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Fischer–Tropsch synthesis: application of clinoptilolite (natural zeolite) as catalyst support

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ABSTRACT

In this study, clinoptilolite (a naturally occurring zeolite) was used as catalyst support in Fischer Tropsch Synthesis. Prior to its use, raw clinoptilolite was crushed sieved to yield different particle sizes (-212 to +150 μm; -150 to +106 μm; -106 to +75 μm; -75 to +53 μm; -53 to +38 μm; -38 to +25 μm; and less than -25 μm). Seven 10% wt cobalt catalyst supported on different size classes of clinoptilolite were prepared using the incipient wetness impregnation method. A thorough investigation was done on the characteristics of cobalt supported on clinoptilolite particles of different sizes using TPR, XRD, XRF, BET and SEM techniques. It has been demonstrated that these techniques provide insight on the effect of the support particle size, and this could be used as a quality control tool to evaluate the efficacy of the preparation method. Temperature-programmed reduction (TPR) was used to examine the non-isothermal reduction of cobalt oxide using 5% hydrogen in argon at three distinct heating rates (5, 10, 15 ^{o}C/min). When using the Kissinger model, it was discovered that the activation energy (Ea), varied from 102.45 to 254.01 kJ/mol, depending on the support particle size of the catalyst. The lowest activation energy being achieved with a support particle size in the 212 to 150 μm range. Reducing the catalyst reduction temperature has significance in FTS, since it drastically reduces the sum of money spent on the energy input required for reduction. XRD, XRF and SEM confirmed the phases making up the catalyst, loading of the catalyst and the particle size distribution respectively. It is worth noting that though differences exist between different size classes, no clear trend was obtained for any of the BET parameters.

For this study, three size classes were investigated as the support for an FT catalyst: -75 to +53 μm; -53 to +38 μm; less than 25 μm. Using a fixed bed reactor at 220 ^{o}C and 10.85 bar(abs), the maximum CO conversion obtained was 44.97% when using the -53 to +38 μm size class (-78 to +53 μm size class giving 32.06 %, and < 25 μm

μm giving 31.29% Co conversion). At the conditions studied, methane selectivity ranged between 14.95 and 16.97% for the support class size studied, while C_2-C_4 selectivity ranged between 14.55 and 19.01%, and C_{5+} selectivity ranged between 66.04 and 70.29%. The acquired product selectivity results are similar to those reported in the literature, which validates the use of this support. Statistical analysis done on the FT results obtained, one-way analysis of variance (ANOVA) and post-hoc Bonferroni adjustment indicated that utilization of different support size classes had an effect on CO conversion. An innovative data simulation technique based on response surface methodology (RSM) was used as part of the design

of experiments (DOE) to thoroughly investigate the effect of the various operating FTS conditions for both cobalt and Iron based catalyst. These discoveries might be have valuable implications for the design of a catalyst that can be used in the coal/biomass to liquid process.