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CO-PD/Γ-AL2O3 CATALYST FOR HEAVY OIL UPGRADING: DESORPTION KINETICS, REDUCIBILITY AND CATALYTIC ACTIVITY

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ABSTRACT

The influence of Pd on a Co-Pd/γ-Al2O3 catalyst is investigated using different physicochemical and reactive characterization techniques. Nitrogen adsorption isotherm shows that the specific surface area and porosity of support alumina is decreased by the addition of cobalt species. TPR experiments show that the reducibility of the catalyst is improved by the presence of Pd. This is due to high metal dispersion and hydrogen spillover effects. Also the Co-Pd/γ-Al2O3 promoted catalyst showed better HDS and HC activities than the unpromoted catalyst. Further methods to improve the catalytic activity of the catalyst are suggested for eg. OMXC, nanomaterial etc.

Introduction

Supported cobalt catalysts are industrially important catalytic materials. The metal component is deposited on a high surface area support such as Al2O3 in order to obtain maximum number of active sites. Metallic promoters like Pd are often employed to increase the catalytic activity of these active sites. In addition, the promoters are very effective in establishing the synergetic effects which enhances the catalytic activity. Noble metals have excellent promotional effects and reduce coke deposition on the catalyst. The purpose of this term paper is to provide an insight on the promotional effects of Pd on a Co-Pd/γ- Al2O3 catalyst. Various experiments like N2 Adsorption isotherm, Temperature Programmed Desorption, Temperature Programmed Reduction, Pulse Chemisorption, Batch Autoclave Evaluations etc are conducted to study the microstructure properties, distribution of acid sites, availability of active metal Co sites, metal dispersion, metallic surface area and the catalytic activity of the prepared catalysts.

Methodology of Experiments

The activity of the catalysts was tested in a batch autoclave reactor using vacuum gas oil as feedstock. Batch Autoclave Reactor trials were carried out at 400°C and 13800 kPa. Characterization of VGO and liquid product was carried out by Gas Chromatography Method was used to analyse the gas sample, while the liquid product was analysed for boiling point distribution using GC simulated distillation. The boiling range distribution of VGO feedstock and liquid products was measured. The feedstock VGO and liquid product samples were also analysed for carbon, hydrogen, nitrogen, and sulphur using an analyser. Finally, these products are separated using separate adsorption columns and detected by a TCD detector. The spent catalyst from the batch autoclave reactor was also analysed for the amount of coke deposition after reaction using the same analyser. The catalyst was washed with n-hexane to extract the coke and the resulting solution was analysed for amount of coke. The specific surface area, pore size and its distribution of catalyst samples were studied by N2 adsorption analysis and calculated by BET equation. Total acidity of the catalyst is determined by the area, position and shape of the peak of the NH3 desorption peak.
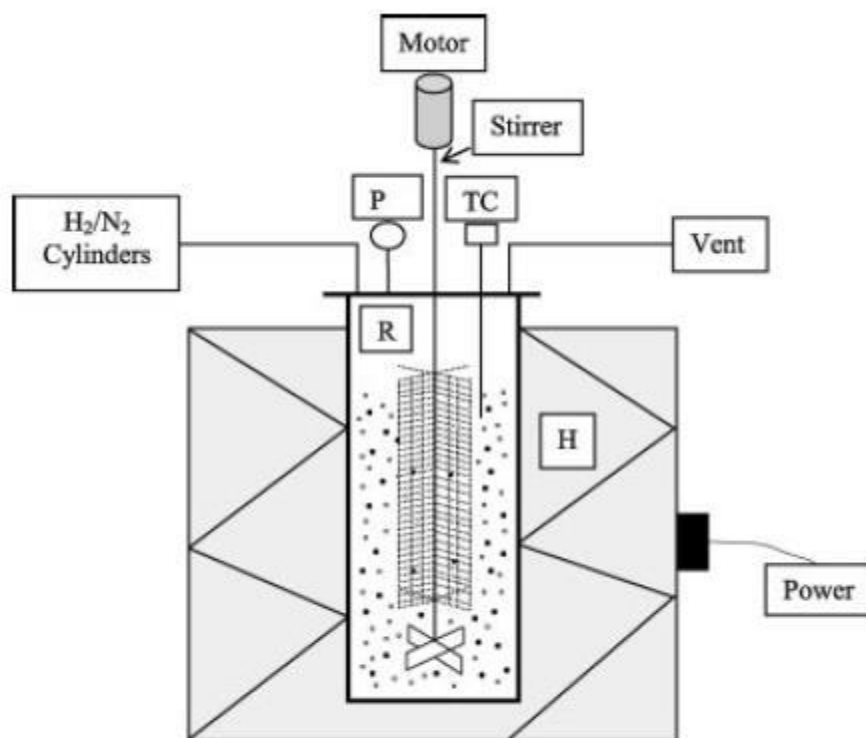
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Figure 1. Schematic diagram of the batch autoclave reactor system.

Promotional Effects Of Noble Metals

Noble metal promotional effect has been explained in the literature in the following ways:

(a) noble metals might reduce the activation energy of the cobalt oxide reduction reaction.

(b) the dispersion of cobalt oxide on HPS can also be enhanced in such a way that it is reduced at a comparatively lower temperature.

(c) an increase in the number of nucleation sites for reduction.

The promotional effects can be explained as follows:

Sulphur bearing hetero-atoms, as well as the heavy hydrocarbon molecules, crack on the acidic HPS sites to produce unstable reaction intermediates. Meanwhile, the noble metal(s) supply reactive hydrogen via the dissociation of molecular hydrogen. The cracked reaction intermediates react with the hydrogen species to produce stable products. As a result the rate of the reaction and the activity become higher.

Hydrogen Spillover Effect

In Hydrogen Spillover Effect, the hydrogen species give rise to highly reactive hydrogen species i.e. $H+$, $H-$ or $H3+$ or ion pair that generate Bronsted acid sites on the Co sites, and such reactive species which can easily attack the cobalt oxide(s) and reduce them at comparatively lower temperatures. This eventually leads to an increase in cracking as well as the hydrogenation activity.

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Comparison Of Promoted And Unpromoted Co-Pd/Γ-Al2o3 Catalyst
For all noble metal promoted catalysts, it can be clearly seen that the formation rate of gaseous hydrocarbon (C1–C5) was considerably lower than that of the unpromoted Co/HPS.
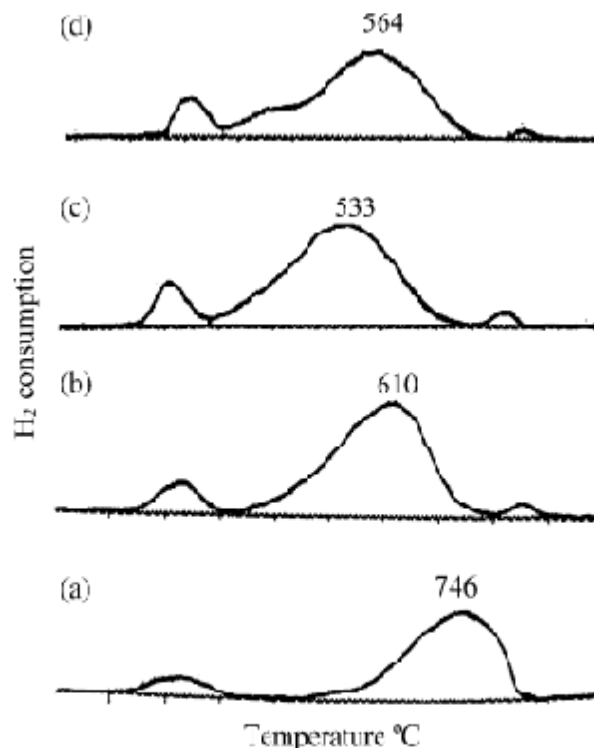
Fig. 1. TPR profiles of (a) Co/HPS, (b) Pd–Co/HPS, (c) Rh–Co/HPS and (d) Pd–Rh–Co/HPS catalysts.

The first peak is due to the easily reducible large particle of cobalt oxides, while the second peak is due to the reduction of highly dispersed amorphous over layer of cobalt oxide. The noble metal promoted catalysts exhibits a significantly low-temperature reduction. The shifting of the peak temperature, which occurred in the range of 140–2158°C, was clearly due to the promotional effects by the noble metals.

Methods To Improve The Catalytic Activity
Nano-material based catalyst
It is usually broken up into metal nano-particles in order to speed up the catalytic process. Metal nanoparticles have a higher surface area and thus increase the catalytic activity. These have two functions – they act as the site of catalysis as well as a support for catalytic activity.
Organometallic functionalized nano particles
Ligands like EDTA etc can be coordinated to the metal centre to prevent aggregation which further prevents the lowering of surface area of the catalyst.

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Functionalized with polymers
They polymers sterically stabilize the nanoparticles by providing a protective layer that prevents the nanoparticles from interacting with each other.
Bimetallic nanoparticles
Using the alloys of two metals creates synergistic effect on the catalysis between two metals.
Genetic engineering
The efficiency of enzymes (also considered as catalyst) can be improved using this technique. Thermo-stable mutants are isolated after sequential rounds of error-prone PCR performed to introduce random mutations which enhance the capability of performing in extreme conditions.

Improvements Suggested
1. As stated in the paper, over cracking leads to the formation of stable, unwanted intermediates in the reaction system. So an efficient mechanism needs to be developed to remove the intermediates.

2. Since there is a need for free catalyst surface, coke deposition needs to be removed. Deactivation due to coke deposition is inhibited by ZrO_2 as it enhances the dissociation of CO_2 forming oxygen intermediates near the contact between ZrO_2 and Co where deposited coke is gasified afterwards.

3. Addition of citric acid as a chelating agent can increase the catalytic activity.
4. Rhodium can be used to enhance the number of active sites and increase the hydrogenation function. It exhibited a more pronounced promotional effect compared to Pd in the reduction of Co species on HPS.

5. Nano-crystalline Al_2O_3 can enhance cobalt active sites and hydrogenation activities when employed as supports for preparation of alumina catalyst.

6. Noble metals such as ruthenium can be used to decrease the reduction temperature of the cobalt oxides and increase the dispersion of cobalt clusters.

7. A new process called the OMXC or Organometallic Matrix Combustion Decomposition can be used to prepare the Co and Mo oxide catalyst for HDS. Mo-Co/γ- Al_2O_3 has the highest activity for HDS (Hydrodesulphurization).

8. Co/ γ- Al_2O_3 catalyst prepared by controlled adsorption have higher activity and slower deactivation than the catalyst prepared by dry impregnation.

Conclusion
1. The incorporation of cobalt blocked some of the pores of the alumina support as is revealed by the nitrogen adsorption experiment. Therefore, the specific surface area, average pore volume was significantly decreased. But the addition of Pd to the catalyst has negligible effect on it.
2. The total acidity of the Co/γ- Al_2O_3catalyst was sharply decreased after cobalt addition on the support due to coverage of the acid sites on the alumina sites. However acidity of the Pd promoted Co-Pd/γ- Al_2O_3 sample was higher than that of the unpromoted sample. This was shown by the desorption kinetics analysis.

3. TPR experiments show that the reducibility of the Co-Pd/ Al_2O_3 catalysts is enhanced by the promotional effects of Pd, indicating an increased amount of active Co species and improved metal dispersion.
4. In batch autoclave reactor trials, the promoted catalyst showed higher HDS and HC activities than the unpromoted catalyst. The addition of Pd influences the surface acidity and availability of reactive hydrogen to minimize coke formation.

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