

A Kinetic Approach to the Evaluation of Active Sites in Working Bifunctional Zeolite Catalysts

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Introduction

In this presentation, we consider a detailed kinetic approach to the evaluation of the different active sites in working bifunctional zeolite catalysts that relies on analysis of the rates of formation of certain reaction products that can be associated with the active sites of a particular type. Our approach develops further previous kinetic characterization of the acid sites in zeolites [1-3], and was used recently for the first time for characterization of gallium (Ga) and acid sites in working GaH-TON aromatization catalysts [4]. This study extends the proposed approach to investigation of the active sites in working GaH-MFI aromatization catalysts and, as a result, leads to the quantitative comparison of the steady-state normalized activities of the acid and Ga sites (i.e. turnover frequencies) present in the GaH-MFI and GaH-TON bifunctional catalysts.

Materials and Methods

MFI (ZSM-5) and TON (theta-1) zeolites were provided in H-form by BP Chemicals. The Si/Al atomic ratio was 40 and 37 for MFI and TON zeolites; respectively, and the Na content was below 0.01 wt.% for both zeolites. These two zeolites, H-TON and H-MFI, were used as catalysts without any modification. The Ga containing zeolite catalysts, GaH-MFI and GaH-TON, were prepared by incipient wetness impregnation of the parent zeolites with an aqueous solution of Ga(NO₃)₃. The Ga content was 1.5 wt.% in both catalysts. The kinetic studies of n-butane transformation were carried out at atmospheric pressure in a continuous flow micro-reactor with 100% n-butane as feed. The reaction temperature was 530°C. The acidity (type and number of acid sites) of the catalysts was characterized by FTIR spectroscopy using ammonia and pyridine as test molecules. The detailed procedures of catalyst preparation, FTIR characterization, and kinetic experiments are described elsewhere [4,5].

Results and Discussion

In this study, a kinetic evaluation of the acid and Ga active sites in working GaH-MFI and GaH-TON catalysts was carried out using the rates of formation of the primary products of n-butane aromatization reaction. Analysis of these rates together with the IR spectra of the purely acidic and Ga containing MFI and TON catalysts has demonstrated that the rate of ethane formation at low conversions of n-butane can be used for the quantitative characterization of the number of Brønsted acid sites (BAS) present in working Ga containing catalysts. Based on this finding, we have shown that the number of BAS in the GaH-MFI and GaH-TON catalysts is decreasing considerably during initial period of n-butane reaction and stabilizes after 15-20 min on stream. These results together with the results reported recently [5] lead to conclusion that the evolution of the Ga containing MFI and TON catalysts under reaction conditions is associated with the formation of catalytically active Ga⁺ species and

related consumption of BAS according to the chemistry (see Eq. (1)) that was first postulated by Price and Kanazirev [6]:



As a consequence of this process, introduction of Ga (1.5 wt.%) into H-MFI and H-TON zeolites has a very weak effect on the overall steady-state catalyst activity in n-butane conversion, as the gain in n-butane dehydrogenation activity (due to Ga active sites) is nearly compensated by the loss in n-butane protolytic cracking activity. For the steady-state reaction conditions, we have obtained, for the first time, quantitative estimates for the numbers of the BAS and Ga active sites in the working GaH-MFI and GaH-TON catalysts as well as for the turnover frequencies of these sites in n-butane transformation. We anticipate that these results will facilitate understanding of the precise roles of the acid and Ga sites in the mechanisms of alkane aromatization and, as a far-reaching implication, will prompt wider use of detailed kinetic studies for evaluation of active sites in working catalysts.

Significance

In this paper we describe a detailed kinetic approach to the quantitative evaluation of active sites in working Ga containing bifunctional zeolite catalysts. In our opinion, this approach goes far beyond this particular reaction, since it can be used for different catalytic systems where formation of certain reaction products is associated with the active sites of a particular type.

References

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