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ALKYLATION OF TOLUENE WITH ETHYLENE ON HZSM-5

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Alkylation of toluene with ethylene on unmodified large-crystal HZSM-5 has been studied in a flow system at 673 K, atmospheric pressure. The yield of ethyltoluenes increased and that of benzene and xylenes decreased with time on stream. This change in yields was accelerated by increasing the ethylene content of feed and by pretreating the catalyst with ethylene. Selectivity for toluene ethylation increase with increasing space velocity.

Алкилирование толуола этиленом на немодифицированном цеолите HZSM-5 с крупными кристаллами исследовали в проточной системе при 673 К и атмосферном давлении. Выход этилтолуолов увеличивается, выход бензола и ксилола уменьшается со временем на струе. Это изменение в выходах было усилено увеличением содержания этилена на питании и предварительной обработкой катализатора этиленом. Селективность этилирования толуола увеличивается с увеличением объемной скорости.

INTRODUCTION

Different reactions of alkylaromatic hydrocarbons have been recently studied over shape-selective ZSM-t catalysts [1-5]. The effect of different catalyst modifications on the selectivity observed in alkylation of toluene with ethylene was described by Kaeding et al. [6].

In our work we aimed to shed some light on how the activity of ZSM-5 in alkylation of toluene with ethylene is influenced by the reactants themselves.

EXPERIMENTAL

ZSM-5 powder (T3-ZIPC, Acade. Sci. GDR, Si/Al=15, crystal size: 70% between 3 and 10 µm) was ion-exchanged with 1 N aqueous solution of NH_4Cl. After drying at 105 °C for 4 h the catalyst was pressed into pellets without binder.

Alkylation experiments were carried out in a fixed-bed flow reactor made of quartz. Before reaction, catalyst was heated to 500 °C in streaming hydrogen, kept under these conditions for 2 h, then in a stationary hydrogen atmosphere overnight, and finally cooled to the reaction temperature in hydrogen flow. Hydrogen served as diluent as well, toluene was fed continuously into the stream of ehtylene and hydrogen by a micro pump. The effluents from the reactor were cooled to 15 °C and the condensate collected in a trap was analyzed periodically by gas chromatography.

Reaction conditions were as follows: 2 g of catalyst, atmospheric pressure, reaction temperature = 400 °C, toluene/ /ethylene/hydrogen = 5:1:5 mol/mol except when mentioned otherwise.

The yield of products was calculated by correlation to the amount of toluene fed.

RESULTS

Results obtained in three different experiments are shown in Fig. 1. In expt. 1 the yield of p-ethyltoluene increases continuously with time on stream, while that of o- and m-ethyltoluene goes through a maximum at 4 and approximately at 25 h, respectively. In contrast to ethyltoluenes, the yield of benzene and xylenes decreases continuously with time on stream.

In expt. 2 (toluene/ethylene/hydrogen = 5:2:4) the higher

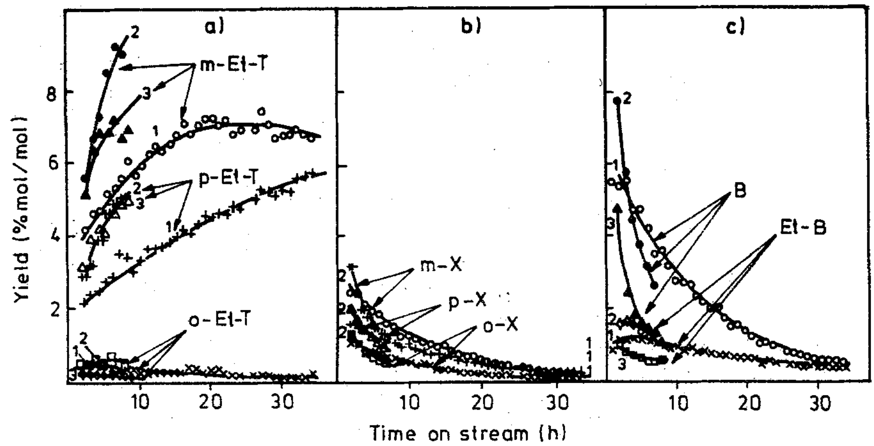

Fig. 1. Yield of ethyltoluenes (a), xylenes (b), benzene and ethylbenzene (c); toluene/ethylene/hydrogen = = 5:1:5 (1,3), 5:2:4 (2) mol/mol; catalyst pretreatment; none (1,2), with ethylene (3)

concentration of ethylene in the feed resulted in a sharper change of yields than in expt. 1. A similar fast change in yields was observed in expt. 3, here before feeding the mixture of reactants, ethylene only was fed for 2 h.

Without ethylene in the feed, i.e. when only disproportionation and demethylation of toluene can take place, the yield of both benzene and xylenes increases with time on stream (Fig.2).

At different space velocities, the change of the yields shows similar characteristics as a function of time on stream. The average values obtained in the 5-7th hours of experiments is plotted as a function of the reciprocal space velocity in Fig. 3. At high space velocities there is a maximum in the yield of p- and m-ethyltoluenes.

The yield of other aromatics increases continuously with the increase of reciprocal space velocity, as it was expected. At the lowest space velocity used by us, the composition of xylenes is close to and that of ethyltoluenes is not far from their thermodynamic equilibrium values (indicated at the right of Fig. 3a and b).

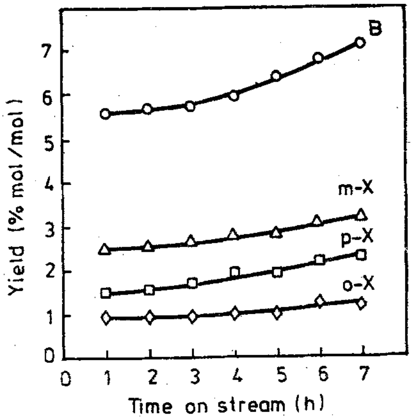

Fig. 2. Yield of benzene and xylenes; toluene/hydrogen = 5:1 mol/mol

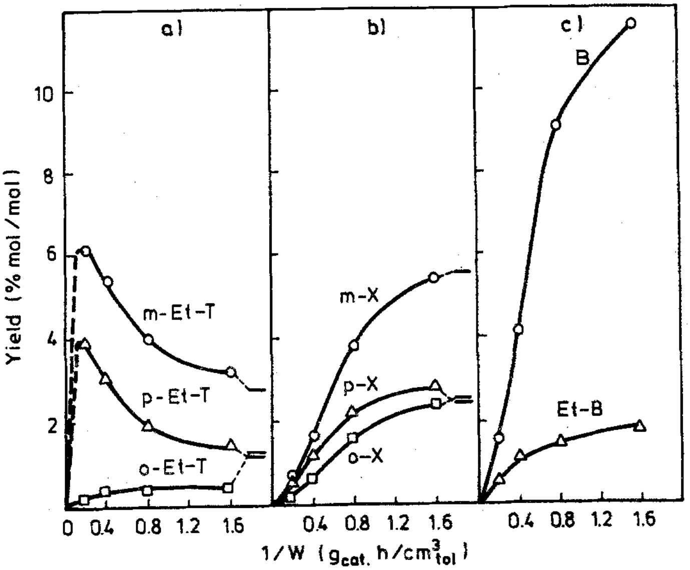

Fig. 3. Average yield of ethyltoluenes (a), xylenes (b), benzene and ethylbenzene (c); thermodynamic equilibrium composition of ethyltoluene and xylene on the right of a and b

DISCUSSION

The products in the toluene/ethylene/HZSM-5 system result from a rather complex set of reactions. The main processes are the ethylation and disproportionation of toluene. The source of ethylbenzene, however, is not clear. It might be thought most likely that it stems from ethylation of benzene. In this case the amount of benzene and ethylbenzene should be equal to the amount of xylenes. This is not the situation. Even, especially at low values of time on stream, excess benzene compared to xylenes was found. This can be accounted for by the formation of benzene through demethylation of toluene and aromatization of ethylene [3,5] and the loss of xylenes by their disproportionation. Occurrence of trace C-9 aromatics in the products is an indication for the latter process.

The relatively high toluene to ethylene ratio (5:1) was chosen to suppress the unwanted reactions of ethylene itself. As can be seen (Fig. 1), ethylene plays an important role in the formation of sites active in alkylation and blocking sites active in disproportionation. Obviously, formation of carbonaceous deposits on the catalyst surface is responsible for the varying selectivity with time on stream. If carbonaceous deposit could develop from ethylene, concomitant formation of benzene could not been disclosed.

The shape of curves in Fig. 3 inspires us to draw a surprising conclusion, i.e. p- and m-ethyltoluene seem to be intermediates, while xylenes and benzene secondary products. It is obvious that benzene and xylenes do not form from ethyltoluenes. A more detailed kinetic study is in progress to shed light on this anomalous phenomenon. For the time being, we can conclude that the higher is the space velocity, the higher is the selectivity for toluene ethylation.

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