Silica gel-supported, metal-promoted MoS_2 catalysts for HDS reactions

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Silica-supported, metal-promoted MoS_2 catalysts were prepared. Sol–gel method was used for providing the SiO_2 support as well as for including the catalyst precursors and promoter in one single step of preparation. The general idea in this approach is to obtain the promoted MoS_2 catalyst phase finely and uniformly distributed in the SiO_2 support. Scanning electron microscopy of the obtained catalysts shows a fine and homogeneous distribution of the metal-promoted MoS_2 particles on the SiO_2 matrix with surface area between 62 and 104 m^2/g. Metal promoter affects the surface area, pore size distribution and the hydrodesulfurization (HDS) activity and selectivity. When different promoters were used at the same amount, the highest selectivity for direct C—S bound cleavage is observed for $Ru/MoS_2/SiO_2$ catalyst, and at different amounts of Co the highest selectivity was occurred with $Co/MoS_2/SiO_2$ at 12% of Co/MoS_2, X-ray diffraction studies showed that the catalysts are poorly crystallized with a very weak intensity of the (002) line of 2H-MoS_2. Comparison on the catalytic activities of the catalysts with different metal promoters was made. Catalytic activity results showed the method of preparation used in this study is successful in producing very efficient catalysts for the HDS of dibenzothiophene (DBT). Silica-supported, cobalt-promoted MoS_2 catalyst showed the highest activity.

KEY WORDS: MoS_2 catalyst; metal-promoted; hydrodesulfurization; sol–gel method.

1. Introduction

It has been a challenge to process petroleum residues because of the large sizes and structural complexity of their molecules, high boiling point range, and high contents of sulfur, nitrogen and metals. At the same time, it has become clear that crude oils in many existing reserves are heavier and higher in sulfur contents than those already recovered [1]. As a consequence, there is a growing interest in research and development for converting heavy feedstock (petroleum residues and heavy oils) into lower boiling products of high quality with the least amount of sulfur content. Therefore, hydrodesulfurization (HDS) of heavy petroleum feedstock to produce distillate fuels, particularly diesel fuels and gasoline (either directly or via subsequent fluid catalytic cracking) has become an important research subject.

Earlier research has shown that certain sulfur compounds are easier to convert and the reactivities of the 1- to 3-ring sulfur compounds decrease in the order of thiophenes > benzothiophenes > dibenzothiophenes [2,3]. It has also been shown that under mild conditions, conventional catalysts are not effective for converting bulky organo-sulfur compounds, particularly 4-methyl and 4,6-dimethyl substituted benzothiophenes [3,4].

Hence, it deems necessary to explore catalysts for converting bulky sulfur compounds in order to produce environmentally friendly transportation fuels.

Unsupported HDS catalysts have been prepared by different methods, including comaceration [5], homogeneous sulfide precipitation [6], and thiosalt decomposition. The thiosalt decomposition method has been widely used in the preparation of molybdenum and tungsten sulfide catalysts for hydro-treating processes [7]. The catalytic properties of MoS_2 and WS_2 obtained by these methods are reported to depend strongly on the processing atmosphere, as well as heating conditions [5,6]. Large variations in surface area have been observed for MoS_2 and WS_2 catalysts, from a few to several hundred squared meters per gram, depending on the decomposition conditions [8,9]. Metal-promoted unsupported catalysts prepared from decomposition of thiosalts have shown higher catalytic activities than catalysts prepared by other techniques [10,11].

Since Weisser and Landa wrote their classic book "Sulfide Catalysts: Their Properties and Applications" [12] more than 25 years ago, considerable progress has been made in understanding the basis for the activity and selectivity of Mo- and W-based hydrotreating catalysts. Since the 1970s, different models were proposed to explain the promoter effect of Co or Ni on alumina-supported MoS_2 or WS_2 [13–16]. But, the first physical proof of a specific cobalt environment was presented by Topsøe and his group [17]: Co atoms are located on the edges of MoS_2 platelets giving rise to a specific Mössbauer signal, the "CoMoS" phase, different from the usual signal for Co_9S_8.

Supported catalysts have been prepared by different methods. The incipient impregnation into a porous support is the most popular technique [18]. Alumina and

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silica based materials have been used as support for those catalysts.

In this work, however, a new, easy and cost-effective method for preparing active catalysts embedded in sol–gel SiO$_2$ derived matrix is introduced. The most unique feature of this method is the simultaneous incorporation of the catalyst precursor(s) as well as the promoter precursor(s) during the mixing of the sol–gel precursors in the overall sol–gel process. It is expected that the catalyst/promoter precursors would finely and uniformly adhere to the high surface area generated in the SiO$_2$ matrix upon drying of the gel. One further step is the conversion of the catalyst/promoter precursors to the final SiO$_2$-supported catalyst. This step involves sulfidation of the precursors in a sulfiding environment of H$_2$/H$_2$S and heat of sufficient degree. It is again expected that the finely and uniformly distributed precursors would convert to the final catalyst particles while still adhered to the high surface area of the SiO$_2$ support just as finely and uniformly distributed as they were precursor particles prior to sulfidation step.

The aim of this work is to show a new, easy and cost-effective procedure to obtain an efficient silica-supported and metal-promoted MoS$_2$ catalyst for HDS reactions. The properties of the resulting catalysts prepared with different metals as promoter are compared. Experimental HDS activity and selectivity, along with microstructural and textural features are also discussed.

2. Experimental procedure

2.1. Sol–gel preparation

2.1.1. Different metal promoters

The basic procedure to obtain silica-supported MoS$_2$ catalysts using any of the 4th period metals as promoters is shown in figure 1.

In order to maintain consistency throughout the process, the same amount of the following reactants were used in all cases: 11.2 mL of tetraethyl orthosilicate (TEOS) (Aldrich Chem. Co., reactive grade), 21 mL of distilled water, 17.6 mL of ethanol (Baker, reactive grade), 1.4 g of ammonium thiomolybdate (ATM) [(NH$_4$)$_2$MoS$_4$], 1.8 mL of glycerin and 2 mL of HF acid (Baker, 45 wt%). Under these conditions, the molar composition of the system TEOS : water : ethanol is 1 : 26 : 6.

Three different metals in the form of chlorides were used as promoters: 0.045 g of FeCl$_2$, 0.16 g of CoCl$_2 \cdot 6$H$_2$O and 0.16 g of NiCl$_2 \cdot 6$H$_2$O. In all cases, the final amount of the metal content was the same and then its proportion with respect to MoS$_2$ was 4.5% by wt. The final product would then contain 76.92 wt% of SiO$_2$, 22.05 wt% of MoS$_2$ and 1.03 wt% of the metal promoter.

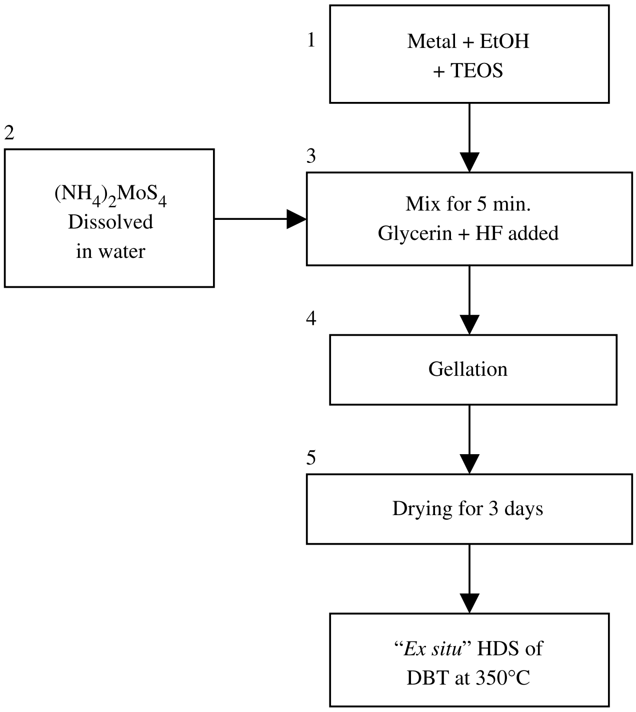

Figure 1. Block diagram showing the process to obtain Metal-promoted MoS$_2$ catalyst supported in silica gels. Steps 1 through 5 at room temperature.

The preparation procedure can be summarized as follows: metal chloride(s) is dissolved in ethanol and then TEOS is added under vigorous stirring to obtain the first solution. ATM is dissolved in water obtaining the second solution. After 5 min of stirring, the ATM solution is poured onto the first solution and keeping under vigorous stirring for other 5 min. Then glycerin is added and finally the sol–gel reaction is catalyzed by adding the HF. Under these conditions the gelation occurs within 2 min. The drying process is carried out at room temperature for three days. Figure 1 summarizes the entire process schematically.

2.1.2. Different cobalt content

Appropriate amounts of CoCl$_2 \cdot 6$H$_2$O were dissolved in 17.6 mL of ethanol (Baker, reactive grade) under vigorous stirring in order to obtain the first solution; then 1.4 g of ATM were dissolved into 21 mL of distilled water obtaining a second solution. The first solution was mixed with 11.2 mL of TEOS under vigorous stirring for 1 min and then were added to the second solution. The molar composition of the system TEOS : water : ethanol was 1 : 26 : 6. Then 1.8 mL of glycerin were added followed by 2 mL of HF (Baker) at 45% by wt was added to catalyze the sol–gel reaction. Under these conditions the gelation occurs within 2 min. The drying process was carried out at room temperature for 3 days. Figure 1 summarizes the entire process, schematically.

Table 1
Final percentage of silica support, catalytic active phase (MoS_2), cobalt promoter and Co/MoS_2 ratio for different amounts of $CoCl_2 \cdot 6H_2O$ used

Sample	Amount of $CoCl_2 \cdot 6H_2O$ (g)	SiO_2 (wt%)	MoS_2 (wt%)	Co (wt%)	Co/MoS_2 ratio (wt%)
Co5	0.16	78.13	20.83	1.04	4.76
Co12	0.48	75.76	21.21	3.03	12.00
Co20	0.80	74.26	20.79	4.95	20.00
Co25	1.14	72.80	20.38	6.80	25.00
Co30	1.45	71.43	20.00	8.57	30.00

The final percentages of silica support and catalyst (MoS_2) as well as the Co promoter for different amounts of $CoCl_2 \cdot 6H_2O$ used are summarized in table 1. Also the Co/MoS_2 ratio is shown.

2.2. Catalyst preparation

Precursor-to-MoS_2 conversion was made "ex situ" in a tube furnace at 350 °C for 2 h. and heating rate of 5 °C/min. A gas mixture of $H_2/10\%H_2S$ with flow rate of 0.75 mL/min was used to provide a sulfiding environment and prevent oxidation.

2.3. Catalytic activity

The HDS of DBT was carried out in a Parr model 4522 high-pressure bath reactor. 1 g of catalyst of each sample along with the dissolved reagent (5 vol% of DBT in decaline) was placed in the reactor, then pressurized to 3.1 MPa with hydrogen and heating to 623 K at a rate of 10 K/min. Once the working temperature was reached, sampling for chromatographic analysis was performed during the course of each run to determine conversion versus time dependence. Reaction runs averaged about 5 h. The reaction products were analyzed using a Perkin Elmer model Auto-system chromatograph with a 6 ft long, 1/8 inch packed column containing OV-3 as separating phase.

Selectivity for a given product was calculated as the weight percentage of the product in the product mixture. There are three main products from the HDS reaction of DBT, namely, biphelyl (BIP), phenylcyclohexane (PCH), and dicyclohexane (DCH). In this case, the variation of selectivity for the main reaction products (BIP, PCH and DCH) is analyzed for MoS_2 catalysts subjected to changes in preparation. The mean standard deviation for catalytic measurements was $\pm 2.5\%$.

2.4. Catalyst characterization

Characterization of catalysts was performed on samples obtained after the catalytic tests. The samples were separated from the reaction mixture by filtration, then washed with isopropanol to remove residual hydrocarbons and dried at room temperature before analysis.

Specific surface area determination was done with a Quantachome model AUTOSORB-1, by nitrogen adsorption at 77 K using the BET isotherm. Samples were degassed under flowing argon at 473 K for 2 h before nitrogen adsorption. The mean standard deviation for surface area measurements was about 2%.

X-ray diffraction (XRD) studies were carried out in a Phillips X Pert MPD diffractometer, equipped with a curved graphite monochromator, using Cu Kα radiation.

Microanalysis and microstructural studies were made in an Environmental Scanning Electron Microscope with EDAX microanalysis unit.

3. Results and discussion

3.1. Different metal promoters

Typical microanalysis results are shown in figure 2. As expected, silicon, oxygen, sulfur, molybdenum and the metal promoter are present in all cases.

X-ray powder diffractograms are shown in figure 3. These patterns are in agreement with those reported for the poorly crystalline structure of MoS_2. As can be observed, all samples show diffraction peaks which are associated with the values of different crystalline planes of MoS_2 as well as a broad peak around 2θ of 20° for the silica gel. Planes marked with (*) are associated with compounds formed during the synthesis process. The identified phases are Nickel Silicide (Ni_3Si_2) in the case of Ni-promoter and cobalt molybdenum oxide in the case of Co-promoter sample.

Table 2 summarizes the data for HDY/HDS ratio calculation after 5 h of reaction time. The HDY/HDS ratio was calculated using (DCH + PCH)/BIP. As can be observed the sample made with Ru promoter showed highest selectivity and higher HDS conversion after 5 h of reaction.

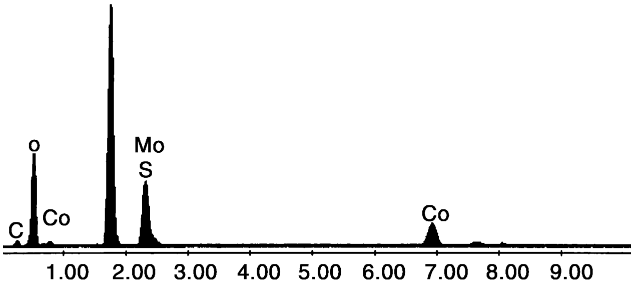

Figure 2. Typical microanalysis (EDX) for samples.

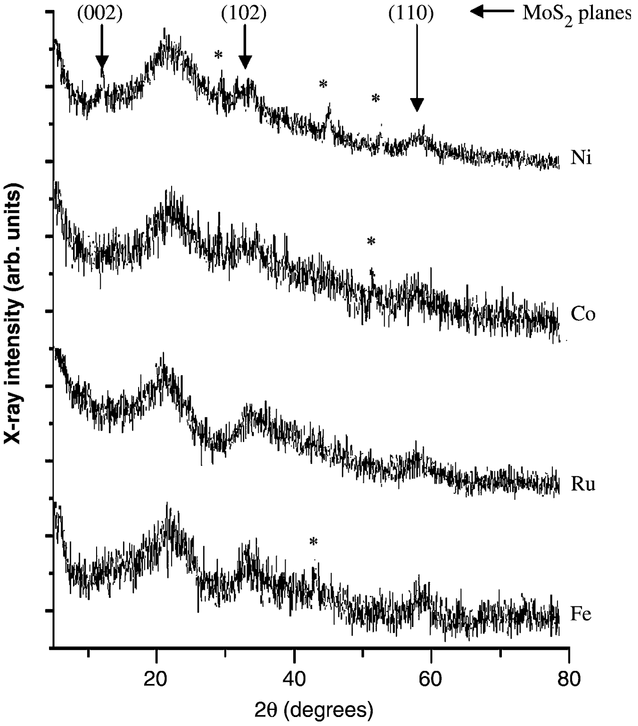

Figure 3. XRD patterns of the samples with different metal promoter.

Table 2
Data for HDY/HDS ratio calculation after 5 h of reaction time for different metal-promoted MoS_2 catalysts

Promoter	%BIP	%PCH	%DCH	HYD/HDS
Fe	69.16	30.84	0.00	0.45
Ru	83.99	16.01	0.00	0.19
Co	72.45	25.40	2.15	0.38
Ni	71.78	28.22	0.00	0.39

Surface area, mean pore size, and initial HDS rate constants of the samples are shown in table 3. There are only slight differences in both surface area and mean pore size, suggesting that the type of metal promoter does not significantly affect necessarily these quantities. The initial HDS rate constant values fall with the same order of magnitude. The Co-promoted sample shows the highest activity.

Figure 4 shows typical micrographs obtained in all cases. It is important to note the size uniformity, and the fine distribution of the catalytic MoS_2 particles on the silica gel matrix as can be observed in figure 4(a). Figure 4(b) corresponds to a higher magnification and as it can be seen the particle size in all cases is lesser than 1 μm. This indicates high surface area availability of the active phase and consequently the high catalytic efficiency achieved with these supported catalysts. This is an excellent result indicating good control in particle size and distribution with this procedure.

Table 3
Specific surface area, mean pore size and initial HDS rate constants for different metal-promoted molybdenum sulfide catalysts

Promoter	Surface area (m^2/g)	Mean pore size (nm)	k (specific) ($\times10^{-7}$ mol/g s)
Fe	104	18	4.62
Ru	109	12	3.77
Co	65	30	7.54
Ni	62	20	5.57

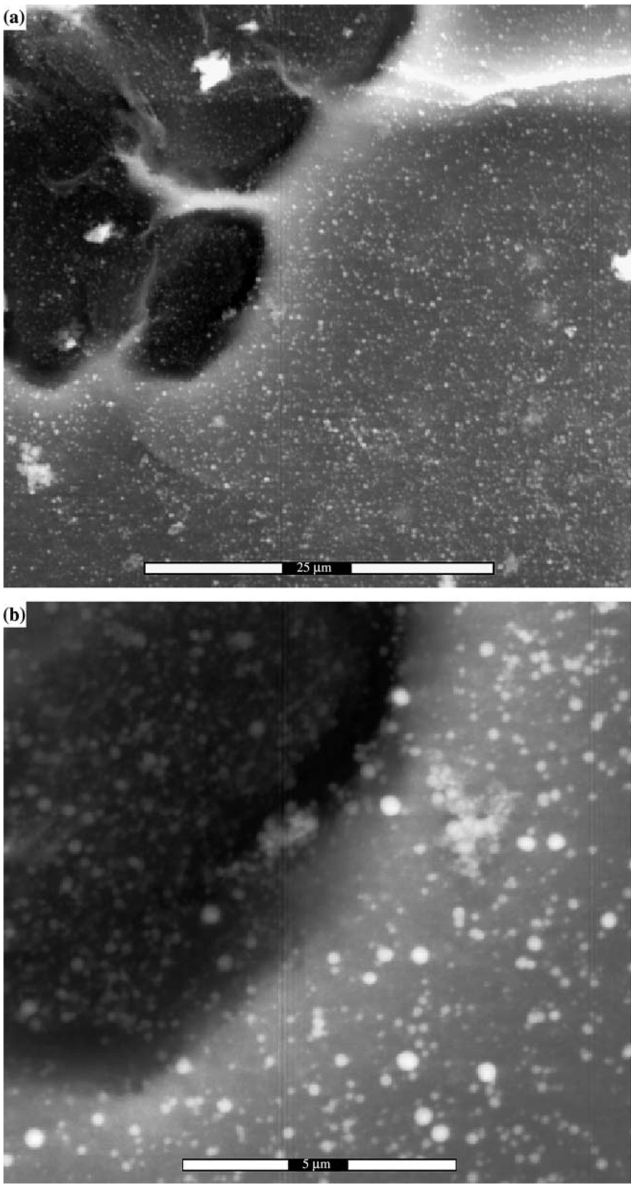

Figure 4. Typical SEM images from the surface of the samples.

3.2. *Different cobalt content*

X-ray powder diffractograms are shown in figure 5. Again, these patterns are in agreement with those reported for the poorly crystalline structure of MoS_2. As can be observed, all samples show diffraction peaks

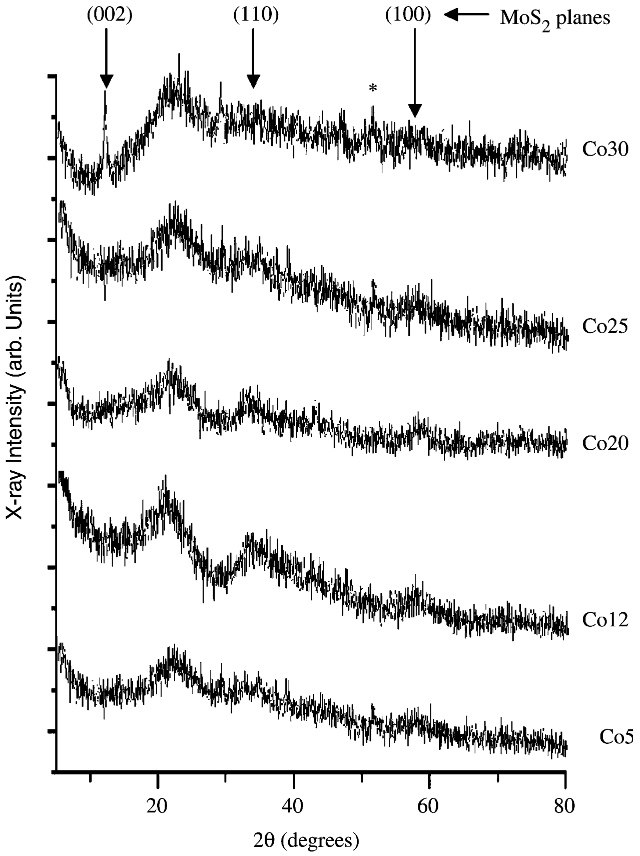

Figure 5. XRD patterns of the samples with different cobalt concentrations.

that are associated with the values of different crystalline planes of MoS_2. The broad peak around 20° is due to the SiO_2 from the silica gel support. The full width half maximum (FWHM) for the (002) reflections for all samples was estimated. Comparison of the FWHM values shows that the stacking of layers in the *c* direction for the MoS_2 catalyst prepared with 30% of cobalt is the largest one. This also indicates that the particle size in that sample must be larger than the others.

Table 4 summarizes the data for HDY/HDS ratio calculation after 5 h of reaction time. The HDY/HDS ratio was calculated using (DCH + PCH)/BIP. It can be observed that hydrogenation decreases with higher amount of promoter and in those cases there are more than 90% of biphenyl conversion. This means that an almost complete hydrodesulfurization conversion could be attained with higher content of cobalt promoter.

Table 4
Data for HDY/HDS ratio calculation after 5 h of reaction time for different amounts of cobalt-promoter MoS_2 catalysts

Sample	%BIP	%PCH	%DCH	HYD/HDS
Co5	72.45	25.40	2.15	0.38
Co12	84.66	15.34	0.00	0.18
Co20	76.20	20.89	2.91	0.31
Co25	91.94	8.06	0.00	0.09
Co30	94.64	5.36	0.00	0.06

Results for surface area, pore size and initial HDS rate constants of the samples are shown in table 5 as well as a comparison with a commercial metal-promoted, supported catalyst. This commercial catalyst, named "CCat" in table 5, is a $Co/MoS_2/Al_2O_3$ catalyst made with a Co/MoS_2 ratio of 30 wt%. As it can be observed, surface area decreases as the promoter content increases while the mean pore size remains almost the same in all cases. Relationship between activity and cobalt content as well as their corresponding surface area is shown in figure 6. It is clear that the more efficient catalyst in terms of initial HDS rate constant is the one with 12 wt% cobalt content. These results indicate that the metal promoter content affect both the catalytic activity and surface area of the samples. The best conditions in order to have the most catalytic efficiency occur with 12 wt% of cobalt content. This is a very good result because previous reports [2–5] indicate that around 25% of

Table 5
Specific surface area, mean pore size and initial HDS rate constants for different amounts of cobalt-promoter molybdenum sulfide catalysts and commercial catalyst (CCat)

Sample	Surface area (m^2/g)	Mean pore size (nm)	*k* (specific) $\times 10^{-7}$ (mol/g s)
Co5	116.59	12	9.39
Co12	70.09	30	12.30
Co20	86.59	31	7.88
Co25	64.84	30	7.54
Co30	64.29	30	4.85
CCat	291.35	6.7	12.00

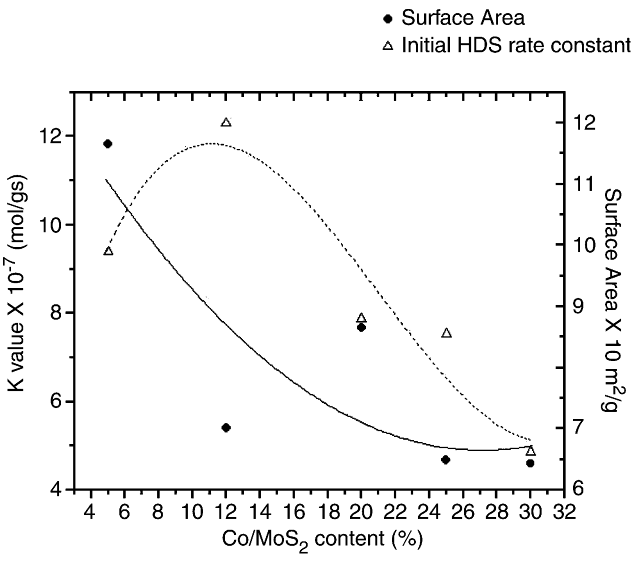

Figure 6. The relationship between activity and cobalt content as well as their corresponding surface area.

metal is needed for the best results in metal promoted catalysts. Comparison between this material and the commercial Al_2O_3-supported, cobalt-promoted MoS_2 catalyst shows the same activity but in the case of the commercial one the Co/MoS_2 ratio is about 30 wt%, 2.5 times the amount mentioned above. This means that the catalyst obtained by the proposed method uses less quantity of metal promoter and results in the same high catalytic activity than commercial catalysts in spite of the difference in surface area. In other words, catalysts obtained by the proposed method show higher efficiency per unit of area than commercial ones and this is attributed to the highly uniform distribution of fine and catalytically active particles on silica matrix observed in figure 4. Moreover, as it has been reported in a previous work [19], this proposed procedure could give cause for a significant reduction in the cost of production of metal-promoted, supported MoS_2 catalysts for HDS reactions.

4. Conclusion

A new, easy and cost-effective method to obtain an efficient silica-supported and metal-promoted MoS_2 catalyst for HDS reactions has been developed. The most unique feature of this method is the simultaneous incorporation of the catalyst precursor(s) as well as the promoter precursor(s) during the mixing of the sol–gel precursors in the overall sol–gel process.

This method requires very few steps and room temperature condition, that means low amount of energy. This has a direct impact on the cost-efficiency relationship and highlights the importance of the sol–gel process as a good option in the manufacture of these supported catalysts.

Highly uniform distribution of fine and catalytically active particles on silica matrix is achieved. The small particle size (under 1 μm) obtained give rise to a high surface area from the catalytic phase and consequently to a high catalytic activity. The SiO_2 matrix shows a surface area between 62 to 104 m^2/g. Metal promoter affects the surface area, pore size distribution and the hydrodesulfurization (HDS) activity and selectivity. At constant promoter content, the highest selectivity for direct C—S bound cleavage is observed for Ru/MoS_2/SiO_2 catalyst, while at different amounts of Co content, the highest selectivity is observed with Co/MoS_2/SiO_2 at 12% of Co/MoS_2, X-ray diffraction studies showed that the catalysts are poorly crystallized with a very weak intensity of the (002) line of 2H-MoS_2.

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References

[1] E.J. Swain, Oil Gas J. 1(March) (1993) 62.
[2] M.J. Girgis and B.C. Gates, Ind. Eng. Chem. Res. 30 (1991) 2021.
[3] M. Houalla, D.H. Broderick, A.V. Sapre, N.K. Nag, V.H.J. De Beer, B.C. Gates and H. Kwart. J. Catal. 61 (1980) 523.
[4] C.G. Frye and J.F. Mosby, Chem. Eng. Prog. 63 (1967) 66.
[5] J.S. Beck, J.C. Vartuli, W.J. Roth, M.E. Leonowicz, C.T. Kresge, K.D. Schmitt, C.T.W. Chu, D.H. Olson, E.W. Sheppard, S.B. McCullen, J.B. Higgins and J.C. Schlenker, J. Am. Chem. Soc. 114 (1992) 10834.
[6] C.T. Kresge, M.E. Leonowicz, W.J. Roth, J.C. Vartuli and J.S. Beck, Nature 359 (1992) 710.
[7] G. Alonso, G. Aguirre, I.R. Rivero and S. Fuentes. Inorg. Chim. Acta 274 (1998) 108.
[8] K. Brownlee, *Statistical Theory and Methodology in Science and Engineering*, 2nd ed. (Wiley, New York, 1965), 590 pp.
[9] H.P. Klug and L.E. Alexander, *X-Ray Diffraction Procedures* (Wiley, London, 1954), ch. 11.
[10] T.P. Prasad, E. Diemann and A. Muller, J. Inorg. Nucl. Chem. 35 (1973) 1895.
[11] M. Vrinat, M. Lacroix, M. Breysse and R. Frety, Bull. Soc. Chim. Belg. 93 (1984) 637.
[12] O. Weisser, S. Landa, in: *Sulphide Catalysts: Their Properties and Applications* (Pergamon, New York, 1973).
[13] R.J.H. Voorhoeve, J. Catal. 23 (1971) 236.
[14] R.J.H. Voorhoeve and J.C.M. Stuiver, J. Catal. 23 (1971) 228.
[15] A.L. Farragher, *Symposium on the Role of Solid State Chemistry in Catalysis* (ACS Meeting, New Orleans, LA, 1977).
[16] G. Hagenbach, Ph. Courty and B. Delmon, J. Catal. 31 (1973) 264.
[17] H. Topsøe, B.S. Clausen, R. Candia, C. Wivel and S. Morup, J. Catal. 68 (1981) 433.
[18] M. Del Valle, M.J. Yañez, M. Avalos-Borja and S. Fuentes, in: *Hydrotreating Technology for Pollution Control*, M.L. Occelli, R. Chianelli (eds.), (Marcel Dekker, New York, 1996), p. 47.
[19] E. Rivera-Muñoz, D. Lardizabal, G. Alonso, A. Aguilar, M.H. Siadati and R.R. Chianelli, Catal. Lett. 85(3–4) (2003) 147.