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DESIGN AND SYNTHESIS OF Cr_2O_3-ZrO_2: TAILORING PROPERTIES OF Pt/Cr_2O_3-ZrO_2 VIA DIFFERENT Cr_2O_3 LOADING FOR CRACKING ACTIVITY

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ABSTRACT

World-wide public concern about the earth's environment and health considerations led into several new legislative action all around the world. Solid acid catalysts play a crucial role in the petrochemical industry, where they have largely replaced traditional acids active in the liquid phase for hydrocarbon transformations. Cr_2O_3-ZrO_2 have been explored to improve the activity, selectivity and stability of catalyst. Cumene hydrocracking selected as a model reaction over Cr_2O_3-ZrO_2 where this cracking has been reported to be a reaction for the simultaneous determination of Brønsted as well as Lewis acidity. The influence of the amount of Cr_2O_3 loading was studied in order to elucidate the effects and limitation of Cr_2O_3 loading on the properties and activity of Pt/Cr_2O_3-ZrO_2. The results of IR studies and catalytic hydrocracking were demonstrated in order to clarify the relationship between Cr_2O_3 loading with the activity of Pt/Cr_2O_3-ZrO_2 in the presence of hydrogen gas. The catalyst with 8 wt.% loading performed with a maximum activity in cumene hydrocracking at 523 K which due to presence of Cr=O band at 1035 cm^{-1} which extensively interacted with H_2 to form protonic acid sites via a hydrogen spillover phenomenon.

Keywords: Pt/Cr_2O_3-ZrO_2, Cr=O stretching band, protonic acid site, Lewis acid site, hydrocracking

1. INTRODUCTION

The demand for stringent environmental regulations of clean fuels is focusing the attention of researchers as well as refiners to the hydrotreatment of various petroleum fractions using new catalytic materials and the development of new and more efficient processes. Development of new type of stable catalyst is required to reduce the cost of industry. Catalysts used in state-of-the-art isomerization-cracking reactors are bifunctional. Since it has been observed that cracking and isomerization of hydrocarbons are the best way in production of liquid fuels or petrol of high quality, solid based acid catalyst plays an important role on providing surface sites in modifying the catalytic performance. Among the catalysts for cracking, sulfated zirconia is widely used and has attracted intensity for its strong acidity and activities in catalysis of hydrocarbon cracking at relatively temperate condition [1,2]. In this study, Cr_2O_3-ZrO_2 was used to generate the active site of the hydrocarbon. The combination of ZrO_2 and CrO_x generates stronger acid sites and more acidity as compared with the separate components [3]. Cr_2O_3-ZrO_2 is seen to be an active catalyst based on the previous study where it has strong acid or base properties and would be more suitable for

industrial applications. In addition, different amount of Cr_2O_3 give different physical and chemical properties on the active site of the catalyst [4].

2. MATERIAL AND METHOD

Chromium oxide zirconia with various weight percentages of Cr_2O_3 were prepared by incipient wetness impregnation of $Zr(OH)_4$ with an aqueous solution of chromium nitrate nanohydrate ($Cr(NO_3)_3 \cdot 9H_2O$, Merck) [5]. The resulting materials were dried overnight at 383 K followed by calcination at 873 K for 3 h in air. 1, 4, 8 and 12 wt.% Cr_2O_3 supported on ZrO_2 were prepared where [wt.%] indicated the wt.% of Cr_2O_3 on the Cr_2O_3-ZrO_2 catalyst. The catalysts then were impregnated with an aqueous solution of hydrogen hexachloroplatinate hydrate ($H_2PtCl_6 \cdot 6H_2O$, Aldrich) and the content of Pt was 0.5 wt.%.

For measurement of IR spectra, about 0.07 g catalyst was ground and pressed in hydraulic press (5000 psi) in order to obtain 13 mm diameter of self-supporting wafer before placed in the purpose-made stainless steel IR cell with CaF_2 windows. The cell is connected to a vacuum-adsorption apparatus. Prior to the adsorption measurements, the catalyst was activated in a vacuo heating at 598 K for 3 h before hydrogen and 2,6-lutidine were introduced into the catalyst. All spectra were recorded on an Agilent Carry 640 FTIR Spectrometer at room temperature and were done in transmission mode.

Cumene hydrocracking was carried out in a microcatalytic pulse reactor at 523 K under hydrogen stream. A dose of reactant (0.5 µL) was injected over the activated catalyst and the products were trapped at 77 K before being flash-evaporated into an online 6090N Agilent Gas Chromatograph equipped with VZ7 packed Column and FID/MSD detectors for quantitative and qualitative analyses.

3. RESULT AND DISCUSSION

Figure 1 (A) shows the mole products of cumene cracking over Pt/ZrO_2 and Pt/Cr_2O_3-ZrO_2 catalysts at 523 K in a microcatalytic pulse reactor in the presence of hydrogen carrier gas. Pt/ZrO_2 shows the lowest activity with only 2.57 µmol of the total products. The introduction of Cr_2O_3 markedly increased the activity by a factor of 2 and 5 for 1 wt% and 8 wt% Cr_2O_3 loading, respectively.

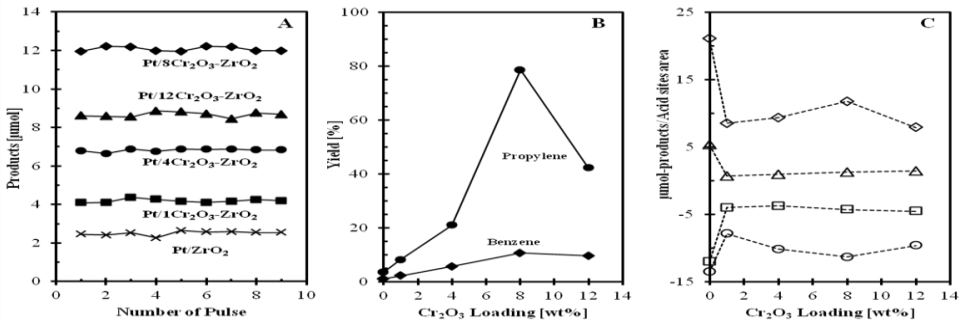

Figure 1. (A) Products for the cumene hydrocracking at 523 K over Pt/ZrO_2, $Pt/1Cr_2O_3$-ZrO_2, $Pt/4Cr_2O_3$-ZrO_2, $Pt/8Cr_2O_3$-ZrO_2, and $Pt/12Cr_2O_3$-ZrO_2 catalysts. (B) Effect of different amount of Cr_2O_3 on the yield of main products (propylene and benzene), and (C) Effect of different amount of Cr_2O_3 on acidic sites. (Δ) Protonic acid sites; (□) Lewis acidic center; (◊) Permanent Brønsted; (○) Permanent Lewis. The Pt/Cr_2O_3-ZrO_2 catalysts were prepared by chromium nitrate solution.

However, the 12 wt% Cr_2O_3 loading increased the activity only by a factor of 3. These results confirmed the Cr_2O_3 loading perks up the yield of propylene and benzene which reaches a maximum at 8 wt%, Figure 1(B). Pt/8Cr_2O_3-ZrO_2 also attributed to the stronger Lewis acidic center at doublets of 1565+1560 cm^{-1} which acts as electrons stabilizer during the generation of protonic acid sites from molecular hydrogen through a hydrogen spillover mechanism. In particular, the presence of small amount of bulk crystalline Cr_2O_3 on Pt/8Cr_2O_3-ZrO_2 may enhance the generation of protonic acid sites from molecular hydrogen which the bulk crystalline Cr_2O_3 act as active sites in the dissociative-adsorption of molecular hydrogen to form hydrogen atoms. But higher amount of bulk crystalline Cr_2O_3 on 12 wt% loading may consists a polychromate structure that exceed the monolayer dispersion of Cr_2O_3 [6]. The excessive amount of Cr_2O_3 on the surface catalyst may lead to decrease the number of molecular hydrogen-originated protonic acid sites. In addition, low activity was determined on Pt/ZrO_2 due to the absence of strong Lewis acidic center which led to a low ability in the generation of protonic acid sites from molecular hydrogen [7]. From the results, it can be summarized that the catalytic activity of cumene cracking increased when the reaction was carried out under hydrogen gas. This high activity can be correlated to the presence of Cr=O band at 1035 cm^{-1} which extensively interacted with H_2 to form protonic acid sites and the presence of strong permanent Lewis acid sites which facilitating in the stabilization of electrons during the formation of protonic acid sites. Besides, the presence of Pt also facilitates the formation of protonic acid sites from molecular hydrogen. This result also shows a direct correlation with the cumene cracking activity at 523 K in which 8 wt% of Cr_2O_3 demonstrated the highest amount of products.

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Kelulusan daripada pihak YBhg. Profesor dalam perkara ini amat dihargai.

Sekian, terima kasih.

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