Synthesis, characterization and hydrodesulphurisation activity of CoMo/γ-Al₂O₃ catalyst prepared through molecular designed dispersion method

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Abstract

CoMo/γ-Al₂O₃ catalysts for hydrodesulphurisation activity were prepared by making use of the molecular designed dispersion (MDD) method. Molybdenum and cobalt pyrrolidine-*N*-carbodithioate (Pydtc) complexes were used for the incorporation of metals on the support. The catalysts were characterized by elemental analysis, low temperature oxygen chemisorption, temperature programmed reduction (TPR) and laser Raman spectroscopy. The hydrodesulphurisation activity of all the catalysts were carried out and results were compared with those of the catalysts prepared through the conventional method. Higher molybdenum dispersion, smaller molybdenum clusters, lower reduction temperature of catalyst and better hydrodesulphurisation activity were observed for the catalysts prepared through the MDD method.
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1. Introduction

Hydrodesulphurisation still attracts the attention of both academia and industry, even though the reforming of crude oil has continued for the last 60 years. This may be because of the variation in the quality of oil feed stocks and the constant pressure on the refining industry to meet more stringent specifications. These specification changes are effected by environmental concerns.

Usually supported catalysts are prepared by aqueous impregnation of support with soluble metal salts, and the impregnated supports are heated in controlled atmosphere to activate the catalysts. This method may not result in a surface with uniform catalyst distribution. In the case of hydrodesulphurisation catalysts, there is a linear correlation between the molybdenum dispersion and the hydrodesulphurisation activity [1]. Molecular designed dispersion (MDD) method is a useful method to develop highly dispersed transition metal oxide on supports [2,3]. The molecular designed dispersion method involves the anchoring of neutral transition metal complexes to the surface of a high

surface area support and subsequent decomposition of the anchored complexes in an oxygen containing atmosphere at elevated temperatures. MDD method involving the use of acetylacetonate (acac) complexes: MoO₂(acac)₂, Cu(acac)₂ and VO(acac)₂, supported on silica/alumina was studied [4–8]. We thought the MDD method using dithiocarbamato complexes of molybdenum and cobalt would lead to more active hydrodesulphurisation catalysts, and have used pyrrolidene-*N*-carbodithioate (Pydtc) complexes of molybdenum and cobalt as the source of the active metals of the hydrodesulphurisation catalyst. Details regarding the preparation, characterization and the catalytic activity for hydrodesulphurisation reactions of straight run diesel of these new catalysts are presented in this paper.

2. Experimental

2.1. Physicochemical measurements

An atomic absorption spectrophotometer (Perlein Elmes 3110) was used to estimate the molybdenum and cobalt in the sample after extracting the samples with concentrated sulfuric acid. The surface area of the samples were

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determined by nitrogen adsorption method on a Micromeritics Gemini 2360 surface area analyzer at liquid nitrogen temperature. The pore volume was determined by mercury penetration method using a Micromeritics Poresizer 9320. Laser Raman spectra were recorded on a Coherent Inc. USA (Model DPSS532-400) spectrometer. A fabricated temperature programmed reduction (TPR) apparatus was used to investigate the surface structure and reducibility of the samples [9]. Low temperature oxygen chemisorption was carried out to get an idea about the extent of molybdenum dispersion on the alumina support.

2.2. Sample preparation and treatment

γ-Alumina extrusions of Sud-Chemie India Ltd., with 5% MoO_3 (incorporated during the mix-mulling stage), and having 1/20 in. diameter and surface area of 245 m^2/g were used as the carrier for further processing. Pyrrolidene-*N*-carbodithioate and its molybdenum and cobalt complexes were prepared according to the literature procedure [10–12].

Five preparations were carried out, of which the first was the conventional method, i.e. the carrier was dipped in an ammoniacal solution of cobalt nitrate and molybdic acid followed by calcining at 500 °C [13]. This is designated as catalyst A.

Molecular designed dispersion of $MoO_2(Pydtc)_2$ was used for the next four preparations. The γ-Al_2O_3 extrusion (50 g) was dipped in a solution of $MoO_2(Pydtc)_2$ (20 g) in dichloromethane and kept for 1 week at room temperature. After 1-week period, the complex in the solution was found to be colourless, suggesting complete and selective adsorption of the complex on the carrier. The extrusions were filtered and washed with the solvent and dried at 120 °C for 2 h. Thus, prepared sample was used as the support for further preparations. This support was divided into four portions. The first portion was calcined at 500 °C for 2 h at a heating rate of 10 °C/min, cooled, dipped in a solution of cobalt acetate in ethanol by pore filling method, filtered and calcined at 500 °C for 2 h. This sample is designated as catalyst B. In the second method, the support was dipped in cobalt acetate solution in ethanol, filtered, dried and then calcined at 500 °C for 2 h, and this sample was designated as catalyst C.

The method of processing for the catalysts D and E was similar to that of catalysts B and C, respectively, using $Co(Pydtc)_2$ as the metal source instead of cobalt acetate. These samples were designated as catalysts D and E, respectively.

2.3. Hydrodesulphurisation (HDS) activity

Hydrodesulphurisation activity of the prepared catalysts for straight run diesel containing 0.9–1.1% sulphur was carried out. A bench-scale co-current down-flow trickle bed rector was used for this purpose [14]. The hydrodesulphurisation of diesel over the catalyst was conducted at 340 °C

and 34 bar pressure, after presulfiding the catalyst. Presulphiding was done using the feed diesel doped with 1% dimethyl sulphide. The hydrotreated diesel samples were withdrawn after 8 h, and the sulphur content was estimated by X-ray fluorescence spectrometry (Oxford, Lab-X 2000 spectrophotometer) after the removal of dissolved H_2S.

3. Results and discussion

3.1. Physicochemical analysis

The analytical and physicochemical data (Table 1) reveal that the surface area and pore volume were decreased upon impregnation. This is because of the pore blocking and surface smoothing by the deposition of the metal oxide on the support. The percentage drop in surface area of catalysts prepared through MDD method was smaller than those prepared though the conventional method. However, the drop in surface area cannot be attributed to the catalyst preparation method, since the loadings of metal are not same for both methods.

The analytical data reveal that the percentage molybdenum content was as expected in all the cases. Thus, the selective adsorption of $MoO_2(Pydtc)_2$ is as effective as that of the pore filling method. The cobalt loading was also as expected; but in those cases, where $Co(Pydtc)_2$ was used as a precursor for the metal source, the loading was low. The reason for the low loading is due to the poor solubility of $Co(Pydtc)_2$ and hence negligible selective adsorption. So, in these cases the pore filling method with multiple impregnations was carried out. Even then, the cobalt loading was found to be low in comparison with that of cobalt acetate solution.

3.2. Oxygen chemisorption

Oxygen has been used as a selective probe for the active sites in hydrotreating catalysts, and many studies have been carried out using oxygen chemisorption [15–17]. The low temperature oxygen chemisorptions of the samples were carried out. A dry ice acetone mixture was used to get the required temperature (−78 °C). The oxygen chemisorption data are given in Table 1. About 25% increase in percent

Table 1
Analytical and physicochemical data

Catalysts	MoO_3 (%)	CoO (%)	Surface area (m^2/g)	Pore volume (ml/g)	Molybdenum dispersion (%)
γ-Al_2O_3	–	–	245	0.51	–
A	20.0	4.9	203	0.44	19.0
B	17.2	3.9	219	0.45	23.0
C	17.3	4.0	214	0.44	22.0
D	17.8	1.7	214	0.45	24.0
E	18.0	1.8	216	0.43	23.0

metal dispersion was observed in the case of catalysts prepared though the molecular designed dispersion method.

3.3. Temperature programmed reduction

Reducibility of the hydrodesulphurisation catalyst was closely related to the activity [18]. TPR experiments were performed to examine the effect of the method of preparation on the reducibility of the catalyst. The reaction conditions for TPR studies are as follows:

Catalyst weight (g)	0.1
Carrier	2% hydrogen in argon
Flow rate (ml/min)	30
Heating rate (°C/min)	10

Normally there are two reduction temperature peaks for MoO_3: one at lower temperature, (between 500 and 600 °C) and the other one at higher temperature (between 800 and 950 °C). It was observed that the lower and higher temperature peaks are due to the reduction of MoO_3 to MoO_2 and MoO_2 to Mo, respectively. The present TPR study was limited to the lower temperature range, as the activity of the catalyst is known to be related to the reduction of MoO_3 to MoO_2 [19]. Fig. 1 gives the TPR profile of the five samples (catalysts C–E). From the patterns it is clear that the catalysts prepared through MDD method consume more hydrogen remarkably than catalyst A. Moreover, the reduction temperature of the samples D and E shows a shift towards lower temperature (the reduction temperature is shifted from 600 to 525–545 °C). In these two samples, Co(Pydtc)$_2$ was used as the metal precursor. So the use of the cobalt complex further enhances the lowering of reduction temperature.

3.4. Raman spectra

Raman spectroscopy has probably been the greatest contributor to the rapid progress in the area of supported metal oxide catalysts characterization, because of its ability to discriminate between metal oxide structures and its in situ capabilities. The supports such as alumina and silica shows no specific peaks in Raman spectroscopy. A number of studies on the assignment of Raman band positions have been reported for supported molybdenum catalysts [20,21].

Raman spectra of the samples are given in Fig. 2. Catalyst A shows a peak at 980 cm^{-1}, which can be attributed to high metal content and to the large polymeric octahedral $Mo_7O_{24}{}^{6-}$ clusters. In the case of catalysts prepared through MDD method, this peak was found to be less intense suggesting the formation of less octahedral clusters and more tetrahedral $MoO_4{}^{2-}$ species [22]. A weak peak at 940 cm^{-1} was observed in catalyst E, and can be assigned to the symmetric Mo=O stretching of $MoO_4{}^{2-}$ in tetrahedral coordination [23]. Thus, higher dispersion of molybdenum is achieved through the MDD method.

3.5. Hydrodesulphurisation activity

A straight run diesel supplied by Kochi Refineries was used for the activity evaluation. The details of the feed is given in Table 2. At first, the catalyst was dried with nitrogen purge at 120 °C for 2 h to remove the moisture present in the catalyst. And then it was sulphided using the feed diesel doped with 1% dimethyl disulphide (DMDS). The reaction
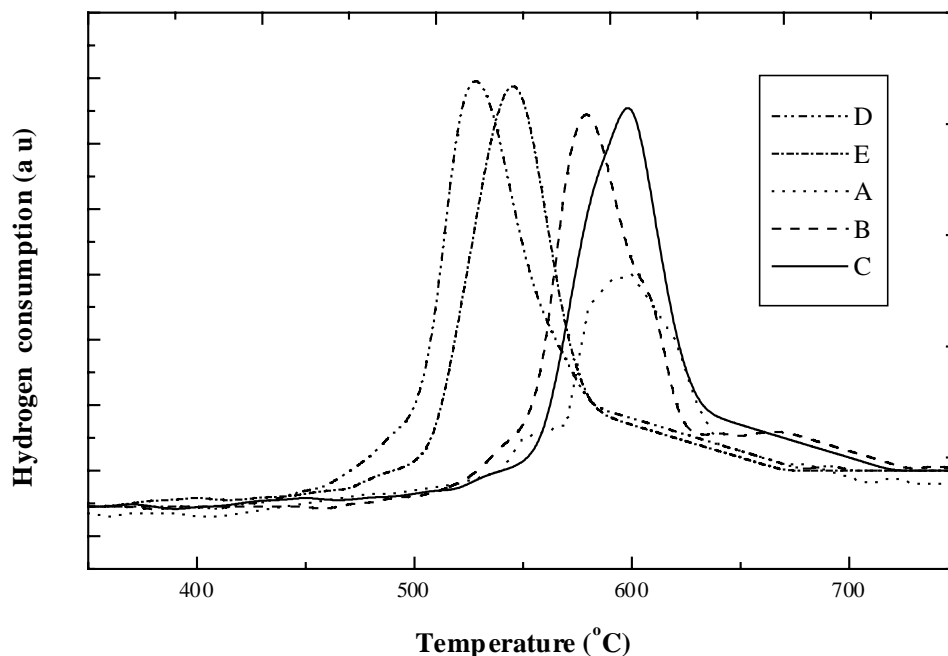

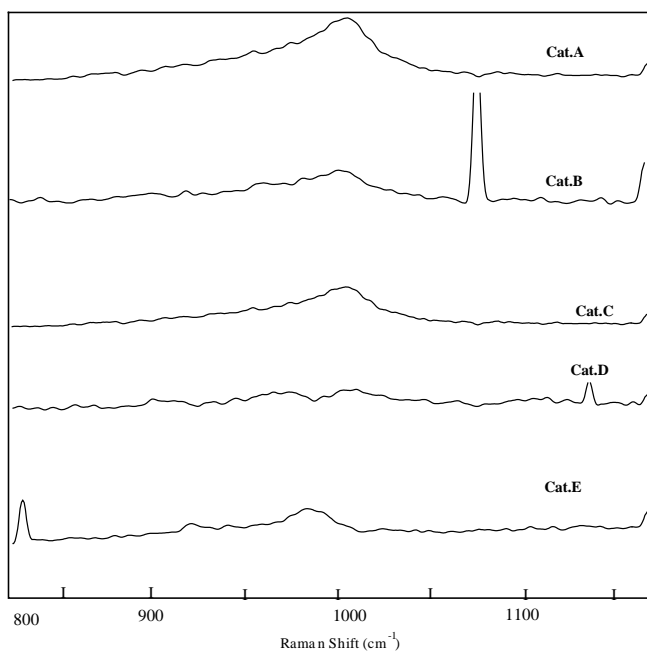Fig. 1. TPR profile of the catalysts.

Fig. 2. Laser Raman spectra.

condition for the presulfidation are as follows:

Catalyst weight (g)	10
Feed	SR diesel doped with 1% DMDS
Pressure (kg)	30
H_2/hydrocarbon	300
Liquid hourly space (h^{-1}) Velocity (LHSV)	3
Duration (h)	8

The temperature profile for the presulphidation is as follows:

The catalyst was heated from room temperature to 175 °C and kept for 2 h and then increased to 250 °C and held for 4 h; after that, the temperature was increased to 300 °C and the sulphiding was continued for 8 h.

The sulphided catalysts were then subjected to desulphurization activity using the SR diesel containing 1.105% sulphur. The reaction conditions for the activity evaluation are as follows:

Feed	SR diesel
Temperature (°C)	340
Pressure (kg)	35
H_2/hydrocarbon	300
Liquid hourly space (h^{-1}) Velocity (LHSV)	3
Duration (h)	8

After the activity evaluation, samples were collected and the percent sulphur was evaluated using X-ray fluorescence spectroscopy. The results obtained are given in Table 3.

Table 2
Properties of the feed

Sulphur (%)	1.105
Initial boiling point (°C)	242.6
Final boiling point (°C)	369.6

Table 3
Catalytic activity data

Catalyst	Sulfur in the outlet (ppm)	Conversion (%)
A	1175	89.00
B	689	93.76
C	875	92.08
D	625	94.35
E	666	93.97

4. Conclusion

All the catalysts developed by molecular designed dispersion method show more or less comparable activity. The catalysts D and E shows slightly higher activity than the other two (catalysts B and C). In these cases, the cobalt was also impregnated as the dithiocarbamate complex. In these catalysts the molybdenum exhibited higher dispersion. The higher amount of active sites available enhances the catalytic activity. Studies also indicate that an enhancement in reducibility, dispersion and the decomposition of cluster complexes into smaller ones happens in the case of molecular designed dispersion method. Simultaneous dipping of cobalt and molybdenum complexes was tried, but it was not successful since the molybdenum complex has higher affinity towards the alumina than the cobalt complex, as evidenced by the analytical data of the samples. It can be concluded that higher molybdenum dispersion, smaller molybdenum clusters, high reducibility of MoO_3 and lower reduction temperature can be achieved through molecular designed dispersion method involving the complexes: such properties are required for a better hydrodesulphurisation activity.

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