Test reaction for low-temperature hydride transfer activity of solid acids

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Introduction

Hydride transfer (HT) is an important process that accompanies acid-catalyzed reactions of hydrocarbons. It is responsible for the early interruption of catalytic cracking reaction chains at elevated temperatures, whereas at the lower temperatures characteristic of the isobutane/olefin alkylation on solid acids it is the limiting step involved in the production of high octane rating isoalkanes. Especially in this latter case, knowledge of HT catalytic activities is essential in the evaluation and selection of successful solid acid catalysts. Model reactions previously used to estimate HT activities are essentially focused on reactants and reaction temperatures that are meaningful for the commercial catalytic cracking process [1-3]. Activities measured this way do not usually differentiate between the Rideal-type HT and disproportionation/hydrogen transfer (DHT), as defined by Corma et al.[4].

In this work, a method involving the reaction between cyclohexene (CHXE) and isobutane (IBU) was tested for the measurement of HT activities in several solid acids at 80°C. The contribution from DHT processes was identified and eliminated using control experiments without isobutane. The effect of catalytic material type and characteristics on the measured HT activity was evaluated and HT results were compared with separately measured isobutane/ butene alkylation activities.

Materials and Methods

The catalytic materials tested were zeolites Beta with molar silica/alumina ratios (SAR) of 25 and 75, zeolites ZSM-5 with SAR=80 and sulfated zirconia. The zeolites powders obtained from Zeolyst Int. were incorporated in silica to produce larger particles (65% zeolite). The catalysts (25BEA65, 75BEA65, 80ZSM565 and SZ, respectively) were analyzed by TGA/MS (decomposition into acid form, dry weight) and adsorption analysis (BET surface area, NH_3 chemisorption and IBU adsorption capacity using the volumetric method). HT measurements were performed in a PFR at constant CHXE/acid molar space velocity, 80°C and atmospheric pressure. CHXE vapors from an ice-cooled saturator were mixed with IBU and helium in a constant molar ratio before being fed to the reactor. In control experiments, IBU was replaced by an equivalent flow of helium in order to measure DHT activity. The observed products were cyclohexane (CHX), methylcyclopentane (MCP) and methylcyclopentene (MCPE). Alkylation activity measurements were performed in the gas phase in a batch, stirred reactor, at 80°C and 4.0–4.4 bar, with IBU and 1-butene as reactants and a constant butene/acid feed ratio. The main alkylation product considered was 2,2,4-trimethylpentane (TMP). Product analysis was performed by GC/MS. For both HT and alkylation tests, measured product amounts were normalized to the total number of acid sited as measured by NH_3 chemisorption.

Results and Discussion

In theory, hydride transfer from isobutane to adsorbed cyclohexene should produce a surface C_4 intermediate. No product derived from the C_4 intermediate could be identified in the effluent, while HT products peaked and declined within tens of minutes on stream. It was concluded that the intermediate remained irreversibly attached to the active sites involved in HT. These sites could therefore be titrated by measuring the total amount of HT products (CHX+MCP). The difference in amounts produced with and without IBU was interpreted as a fraction of acid sites available for hydride transfer from isobutane (AHT).

Cumulative results from the characterization and activity measurements are presented in Table 1. For zeolite Beta, a higher acid density (lower SAR) resulted in an elevated AHT, as expected from previous estimations [5]. Of a much higher surface acid density, SZ had a lower AHT probably due to its lower IBU adsorption capacity. ZSM-5 was completely inactive for HT, although it had a significant DHT activity. In this zeolite the narrower, parallel pores interfere with the bimolecular HT from IBU, unlike the intersecting and slightly wider pores in Beta zeolites that seem to facilitate this process. More importantly, the measured AHT values correlated well with alkylation activities. SZ produced more TMP than expected from the AHT, via oligomerization-cracking promoted by its high acid strength and density.

Table 1. Characterization and activity test results

	BET S.A.	NH_3 chemisorption		IBU total adsorption		AHT	TMP produced
material	m^2/g	mmol/g	$\mu mol/m^2$	mmol/g	IBU:acid	mol/mol acid	mol/mol acid
75BEA65	441	0.254	0.58	0.733	2.89	0.065	0.020
25BEA65	444	0.572	1.29	0.780	1.36	0.073	0.040
SZ	90	0.230	2.56	0.034	0.15	0.029	0.023
80ZSM565	333	0.336	1.01	0.377	1.12	0	0

Significance

The test reaction proposed allows for the measurement of hydride transfer activities of solid acids under conditions relevant for the isobutane/olefin alkylation process and can help in the identification of successful solid acid catalysts for alkylation.

References

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