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Performance of mesoporous ZSM-5 for the upgrading of straw derived pyrolysis vapors

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1. Introduction

Fast pyrolysis of biomass produces a high yield of bio-oil through well-established technologies at optimized temperature, pressure, and residence time of the liberated pyrolysis vapors [1], [2]. In order to allow processing in oil refineries, further conversion that reduces the oil's oxygen content and acid number deserve prioritized attention [3]. Deoxygenation can be obtained by catalytic upgrading over solid acid catalysts. A close coupled process operating at temperature and pressure conditions close to those for optimum liquid yields in pyrolysis units offers potential economic advantages for zeolite deoxygenation over high pressure hydrotreating [4]. To date, the medium pore size ZSM-5 zeolite provides a high aromatic yield and the least amount of coke [5] in upgrading of pyrolysis vapors. The coke caused by reactive pyrolysis vapors may form an envelope covering the zeolite crystals and block the pore mouth entries. The rapid decay in site accessibility requires frequent regeneration to recover activity. In addition, irreversible dealumination can be caused by steam from the pyrolysis process, the dehydration reactions during upgrading and the steam produced during oxidative regeneration. We address the reversible deactivation due to coke by introducing an auxiliary mesopores network to improve the accessibility and prolong the zeolite's active time on stream. In order to minimize the irreversible deactivation, the zeolites acid site strength and density have to be carefully balanced with additional metal promoters or modification by phosphorous.

2. Experimental

The screening of the modified ZSM-5 zeolites was performed with 20 -150g of catalyst in a fixed bed reactor downstream an ablative type pyrolysis unit. Crushed wheat straw pellets (Denmark) were used as feedstock at a feeding rate of ~2g/min. By varying the runtime and amount of catalyst, a wide range of biomass feed to catalyst (B:C) ratios is covered and real upgraded product is collected at an optimized condensation train, followed by detailed analysis of the liquid in terms of moisture, elemental analysis, size exclusion chromatography (SEC) and quantification of ~200 components by GC-MS/FID. The micro and mesoporous versions of ZSM-5 tested in this investigation cover the molar Si/Al range of 12.5 to 29.5. Catalyst characterization was performed with ICP, NH₃-TPD, N₂ and Ar-physorption, TEM and XRD.

3. Results and discussion

Mass and energy-balances in the range 90-100% were obtained. At higher amounts of biomass converted, the obtained oil is the cumulative result of fully upgraded products when the catalyst was fresh and products from periods with partial breakthrough of primary pyrolysis vapors. In order to unravel the change in oil-quality with increased B:C ratio, a series of successive conversion steps was performed, as illustrated in Fig. 1a) for ZSM-5 with Si/Al=29.5. A clear reduction in the oxygen content of the oil fractions is observed at low B:C ratio over the steamed ZSM-5 with Si/Al=29.5 in comparison to oil obtained from passing the vapors over a silicon carbide bed at the same temperature (500°C), see e.g. Fig. 1b for CBV30, B:C = 0.6. After the conversion up to B:C=1.1, the additional conversion to reach B:C=2.5 reduces the selectivity for monoaromatics, especially the BTX fraction. When comparing the molar H/C and O/C ratio of the oils obtained from micro and mesoporous ZSM-5 at an operating temperature of 500°C (Fig. 1b), the benefit of the auxiliary mesopore network becomes apparent: while the microporous counterpart rapidly loses its deoxygenation ability, the mesoporous ZSM-5 maintains a similar degree of deoxygenation for almost four times higher B:C ratio.

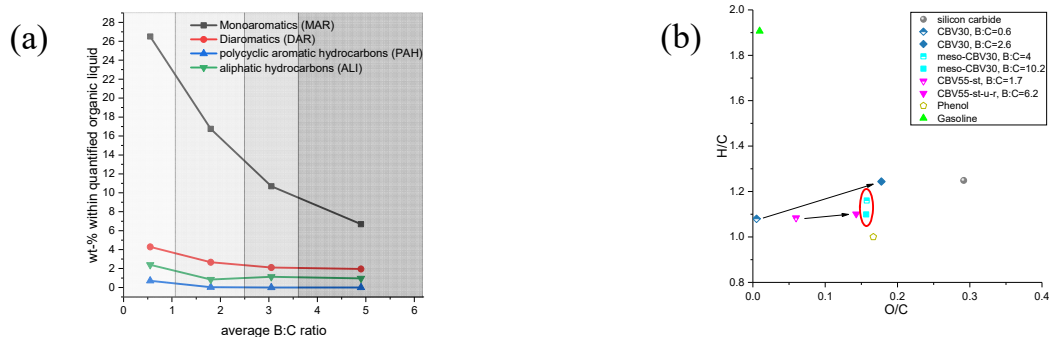


Figure 1: (a) Change of deoxygenated liquid products with increasing catalyst deactivation by coke, here shown for steamed ZSM-5 (Si/Al=29.5); (b) Performance of micro and mesoporous ZSM-5 at operating temperature of 500°C based on molar H/C and O/C ratio

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