REMOVAL OF ISOPROPYL MERCAPTAN FROM GAS STREAM USING Co-Mo SUPPORTED CARBON NANOTUBE NANO CATALYST

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Introduction

Because of all problems that mercaptans cause in petroleum industries or natural gas processing, the scientist interested in their removal from gas or liquid streams. in this respect different methods have been suggested such as: using of physical solvents, chemical reaction (alkalin solution),or adsorption methods [1]. These methods ,all, expose some problems in mercaptans removing process like as: process selectivity for another component (hydrocarbons) instead of mercaptans, alkalin wasting and finally their incapability in reducing mercaptans content of stream to desired value.

In adsorption methods for removing of mercaptans from gas stream many different catalysts such as Copper chloride supported activated carbon[2] ,virgin or various types of modified activated carbon [3,4] have been applied. cobalt-molybdenum ,nickel-molybdenum on optionally catalyst supports like alumina, zirconia and silica have been tested as hydrodesulphurization catalyst for the conversion of mercaptans to H_2S [5]. To the best of our knowledge, no studies on the catalysts with CNTs as support for mercaptans removal process from gas stream have been reported. In this paper CNTs have been chosen as support because of its mesoporosity, high purities, high mechanical strengths, high thermal stability and tunable bulk density [6,7] and high selectivity for sulphur compounds ,not hydrocarbons. Therefor, present work aims at using CNTs supported cobalt-molybdenum catalyst for Oxidative adsorption of iso propyl mercaptans from gas stream in the presence of oxygen.

Experimental

In this study Multi Wall Carbon Nano tubes (MWNTs) have been used as support. It has been prepared by CVD method over Co-Mo/MgO catalyst by methan decomposition at 600-900˚C [8].

Co/Mo catalyst with different loading of 7wt% and 15wt% of Co and Mo were prepared using the incipient wetness impregnation method. For this bimetallic catalyst, a two-step incipient wetness method was used: ammonium hepta molybdat $(NH_4)6Mo_7O_{24}$ _$4H_2O$ was first applied to the support, then the sample was dried at 100 ˚C for 4 h, and after that $Co(NO_3)_2.6H_2O$(99%,Fluka) was added and the sample was dried at 100 ˚C overnight. The molar ratio of Co/Mo is 1:3,therefore, for٧٠ and 15 wt% bimetallic catalyst, different loading of Co successively are ;2.5 and 3.75wt% and different loading of Mo successively are;7.5 and 11.25 wt%.Then prepared catalysts,Co-Mo/CNTs, were calcined in flowing He at 450˚C for 270 min with a ramp rate of 2˚C/ min.

The tests has been done at different experimental condition like as reaction temperature, catalyst loading, ratio of O2 /i-propyl mercaptan and Gas Hour Space Velocity(GHSV,h-1).
4 mlit of prepared catalyst has been loaded in a fixed-bed reactor that used for this study and constructed from stainless steel-314 tube 12.5 mm i.d. and 450 mm length. The gas mixture was passed downwards through the catalytic bed. The reactor was vertically mounted in an electrical furnace; the temperature was controlled by thermal indicator controller. The flow rates of gases (O2, He) were monitored and controlled with Bronkhorst mass flowmeters linked to a JUMO (dTRON 304) electronic control unit. The catalyst was heated from room temperature to the reaction temperature (heating rate of 5oC min-1) in presence of He. At this point the reactant flow was added.
feed is a mixture of n-hexan (99.5wt%) and iso propyl mercaptan (0.5 wt%) with mercaptans content of 4000 ppm that flows at rate of 70 mL/min, then it was mixed with O2 and He in proportional to determined O2 ratio and GHSV. All the lines were maintained at 120oC with electrical tracing tapes to avoid any condensation before the analysis. Finally this mixture passes downward through the reactor.
The product stream has been passed through KOH solution (25%) in different times each time for 10 min. Mercaptan was measured with a KEM potentiometer (AT-500) and UOP 163 method with detection threshold of less than 2 ppm.

The catalyst were characterized by X-ray diffraction (XRD), Scanning electron microscopy (SEM),ICP, transmission electron microscopy(TEM),BET tests of catalysts has been recorded.

Results and Discussion

Some properties of prepared catalysts that has been gained with BET and ICP analyses is presented in table 1.

The results of some experiments has been shown in Fig. 1.The curves present the change of mercaptan not reacted in product stream as a function of time. curve (a) that shows the operating condition of; Load:7% ,T:60˚c, GHSV:4000h-1, 02 R:15, is detached from X axis at the beginning minutes of reaction and ascends sharply. But with increasing temperature and loading of catalyst to 300˚C and 15% in curve (d) and (e) the time of detaching has postponed to 110 and 180 min respectively. The rate of ascending decreases with increasing loading from10% to 15% and decreasing GHSV from 4000 to 2000 h^{-1} in curve (b) comparative to curve (a).However, at experimental condition of curve (b) the loading is higher than curve(c) , but curve (c) represents much better results. At first that because of increasing in temperature level and then because of increasing O_2 ratio and decreasing GHSV.It seems that in high temperature the probability of reaction is more than lower one and in addition to adsorption mechanism, reaction take place with increasing temperature. By increasing

loading activated sites become more. Increasing O_2 ratio and decreasing GHSV give more chance to gas for better contacting with catalyst and in result of that better conversion of mercaptan.

X-ray diffraction patterns of the carbon nanotube, CoMoO/CNT is presented in Figure 2. For the CNT, a strong peak at a 2θ value of 26.05o can be observed, representing the (002) graphitic basal plane. In addition, a weaker broad peak near 2θ of 43.0o also can be found.In the XRD pattern of the oxide CoMoO/CNT, new diffraction peaks are clearly observed at the 2θ values of 36.9o and 53.49o, respectively. These peaks are Characteristics of MoO2, but not those of the expected MoO3 , indicating that the main active phase on the surface of CNT is the low valence state Mo, and the active phase conglomerates into crystallites.

Table 1.Properties of Two Prepared catalysts and virgin CNT.

	BET (m^2/g)	ICP	
		Co (%)	Mo (%)
CNT	136	–	–
Co-Mo/CNT(10%)	110	2.3	7.2
Co-Mo/CNT(15%)	95	3.65	11.05

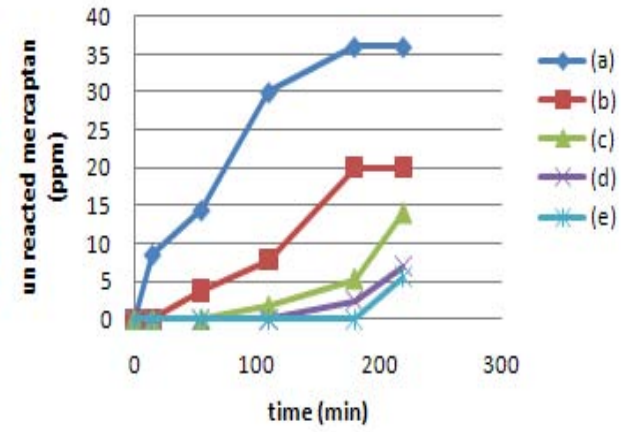

Fig.1 . The changes of iso propyl mercaptan content in exit stream during time;(a)Load:10% ,T:60˚c, GHSV:4000h-1, 02 R:15,(b)Load:15% ,T:60˚c, GHSV:2000h-1, 02 R:15,(c)Load:10% ,T:300˚c, GHSV:2000h-1, 02 R:15,(d)Load:15% ,T:300˚c, GHSV:4000h-1, 02 R:15, (e) Load:15% ,T:300˚c, GHSV:2000h-1, 02 R:6

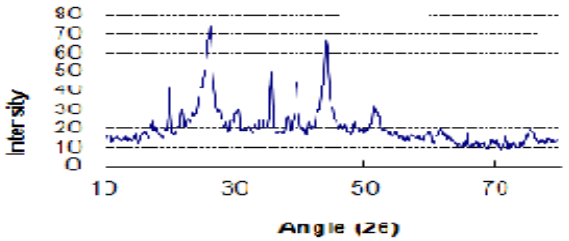

Fig. 2. XRD pattern of Co-Mo/CNT 10%

Conclusion

The results show iso propyl mercaptan was removed from gas stream using Co-Mo/CNT nano catalyst. unreacted mercaptan is reduced with increasing temperature value from 60 ˚C to 300˚C. Increasing in loading offer more activated sites and make the reaction condition more better. Decreasing GHSV from 4000 to 2000 h^{-1} result in increasing residence time of gas and better catalytic contaminant and cause better results. Increasing O_2/ iso propyl mercaptan ratio from 6 to 15 has positive effects in mercaptan conversion too. Among different parameters, temperature has the most effects in results and change them significantly and O_2/ iso propyl mercaptan ratio has the lowest. Increasing of loading causes increase in mercaptan conversion but it has lower significance in comparison with temperature.Finally the concentration of isopropyl mercaptan can be reduced from 4000ppm of the gas to levels in the vicinity of less than 2ppm by Co-Mo/CNT in presence of oxygen in optimized condition of temperature, catalyst loading, O_2/ isopropyl mercaptan and GHSV.

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