

Development of a highly selective Ir/WO_x/ZrO₂ ring opening catalyst

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Introduction

The conversion of light cycle oil (LCO) feedstock to diesel-fuel products requires deep desulfurization and hydrogenation followed by ring opening of the naphthenic cycles to form alkanes (molecules with higher cetane index). In general, opening of a six-membered naphthenic ring C₆ is more difficult than that for C₅ [1]. A suitable catalyst must thus contain an acid function to allow for ring contraction. The cleavage of a C-C bond is, then, followed by hydrogenolysis over the metal. To date, no systematic study of the influence of acidity and metal content on C₆ ring opening activity has been performed. Previous studies have shown that the acidity of zirconia can be modulated with deposition of a controlled amount of W [2]. Hence, a catalytic system consisting of tungstated zirconias and a metal with strong C-C bond cleavage activity such as Ir, appears promising. The present paper is a systematic study of the influence of W and Ir loading on the catalyst activity for ring-opening of naphthenic molecules using methylcyclohexane (MCH) as model compound.

Materials and Methods

Zirconium hydroxide was synthesized by precipitation from zirconium oxychloride solution with ammonium hydroxide. The W phase (0-12 wt% W) was deposited by impregnation of the support using ammonium metatungstate solution followed by calcination at 1023 K for 3h. The Ir (0-1.2 wt %) was added by impregnation with a basic iridium chloride solution followed by calcination at 723 K under air. The catalyst was reduced in situ at 623 K under H₂ at atmospheric pressure before use. Tungstated zirconias were designated as WZx where x is the W density expressed as at. W/nm².

The MCH ring opening reaction was performed in a plug flow reactor between 523 and 598 K under hydrogen at a total pressure of 50 bar with a MCH partial pressure of 2 bar for different contact times. The catalyst activity was stable for at least one week.

The acid properties were measured by FTIR at 100 K using CO as probe molecule. The catalyst was pressed into a self-supported wafer, activated in situ as for the activity test, evacuated and finally contacted with CO at equilibrium.

Results and Discussion

The initial rates k_i were determined on the basis of Scheme 1. In the proposed scheme, all reactions are presumed to be first order. Isomerization includes all C₇H₁₄ compounds. Ring-opening products designate C₇H₁₆ isomers. Cracking refers to all compounds with a number of carbon atoms lower than 7.

ZrO₂ and WZx : The ZrO₂ support exhibited no isomerization activity. This was attributed to the low Brønsted acidity of ZrO₂ evidenced by infrared study of low temperature CO adsorption. The isomerization (k_1) and cracking (k_4 , k_5) rates increased with W loading. This was correlated with the observed increase in Brønsted acidity with W content. The ring opening activity was very low for all samples.

Ir/ZrO₂ : A progressive increase in direct ring opening activity (k_2) with Ir content was observed. The catalysts, however, exhibited no isomerization activity illustrating the ability of Ir for direct opening of a cyclohexane ring [1].

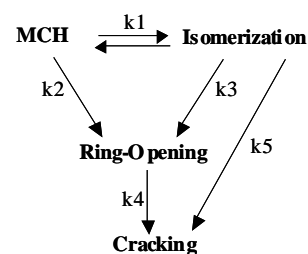
Ir/WZx : Figure 1 shows, for two W surface densities the variation of ring opening and isomerization rates as a function of Ir content. Direct cracking of isomerization products (k_5) increased with W loading but was little affected by Ir content. The rate k_4 increases with Ir content for the WZ1.5 series, but is hardly affected by Ir on WZ3.5. W addition increases the activity for ring opening of isomerized product (k_3) relative to direct ring opening. The rates k_2 , k_4 et k_5 were too low compared to k_1 et k_3 and thus were not included in the Figure.

For all Ir contents the isomerization rate (k_1) was higher for W rich samples WZ3.5. The ring opening rate (k_3) increases with Ir content for WZ1.5 but remains low for WZ3.5. For the latter series, the coverage of the support by the W phase is near monolayer. The results suggest that the hydrogenolysis activity of Ir is inhibited when it is deposited over the W phase.

This study shows that selectivity for ring opening requires a minimum of acidity to promote ring contraction. A strong Brønsted acidity as in the WZ3.5 catalyst (comparable to zeolite HY) favors cracking and appears to be detrimental for Ir hydrogenolysis activity.

Significance

This study contributes to the valorization of LCO, instead of blending with domestic fuel, which is becoming an important issue for petroleum refiners.



Scheme 1. Reaction scheme for MCH conversion.

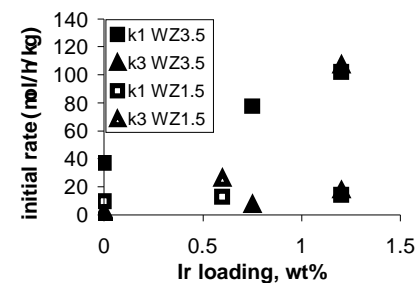


Figure 1. Initial rates at 523 K versus Ir loading for two W densities.

References

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