SULFATED ZIRCONIA AS A CO-CATALYST IN FISCHER-TROPSCH SYNTHESIS

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INTRODUCTION

During the last decade, the average composition of gasoline underwent dramatic changes to make up for the gradual removal of lead compounds, and to meet a strong market demand for premium high octane gasoline. From 1980 to 1988, the average aromatic content in gasoline increased from 22 to 32% and consequently the average octane number increased from 83 to 88.4 [1,2]. Modest increases in olefin and light paraffin (butane) contents also took place. The same tendency was observed in Western Europe [3].

At present, most of the compounds whose concentrations have increased are considered to be directly or indirectly as a threat to the environment and/or human health [2,4]. The challenge is to bring down aromatics, olefins and light hydrocarbons in gasoline to more acceptable levels without adverse effects on the gasoline performance [4]. The most common approach to address this problem is the addition of oxygenated compounds such as MTBE, TAME or ethanol into gasoline. Another approach is to increase the concentration of branched hydrocarbons in gasoline. Indeed, such hydrocarbons have high octane numbers and no major environmental drawbacks. However, according to Unzelman [5], within the limits of existing technologies, isoparaffins cannot be made via isomerization and alkylation in sufficient amounts to replace aromatics below 30%. The objective of the present work is to synthesize branched hydrocarbons from carbon sources other than petroleum. The most obvious choice is synthesis gas (CO/H_2).

The approach we have taken is to use a hybrid catalyst comprised of a Fischer-Tropsch synthesis (FTS) catalyst and a hydroisomerization acid catalyst. The purpose is that the mainly linear hydrocarbons generated on the FTS catalyst would isomerize on the acid catalyst before leaving the reactor. Solid superacid catalysts such as sulfated zirconia (SO_4^{2-}/ZrO_2) exhibit excellent hydroisomerization properties with the formation of significant amounts of branched hydrocarbons [6]. Therefore, we chose to combine Ru loaded on Y zeolite as the FTS catalyst and SO_4^{2-}/ZrO_2 as the isomerization catalyst. In a previous paper [7], we reported data obtained using the hydrogen bracketing technique at atmospheric pressure. In the present communication, we deal with reaction studies in a continuous flow reactor at elevated pressures (mostly at 10 atm).

EXPERIMENTAL

SO_4^{2-}/ZrO_2 and $Pt/SO_4^{2-}/ZrO_2$ catalysts were prepared as described earlier [7]. Surface area and sulfur content of the two catalysts were ca. 90 m^2/g and 1.5 wt%. Pt content in $Pt/SO_4^{2-}/ZrO_2$ was 1 wt%. The FTS catalyst used in this work was 2 wt% Ru loaded on KY zeolite prepared by ion exchange using $Ru(NH_3)_6Cl_3$. Procedures for the preparation of RuKY, the decomposition of the ruthenium complex, and the prereduction of RuKY are the same as those described in [7] for RuNaY. The catalyst thus formed was exchanged again with a dilute solution of K_2CO_3 (0.006 M) to neutralize the protons formed during the decomposition of the Ru complex, and eliminate their possible contribution to the formation of branched hydrocarbons. This catalyst, designated as RuKY-K, was then reduced at 420 °C in flowing H_2 for 4 h.

FTS reaction was carried out in a CDS-804 Micro-Pilot Plant coupled with an on-line gas chromatograph (HP 5890 Series II). The reactor part was described in [7]. Product analysis was carried out using flame ionization (FID) and thermoconductivity (TCD) detectors operating in a parallel mode. A capillary column (PONA from HP, 50m x 0.2mm x 0.5μm) and a stainless-steel column (1/8 in. O.D. x 12 ft. long) packed with Porapak Q (80/100 mesh) were linked to FID and TCD respectively, and used for product separation. All valves and transfer lines between the reactor and the GC were heated to prevent the products from condensation. In a typical experiment, the same amount (0.3 g, unless specified otherwise) of prereduced

RuKY-K and SO_4^{2-}/ZrO_2 or $Pt/SO_4^{2-}/ZrO_2$ were loaded in two separate layers in the reactor, with the FTS catalyst being upstream. They were first reduced at 300 °C for 1 h under a H_2 flow of 40 ml/min and then cooled to reaction temperature (250 °C) under flowing helium. The reactor was pressurized to 10 atm with He, before switching to synthesis gas (CO/H_2 = 1:2, 20 ml/min).

RESULTS AND DISCUSSION

Under the experimental conditions used in the present work, the superacid catalyst did not contribute to CO transformation. CO conversion was due to RuKY-Y catalyst only, and was kept below 10% to minimize the effects of heat and mass transfer. The composition of the C_7 hydrocarbon fraction was used to monitor the effect of SO_4^{2-}/ZrO_2 on product selectivity. Fig. 1 shows iC_7% and $C_7^=$% vs. time-on-stream over different catalysts, where iC_7% and $C_7^=$% designate the content of branched C_7 paraffins and of C_7 olefins in the C_7 hydrocarbon fraction, respectively. Over RuKY-Y catalyst, at 10 atm and 250 °C, iC_7% was below 10 wt%, while the amount of C_7 olefins was very high ($C_7^=$% ≈ 67 wt%). When SO_4^{2-}/ZrO_2 was loaded downstream of the RuKY-K catalyst, iC_7% increased significantly, while only negligible amounts of C_7 olefins were produced in the early stages of the reaction. However, a deactivation of SO_4^{2-}/ZrO_2 catalyst was subsequently observed, as shown by the gradual decrease in iC_7% and the increase in $C_7^=$%. Addition of small amounts (1 wt%) of Pt to SO_4^{2-}/ZrO_2 significantly improved the stability of the catalyst. Under steady state, the iC_7% and $C_7^=$% reached 60 wt% and 10 wt%, respectively.

SO_4^{2-}/ZrO_2 and $Pt/SO_4^{2-}/ZrO_2$ showed different degrees of deactivation during reaction. Two possible deactivation mechanisms were proposed: (i) reduction of S^{6+} to lower oxidation states [8,9]; or (ii) coke deposition on acidic sites [8]. Our TPR results [10] showed that no reduction of surface sulfur species on both SO_4^{2-}/ZrO_2 and $Pt/SO_4^{2-}/ZrO_2$ occurs below 350 °C. The deactivation of SO_4^{2-}/ZrO_2 under our experimental conditions was attributed to coke deposition [7]. On the other hand, CO is known to chemisorb on coordinatively unsaturated surface (CUS) cations which are usually considered as strong Lewis acid sites. Pinna et al. [11] reported that CO can adsorb on CUS Zr^{4+} cations, and the adsorption of CO reversibly poisons active sites for n-butane isomerization, suggesting that the presence of Lewis sites made superacidic by the inductive effect of sulfate species is essential for the occurrence of catalytic activity. Other researchers [12-14] proposed a dual-site model to represent the nature of active sites on SO_4^{2-}/ZrO_2. They suggested that the strongly acidic Bronsted sites are responsible for the catalysis [12, 13, 15]. But the strong acidity of the Bronsted sites requires the presence of adjacent Lewis sites [12-14]. Clearfield et al. [12] and Lunsford et al. [13] argued that through an inductive effect, electrons are withdrawn from O-H bond of surface bisulfate by CUS Zr^{4+} cations, thus yielding stronger Bronsted acid sites. Therefore, whatever the nature of the active sites is, the adsorption of CO on Lewis acid sites of SO_4^{2-}/ZrO_2 will adversely influence the acid strength. As a result, isomerization of hydrocarbons, an acid catalyzed reaction, will be suppressed. To further elaborate on this point, the effect of CO on isomerization of n-butane over $Pt/SO_4^{2-}/ZrO_2$ is being investigated in our laboratory.

Hydrocarbon selectivities under steady state are shown in Fig. 2. It is seen that the presence of $Pt/SO_4^{2-}/ZrO_2$ downstream of RuKY-K has two effects: (i) it alters the normal Schulz-Flory distribution by decreasing the selectivity to C_3 hydrocarbons and by increasing that to C_4's; (ii) it shifts product distribution to lighter hydrocarbons (in particular C_1). The first effect was found to be due to an oligomerization-cracking mechanism of C_3 olefin into C_4 hydrocarbons [7]. The second effect implies the involvement of cracking or hydrogenolysis of primary FT products, which was not observed under atmospheric pressure [7]. To investigate the effect of pressure on FTS product cracking or hydrogenolysis, two reaction experiments were performed at 5 atm, with and without $Pt/SO_4^{2-}/ZrO_2$ catalyst respectively. The results are shown in Fig. 3. By comparing Fig. 2 and Fig. 3, it was found that the net increase in selectivity to C_1 due to the presence of $Pt/SO_4^{2-}/ZrO_2$ is higher at 10 atm than at 5 atm, which suggests a favorable hydrogenolysis at a higher pressure.

Table 1 depicts the effect of the amount of $Pt/SO_4^{2-}/ZrO_2$ used in the hybrid catalyst bed on the composition of C_7 hydrocarbons

under steady state. The increase in the amount of the acid component results in a decrease in olefin contents and an increase in branched C_7 paraffins. In addition, the use of a larger amount of $Pt/SO_4^{2-}/ZrO_2$ favors the formation of di-branched C_7 paraffins which have higher octane numbers than mono-branched paraffins.

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TABLE 1
Effect of the amount of $Pt/SO_4^{2-}/ZrO_2$ on the composition of C_7 hydrocarbons (RuKY-K = 0.3 g, P = 10 atm)

Amount of $Pt/SO_4^{2-}/ZrO_2$ (g)	0	0.3	0.6	0.9
$C_7^=$%	66.0	9.7	0	0
iC_7%	7.0	61.0	76.0	78.0
mono-branched C_7	100	64.0	62.2	58.0
di-branched C_7	0	36.0	37.8	42.0

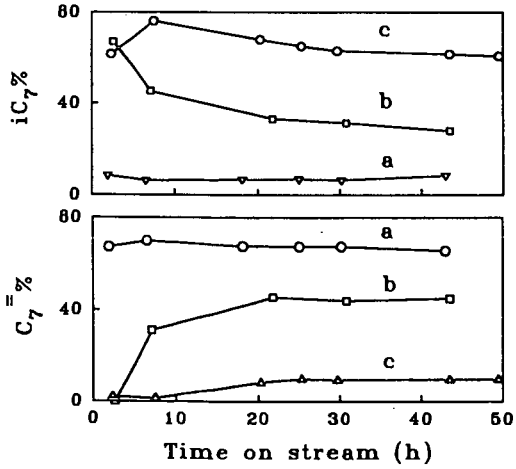

Fig. 1 The composition of C_7 hydrocarbons as a function of time on stream over (a) RuKY-K, (b) RuKY-K + SO_4^{2-}/ZrO_2, and (c) RuKY-K + $Pt/SO_4^{2-}/ZrO_2$.

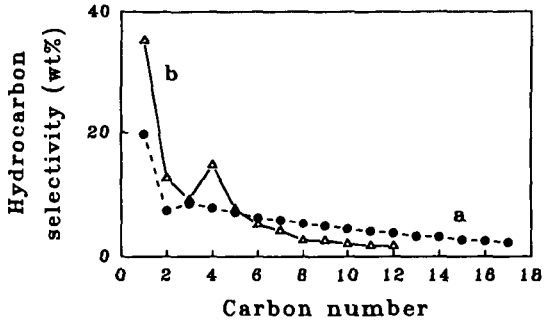

Fig. 2 Hydrocarbon selectivity under steady state at 10 atm over (a)RuKY-K, and (b) RuKY-K + $Pt/SO_4^{2-}/ZrO_2$.

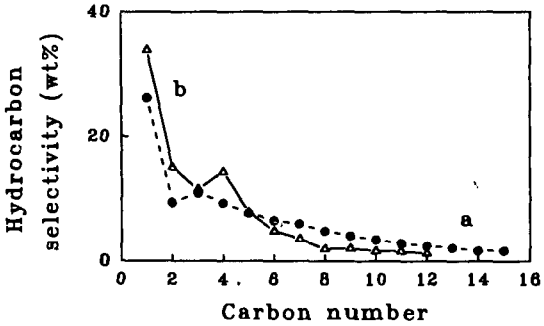

Fig. 3 Hydrocarbon selectivity under steady state at 5 atm over (a)RuKY-K, and (b) RuKY-K + $Pt/SO_4^{2-}/ZrO_2$.