPR), and other surface studies are being carried out to understand how barium affects the species present on the support surface on its addition.

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