Zeolite adsorbents based on transition metals as adsorptive desulfurization fuel

Essay article Presented

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Abstract :-

In the last few decades, much efforts has been addressed a methodology to remove or absorb sulfur compounds from its fuel oil and prevent it to emit it into the atmosphere . This is because sulfur- compounds has a serious negative impact on both human life and environment due to its high toxicity. Zeolites exchange ions is one of these strategies that used to extract sulfur from fuel oil. Zeolites can be immobilized in variety of metal ions such as Fe^{2+}, K^{+}, Ag^{+}, Cu^{+}, Ni^{2+}, Zn^{2+}, and Ce^{4+} and Pd^{2+} via either ion exchange or impregnation methods. This modification can enhance both the absorption ability and selectivity for S-atoms. The purpose of this review is highlighted variety desulphurization method techniques that can apply on diesel, gasoline ,kerosene crude oil and hydrocarbon fuels. Then a conclusion has been reported for these studies.

Introduction:-

There is no doubt that exhaust emissions through gasoline and diesel fuels resulted in sulfur compounds as the main impurities in air in air pollutants[1, 2]. Numerous research reported the harmful role of sulfur compound on both human health and environment[3-5]. For example, in human harmful aspect, the presence sulfur in atmosphere causes; neurological behavioral changes, heart damage, disorder of both stomach and gastrointestinal, and hearing defects[6-8]. While the sulfur harmful role on environments can be summarized in ; causes deforestation, acidify waterways such as river lake and oceans, and finally corrodes building materials and paints[9, 10]. Thus, the long-term of sulfur compounds emissions can amplified these consequences[11, 12].

Transportation fuels such as diesel, gasoline, and jet fuel are the three major sorts of. Fuels that currently contain a high amounts of sulfur[13]. For instance, in gasoline there is up to 300 ppmw sulfur , in Jet fuel it raised up to 500 ppmw while in diesel up to 3000 ppmw[14]. Combustion of these fuels are mainly emitting SO_x, as major air pollutant[15].

According to environment's regulations the allowed normal sulfur should be no more than 10 ppm[15]. Thus, in industry methodology, the scientists are trying to reduce sulfur content to near-zero level in next few years. For this purpose, several techniques were investigated to control emitting of sulfur compounds, such as oxidative desulfurization(ODS), hydro desulfurization (HDS), adsorptive desulfurization (ADS), etc[16]

Hydrodesulfurization (HDS) technique is one of these efforts to remove the sulfur compounds. The overall process of HDS includes a catalytic treatment to provide H_2 to convert sulfur compounds to hydrogen sulfide and that required several operating conditions But, although of the successful results that reported, recently, to remove some sulfur compound. This method is approved to be unfavorable for industrial application due to the limited ability to remove other refractory sulfur compounds that present in jet fuels and diesel. As well as the process of using HDS is required a high temperature and pressure resulting in reduced some of olefines and aromatics continents in the fuels that consequently leads to reduce octane number of fuel[17, 18].

On the second hand, although oxidative desulfurization (ODS) has achieved high catalytic activity, better selectivity and possible recovery, there is still large number of

problems are required to find urgent solution such as; modified ODS materials are often combined or electrostatic interaction instead of bonding resulting in reduces the active sites of catalytic activity and recovery efficiency, the morphology of catalytic is preferred to be powder and sometime this powder does not able to reuse or processing in indudtrail application and finally the desulfurization fuel mechanism is still need to investigated[19, 20].

Among above variety techniques adsorption desulfurization process appears to be promising for ultra- deep desulfurization. This is because it has amazing features such as ; its availability , environmentally friendly, high selectivity, cheap and regenerated approach and can reduce the amount of sulfur to less than 1 ppm. Abroad rang of adsorbent have been applied and reported such as metal adsorbents, metal oxide, metal sufide, silica based adsorbents, carbon based sorbents , metal organic formwork (MOF) and zeolite based adsorbents[20, 21].

Zeolite based adsorbents can provide active cite centers, active separations media, amazing geometry to exhibits different shapes such as channels and cages cavities. A large numbers of reviews reported Zeolite applications such as H_2S removal, coverting biomass to fuel, removal benzene from gasoline and wastewater treatments. However, there is very limited reviews that published to reported the variety uses of zeolite based adsorbents in desulfurization fuel[22, 23].

Utilizing zeolite as adsorptive desulfurization

There are several types of modified adsorbent zeolite for fuel desulfurization can be classified to;

1.1 Natural zeolite

There are more than 50 natural zeolite known and already used for deep desulfurization such as mordenite (MOR), chabazite (CHA), and clinoptilolite (HEU)[24].

In natural zeolite process, the uses of transition metal as exchange ion is approved to enhance the removal of sulfur amount from its compounds. For example, Mahmoudi and Falamaki showed when Ni^{2+} ion exchanged dealuminated clinoptilolite for desulfurization *via* Oxalic acid in special condition that reported, the desulfurization levels significantly raised to high amount up 10.10, 6.33, 3.60 and 2.70 mg s/g in thiophene (T), benzothiophene (BT), dibenzothiophene (DBT) and isopropyl mercaptan (IPM) respectively. This enhancement due to the great π-complexation bonds between both sulfur atoms and d-empty orbital in Ni atoms that immobilized in zeolite[25].

1.2 Faujasite (FAU) zeolites

FAU zeolites has a supercage with 3d dimensional 12-ring pore system. X and Y Zeolites are two main sorts of synthetic forms for FAU type zeolite. As it known Zeolite X can refer to zeolite that has Si/Al ratios between 1 and 1.5 while Zeolite Y refers to zeolites with Si/Al ratios higher than 1.5. X and Y zeolites have been deeply investigated as (ADS) due to their tolerated selectivity regardless of their polar molecules effects[24].

1.2.1 X-zeolite exchanged with transition elements

X-zeolite exchanged with transition elements has been showed promising sulfur removal due to the π-complexation mechanism and it high selectivity. For example, Tong et al. showed when Cupper Ion (Cu^{+}) mixed with lanthanide(III) (La^{+3}) in X-Zeolite. The resulting La3+/Cu+-13X zeolites raises the amount of sulfur adsorption up to 197.3, 159.2, 153.5 and 151 mg/g in series compounds; Thiophene (TP), 3-methylthiophene (3-MT), 2, 5-dimethylthiophene (2,5-DMT) and benzothiophene (BT) dissolved in n-hexane (Model fuel) respectively[26]. Another research utilized nano-Ag X-zeolite as adsorption agent for desulfurization fuel. The methodology were involved comprised metal percentages , adsorption temperature and calcination temperature. The results reported that sulfur adsorption was able to remove amount of sulfur reached up to 48.36 ppm at 83 °C as adsorption temperature[27].

1.2.1 Y-zeolite exchanged with transition elements

Much research demonstrate that Y-zeolite exchanged with transition elements enhances the sulfur adsorption ability and very stable in practical process . This this adsorption depends on metal type and nature of synergistic effects between metal ion and zeolite itself. Zhang et al. reported the removal adsorption of sulfur in dibenzothiophene (DBT) and 4,6 dimethyldibenzothiophene (4,6-DMDBT) on the various ion-exchanged Na-Y zeolites (with single Cu^{2+}, Zn^{2+}, Ag^{+} and the combined Cu^{2+}-Zn^{2+}, Zn^{2+}-Ag^{+}, Ni^{2+}- Nd^{3+}). Under certain reported conditions, result showed that the Ag-Y and Cu-Zn-Y adsorbents have higher adsorption abilities than the other adsorbents. In addition, the reaction time appeal that DBT can be removed in large amount from1500 ppm in the feed to 300 ppm in the product in only first 30min of adsorption process, and the sulfur reduction reached

sulfur reduction reached 42 mg S/g. while the adsorptive removal of 4,6-DMDBT on Ag-Y is as effective as that of pure DBT due to the little steric effects of 4,6- dimethyl group that could hindered π-complexation predominant interaction between 4,6-DMDBT and Ag^{+} site[28]. Lee et .al. reported that ion-exchanged metals on mesoporous Y-zeolite increases removal of sulfur compounds with high kinetic diameter. This is because mesopores allow access to y- zeolite active sites while the metal cations improve the selectivity and/or capacity for sulfur compounds[29].

Conclusion

Recently much research highlighted the desulfurization fuel in order to obtain a clean and healthy environment. Among variety desulfurization fuel techniques, adsorptive desulfurization (ADS) was demonstrated as an effective removal sulfur due to its amazing features such as low in cost, environmental friendly, long-term practical recovery and easily to regenerate . Zeolite based on transition elements can provide active cites, high mesoporous morphology due to its channels, cages and cavities. More research is needed to explore this technique as zeolite adsorbents based transition metals.

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