



Toluene disproportionation and coking on zeolites Y modified with Lewis-connected InO^+ acid sites

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Abstract

The effect of introduction of Lewis acid sites on the reactions of toluene transformation and catalysts coking has been studied over parent ($\text{Si}/\text{Al} = 2.5$) and dealuminated ($\text{Si}/\text{Al} = 3.7$) Y zeolites modified with Lewis connected InO^+ cationic acid sites. The catalysts with prevalent amount of Brønsted acid sites (less than 40% of protons exchanged by InO^+) possess the typical for the proton directed reaction of methyl transfer upon toluene disproportionation long period of activation, the longer the higher the concentration of bridging protons. In contrast, at predominant Lewis sites concentration, the activation period disappear, an enhanced initial activity is observed, followed by deactivation on the expense of a rapid process of accumulation of strongly held reaction products and intermediates. Their further condensation leads to catalysts aging, the faster the higher the concentration of electron acceptor Lewis acid sites. A relation has been found between the initially accelerated processes of alkyl transfer and the reinforced formation of carbonaceous deposits over the In-modified catalysts.

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1. Introduction

Disproportionation is one of the major practical processes for interconversion of aromatics, especially for the production of dialkyl benzenes. Manufacturing of surplus toluene by disproportionation is one of the areas for new process innovations in response to the market situation and legislation changes, and still provokes a growing interest in both academic and industrial research.

Early studies on toluene disproportionation have established that Brønsted acid centers were the seat of catalytic activity [1,2]. Later it is asserted that Lewis acid sites related to non-framework aluminum generated by (hydro) thermal treatment of zeolites have a pronounced promoting effect on ethyl benzene [3] and toluene [4,5] disproportionation. In their thorough review on alkylation and alkyl transfer of aromatics, Cejka and Wichterlova [6] have suggested a direct participation of the Lewis sites in these transformations.

The determination of the amount and the accurate identification of the nature of the extra-framework Al species considered as active ones in alkyl aromatics transformations remains, however, practically impossible. It is still not clear which of the great variety of non-framework cationic Al species, AlO^+ , $\text{Al}(\text{OH})_2^+$, $\text{Al}(\text{OH})_2^{2+}$, etc. actually interact with the reactants and how. It is not clarified, as well, what portion of the bridging protons have remained accessible, not compensated by cationic Al, or not shielded by neutral entities as Al_2O_3 or polymeric oxides [7,8]. This vagueness makes the evaluation of the contribution of these sites quite undefined.

In our previous investigations a model system in which controllable replacement of the protons of Beta and Y zeolites by well defined and stable InO^+ cations (proved to act as electron acceptor Lewis acid sites [9]) has been proposed for studying the role of Lewis acidity in conversions of different alkyl aromatics [10–12]. A partial introduction of InO^+ counter ions have been performed by reductive solid-state ion exchange (RSSIE) followed by oxidation, a method allowing incorporation, together with the bridging protons, of stabilized Lewis acid centers of well-known nature and strength [9]. It was found that the introduc-

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tion of coordinatively unsaturated Lewis acid sites strongly influence the Brønsted-mediated process of toluene disproportionation. A mechanism for the contribution of these sites has been suggested [10,12]. Since these investigations have been performed over catalysts containing both protons and InO^+ cationic sites, it has still remained under question whether the contribution of the latter centers has been independent or it has been assisted by the presence of residual bridging protons.

For to shed a light on this issue, an attempt has been undertaken in the present study to prepare a proton devoided, entirely In exchanged materials, so as to eliminate the role of the Brønsted sites and to evaluate the participation of the Lewis sites only. Also, the effect of the large variation of the Brønsted/Lewis acid sites ratio in directly synthesized parent faujasite and its dealuminated analogue modified with indium has been investigated. The hypothesis about the reinforced coke formation upon toluene disproportionation in presence of In exchanged catalysts proposed formerly [12] has been experimentally checked.

2. Experimental

2.1. Catalysts preparation and characterization

The parent Y (Si/Al = 2.5) and Y zeolite dealuminated with crystalline $(\text{NH}_4)_2[\text{SiF}]_6$ (Si/Al = 3.7) were modified by InO^+ cations according to the following procedure for RSSIE described in Ref. [9]. Ground mixtures of In_2O_3 and NH_4Y in certain In: NH_4 mole ratios were subjected to gradual heating up to 723 K in H_2 flow and maintained at this temperature for 2 h in order to accomplish the RSSIE. Afterwards, an oxidation pretreatment at the same temperature for 1 h was applied in order to transform the In^+ cations to InO^+ . The $\text{InO}^+:\text{NH}_4^+$ mole ratio was varied from 0.16 to 1.0 (Table 1). The process of replacement of the protons by In^+ cations formed upon reduction of the admixed In_2O_3 and the further oxidation of these counter ions to InO^+ ions were followed by IR spectra of adsorbed pyridine (Py). IR spectra were recorded on a Nicolet FTIR spectrometer (Impact 400) using self-supporting wafer transmission technique. Sample

pretreatment at 723 K in high vacuum for 1 h and adsorption of Py at 473 K and 5.7 mbar Py pressure for 30 min were performed in situ in the IR cell. The spectra were registered after cooling down the wafers in pyridine atmosphere to 373 K and degassing in high vacuum at 373 K for 0.5 h.

2.2. Catalytic measurements

The catalytic experiments were carried out in continuous flow reactor at atmospheric pressure [11] at $T_r = 575$ and 723 K and $\text{WHSV} = 1.2 \text{ h}^{-1}$ in N_2 flow. The catalysts were pretreated in the reactor in the same way as it was done for the IR experiments in order to obtain the aimed InO^+ modifications. After this pretreatment the samples were purged in N_2 for 30 min at the chosen reaction temperature and the reactant was introduced (through a saturator kept at 273 K, $P_{\text{tot}} = 0.9 \text{ kPa}$) into the reactor. On-line GC analysis (HP 5890, Series II equipped with FID and a 25 m HP-FFAP capillary column) of the reaction products was performed.

2.3. Coke determinations

Thermogravimetric microbalance (Setaram TG 92) experiments described in Ref. [10] were used for determination of the adsorbed carbonaceous species on the spent catalysts. The preparation procedure of the used catalysts included the following. The catalytic experiments were aborted after chosen time period, the volatiles were eliminated by heating in N_2 for 30 min at the reaction temperature. Then the samples were cooled down, taken out from the reactor, placed in the microbalance and heated first in Ar by raising the temperature (10 K/min) up to 823 K, and then in air at 823 K for another 2 h. The registered weight loss was accepted as a measure of the strongly held intermediates and products desorbed up to 823 K in Ar, as well as of the carbonaceous deposits removed in air at 823 K.

3. Results and discussion

Special precautions have been undertaken in order to assure preparation and reaction conditions at which the desired

Table 1
Chemical composition of the starting, dealuminated and In-modified catalysts

| Samples | Al (mmol/g) | NH_4 (mmol/g) | InO^+ (mmol/g) | $\text{InO}^+:\text{NH}_4^{\text{a}}$ (mol) |
|----------------------------|-------------|------------------------|-------------------------|---|
| $\text{NH}_4\text{Y}(2.5)$ | 4.75 | 2.96 | – | 0 |
| $0.16\text{InY}(2.5)$ | 4.75 | | 0.47 | 0.16 |
| $0.36\text{InY}(2.5)$ | 4.75 | | 1.06 | 0.36 |
| $0.58\text{InY}(2.5)$ | 4.75 | | 1.72 | 0.58 |
| $1.0\text{InY}(2.5)$ | 4.75 | | 2.93 | 0.99 |
| $\text{NH}_4\text{Y}(3.7)$ | 3.53 | 2.91 | – | 0 |
| $0.16\text{InY}(3.7)$ | 3.53 | | 0.47 | 0.16 |
| $0.43\text{InY}(3.7)$ | 3.53 | | 1.25 | 0.43 |
| $1.0\text{InY}(3.7)$ | 3.53 | | 2.85 | 0.98 |

^a Determined according to [9].

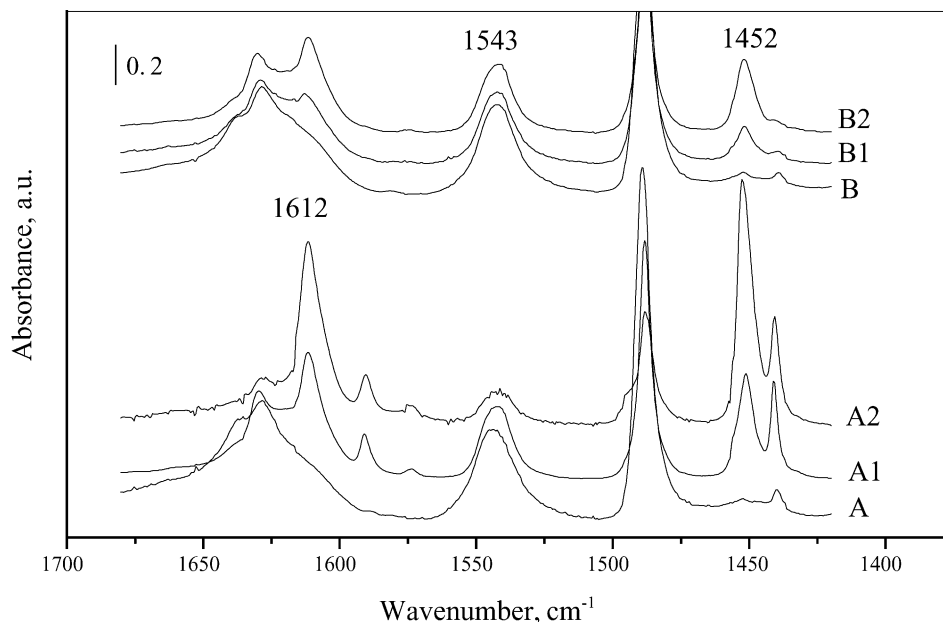


Fig. 1. Spectra of pyridine retained after adsorption at 470 K and subsequent degassing at 370 K on $\text{NH}_4\text{Y}(2.5)$ (A), and $\text{NH}_4\text{Y}(3.7)$ (B), thermally pretreated in HV at 720 K for 0.5 h; $\text{In}_2\text{O}_3/\text{NH}_4\text{Y}(2.5)$ mixtures, viz. $\text{In}/\text{NH}_4 = 0.36$ (A1), 0.58 (A2); $\text{In}_2\text{O}_3/\text{NH}_4\text{Y}(3.7)$ mixtures $\text{In}/\text{NH}_4 = 0.16$ (B1) and 0.43 (B2) subjected to RSSIE at 720 K in flowing H_2 at 670 and 720 K for 0.5 h and oxidized with O_2 at 670 K for 0.5 h.

amounts of indium to be introduced and stabilized in cationic positions as InO^+ and the Lewis to Brönsted ratio to be fixed reliably. Precautions have also been taken for prevention the access of any traces of H_2O impurities in the reactants and in the flow gases during the sample pretreatment preceding both catalytic and IR spectroscopic measurements. Contact with H_2O was excluded by severe drying with highly efficient traps filled with activated molecular sieve 3A.

Fig. 1 shows the IR spectra of Py adsorbed on $\text{NH}_4\text{Y}(2.5)$ (spectrum A) and $\text{NH}_4\text{Y}(3.7)$ (spectrum B) thermally pre-

treated in high vacuum as well as on their mixtures with different amounts of crystalline In_2O_3 subsequently subjected to RSSIE and oxidized (spectra A1, A2 and B1, B2, respectively).

The proportional decrease in the intensity of the pyridinium bands (1543 cm^{-1}) corresponding to the amount of bridging OH left after the RSSIE followed by oxidation is accompanied by the appearance and increase of the bands attributed to pyridine coordinatively bonded to InO^+ cations (1452 and 1612 cm^{-1}). From the release of Py with

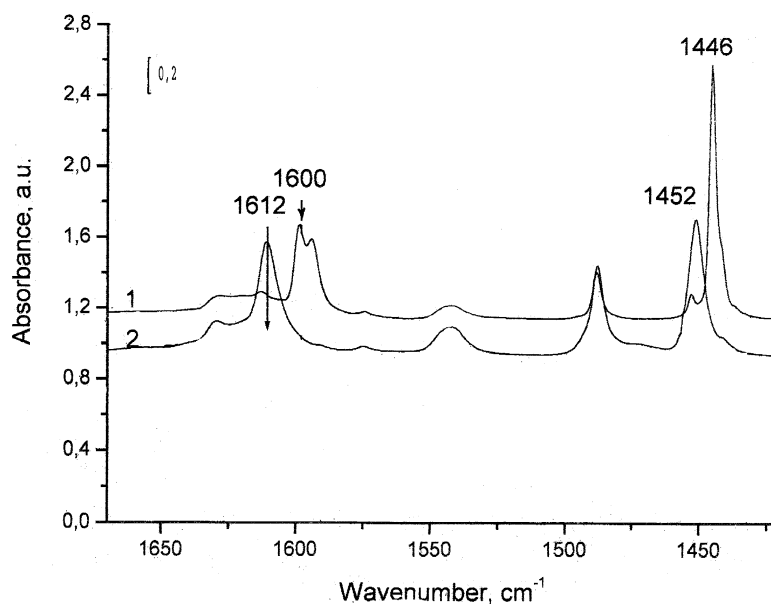


Fig. 2. Spectra of Py retained after adsorption at 470 K and subsequent degassing at 370 K on $\text{In}_2\text{O}_3/\text{NH}_4\text{Y}(3.7)$ mixture with 1:1 $\text{In}:\text{NH}_4$ mole ratio reduced in H_2 (1) and subsequently oxidized in O_2/Ar flow (2).

increasing degassing temperature (not shown), it follows that InO^+ represents a strong Lewis acidity as it was also proved in [13].

In Fig. 2 the IR spectra of Py retained after adsorption at 470 K and subsequent degassing at 370 K on 1.0InY(3.7) firstly reduced with H_2 (curve 1) and then oxidized in O_2/Ar mixture (curve 2) are compared. The very intense bands of Py bonded to In^+ cations (1446 and 1600 cm^{-1}) of the reduced sample show successful accomplishment of the RSSIE. Only hardly notable undulating has remained at about 1543 cm^{-1} . The subsequent oxidation of the univalent In^+ species to cationic InO^+ results in appearance of the band at 1452 and 1612 cm^{-1} corresponding to Py retained by InO^+ Lewis sites. A broad shoulder arises, however, in the hydroxyl stretching region between 3400 and 3700 cm^{-1} (not shown) and an enhancement of the band at 1543 cm^{-1} became visible (Fig. 2, curve 2). This effect suggests a partial restoration of the bridging protons. Hence, an incomplete exchange with InO^+ in 1.0InY(3.7) has occurred, few bridging protons have remained unchanged and the preparation of the aimed 100% exchanged InO^+Y appeared to be unsuccessful. The reasons for the observed effect will be a subject of particular investigation.

In Fig. 3 the time-on-stream (TOS) dependence of toluene conversion over the initial and the In-modified catalysts at the lower (573 K) reaction temperature is shown. The poor ability of the bridging protons in HY to ionize toluene molecules results in a very low activity of the unmodified starting material. The activity is expressed as the sum of the yields of benzene and xylenes, the only products formed

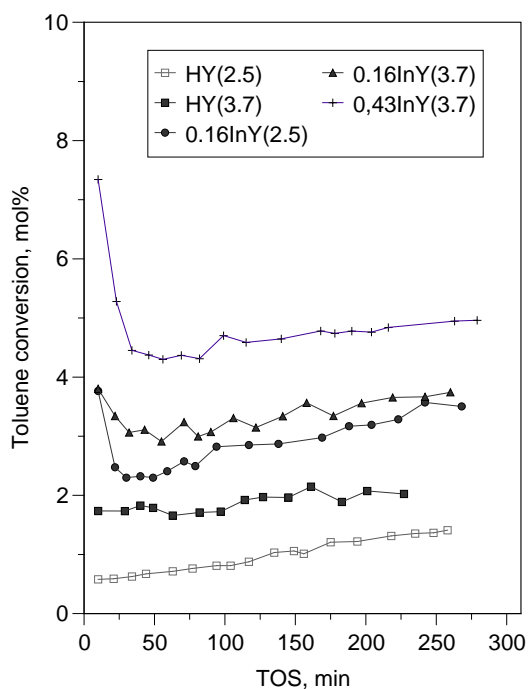


Fig. 3. TOS dependence of toluene conversion over the parent HY(2.5) and dealuminated HY(3.7) and their In-modifications at $T_r = 573\text{ K}$ and $\text{WHSV} = 1.2\text{ h}^{-1}$.

at this reaction temperature. The reduction of the number of acid sites as a result from the dealumination in case of HY(3.7) leads to higher degree of conversion compared to the parent HY(2.5) zeolite.

Compared to the materials containing only Brönsted sites, the partially exchanged with InO^+ (0.16InY(2.5), 0.16InY(3.7) and 0.43InY(3.7)) samples provide much higher initial conversion, followed by a substantial deactivation but only during the first 30 min TOS. A slight, gradual activity increase in the course of the next 4 h follows. Such initial activity decay has been also observed by Rhodes and Rudham [4] for steam dealuminated Y zeolites. In case of HY(3.7) higher activity level is established when the same amount of indium as those in HY(2.5) (Table 1) is introduced.

At the higher reaction temperature (723 K, Fig. 4), very prolonged activation period is also seen for both unmodified catalysts HY(2.5) and HY(3.7). It is shortened, however, for the materials containing less than 40% indium, and deactivation follows, the faster the higher its amount. For the catalysts with lower concentration of residual protons (more than 40% of In introduced), the activity drop starts at the very beginning of the experiment with a rate obviously determined by the Brönsted to Lewis sites ratio (Fig. 4A and B). The elimination of the induction period and the immediate activity decay is most substantial in case of the almost proton devoided samples 1.0InY(2.5) and 1.0InY(3.7). Thus, the prevailing function of the Brönsted acidity for the material with less than 20% protons replaced by InO^+ (0.16InY(3.7), Fig. 4B) manifests itself in retaining a very high and stable activity for the first two hours. When the Lewis acidity predominate, substantial or immediate deactivation follows.

An equilibrium *p*-/*o*-xylene ratio was observed for the initial HY(2.5) and HY(3.7) as well as for the catalyst in which only about 20% of the protons were replaced by InO^+ (Fig. 4A' and B'). Introduction of more indium (0.58InY(2.5) and 0.36InY(2.5)) results in accelerated *p*-xylene production after about 120 min TOS when noticeable deactivation starts (Fig. 4A'). This selectivity arising after the substantial activity loss is most probably a coke-induced *p*-xylene selectivity.

The specific features of the modification with In are most clearly manifested in case of 1.0InY(2.5) and 1.0InY(3.7). A typical deactivation curve is observed for them (Fig. 4A and B) and, in addition, their initial activity is the lowest among the indium containing samples. These effects can be due to enhanced adsorption and retention of products, leading to an increase in their contact time, and consequently, to enhanced formation, still from the beginning, of high molecular weight products-coke precursors, as Cejka et al. [14] have proposed for steam dealuminated HZSM-5 catalysts. The presence of mass-transfer limitations caused by these hardly desorbable products, together with the high amount of bulky InO^+ cations accommodated into the zeolite channels, should be the reason for the relatively lower than expected initial activity detected over these catalysts. Such an

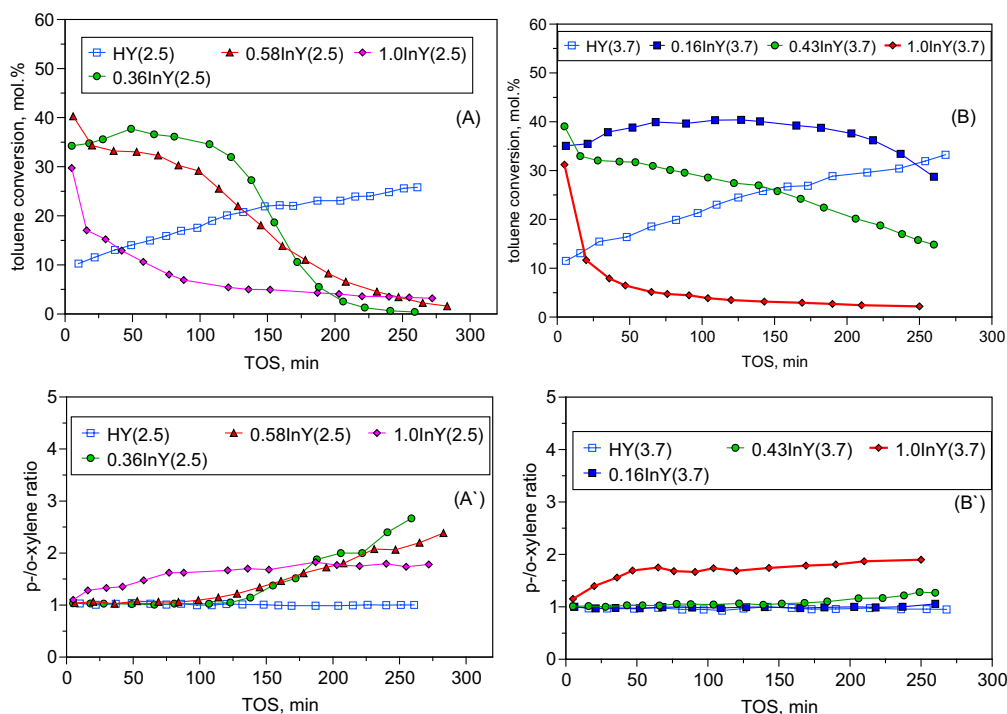


Fig. 4. TOS dependence of toluene conversion (A, B) and *p*-xylene selectivity (A', B') at $T_r = 723$ K over parent HY(2.5) and In-modified HY(2.5) (A and A', respectively), and dealuminated HY(3.7) and In-modified HY(3.7) (B and B', respectively).

effect may also provoke an enhanced *p*-xylene selectivity as actually has been observed (see Fig. 4A' and B'). Favored transfer of methyl group to the less hindered, *p*-position of toluene may also explain the preferential formation of the *p*-isomer on these materials. The as-formed smaller isomer diffuses faster from the pores of the zeolite to the external surface of the catalyst but could not further isomerize there because of the lack of protons left on the exterior.

In Table 2 the composition of the products at $T_r = 723$ K (corresponding to the conversion-TOS dependence in

Fig. 4B) taken at different TOS at which close degree of conversion is attained over the initial HY(3.7) and its In containing modifications is depicted. At the higher reaction temperature studied, and especially at the early stages of the reaction, pronounced dealkylation proceeds in the case of the sample with the highest number of Lewis acid sites in the series. As the data show, benzene to xylenes ratio is the highest (column 2) at the first sampling from 0.43InY(3.7). The selectivity to benzene is also the highest but the selectivity to light gases detected in the gas

Table 2

Yield and selectivity of products at close conversions over HY(3.7) and its In modifications at $T_r = 723$ K and $WHSV = 1.2\text{ h}^{-1}$ (data correspond to the curves in Fig. 4B)

| Samples | 0.43InY(3.7) | 0.43InY(3.7) | 0.16InY(3.7) | 0.16InY(3.7) | HY(3.7) |
|------------------------------|--------------|--------------|--------------|--------------|--------------|
| Conversion, % (mol) | 39.30 | 33.38 | 35.07 | 33.43 | 33.24 |
| Run no. (TOS, min) | 1 (5 min) | 2 (16 min) | 1 (6 min) | 14 (237 min) | 17 (268 min) |
| Yield (%) | | | | | |
| Light gases | 0.57 | 0.96 | 0.41 | 0.91 | 0.67 |
| Benzene | 24.70 | 19.08 | 20.04 | 19.46 | 18.38 |
| <i>p</i> -Xylene | 3.06 | 2.96 | 3.2 | 2.88 | 3.01 |
| <i>m</i> -Xylene | 6.64 | 6.38 | 7.01 | 6.25 | 6.76 |
| <i>o</i> -Xylene | 3.02 | 2.92 | 3.19 | 2.87 | 3.17 |
| Σ xylenes | 12.72 | 12.26 | 13.4 | 11.99 | 12.94 |
| TMB | 1.27 | 1.07 | 1.22 | 1.07 | 1.25 |
| Benzene:xylenes | 1.94 | 1.56 | 1.5 | 1.62 | 1.42 |
| <i>p</i> :- <i>o</i> -xylene | 1.01 | 1.01 | 1.0 | 0.99 | 0.95 |
| $S_{\text{light gases}}$ | 1.5 | 2.89 | 1.2 | 2.7 | 2.1 |
| S_{benzene} | 62.8 | 57.16 | 57.1 | 58.2 | 55.3 |
| S_{xylenes} | 32.40 | 36.75 | 38.2 | 35.9 | 38.9 |
| S_{TMB} | 3.3 | 3.2 | 3.5 | 3.2 | 3.8 |

phase is not. It could be proposed that oligomers of the type $(\text{CH}_2)_n$ have been formed and strongly adsorbed on the surface at the initial stage of the reaction. The second sampling from this experiment over 0.43InY(3.7) (16 min TOS, Table 2, column 3 and Fig. 4A and B) shows very close conversion level to those obtained at the first sampling from 0.16InY(3.7), as well as close selectivity to benzene, xylenes, and to trimethyl benzenes (TMB). On the latter catalyst a high steady-state conversion is established for the following 200 min TOS. In the same time, more than 4 h are needed for the parent material containing only Brønsted acid sites to reach the initial activity and selectivity level to the initial ones of the In containing samples at the reaction conditions used (Fig. 4B and Table 2, last column).

On the basis of the results obtained, it can be concluded that the effect of the prevailing proton sites concentration consists in a presence of activation period and slow deactivation or absence of such, in dependence on the amount of In and the reaction temperature. The predominance of the Lewis acid sites function manifests itself in shortening or disappearance of the period of activation and acceleration of the catalysts aging. The latter is mostly pronounced in the almost fully exchanged materials. It is hard to believe that such an effect might be caused by the even enhanced individual action of the few residual protons in them. A direct participation of the InO^+ Lewis-connected acid sites is rather acceptable. In accordance to our findings, faster initial toluene conversion and activity decay are observed over steam dealuminated Y zeolites containing substantial amount of extraframework Al, compared to their analogues from which the extralattice aluminum is extracted [4].

The bimolecular reaction mechanism of alkyl aromatics disproportionation invoking a diphenyl alkane-like intermediate (DPA) formation is widely accepted in the literature, especially for the large pore zeolites. It is consistent with the presence of an induction period needed for the formation of the so-called chain carriers, benzylic cations and diphenyl methane (DPM) type cations in toluene disproportionation [4,5,15]. As our present data show, about 5 h for HY(3.7), or even more for HY(2.5) are required for these chain carriers to be built up (Fig. 4), so as the highest activity level for the reaction conditions used to be reached. Over the corresponding In-modified materials this process appears to be very fast, due to the presence of the Lewis acid In cationic sites. The duration of the time period necessary for the build up of the reaction intermediates is obviously dependent on the amount of the introduced electron acceptor sites and even is lacking when more than 40% of the protons are replaced by such sites. As it was already assumed in [12], a highly accelerated formation of the chain transfer agent, $\text{C}_6\text{H}_5\text{CH}_2^+$ and respectively, of the diphenyl methane intermediate needed for this reaction pathway in case of toluene reactant occurs in presence of cationic sites. Exactly these intermediates, however, are found to be prerequisites for coking according to Refs. [16,17]. As the authors have proved, these compounds actively participate in further reactions of

condensation to higher polyaromatics, the main coke constituents in toluene disproportionation. Thus, the favorable, much faster initial DPM intermediates formation that assists toluene transformation, becomes detrimental because of the rapid transformation of the latter to coke.

An attempt to evaluate this process was undertaken in the present study. The dynamics of formation of carbonaceous residues in dependence on the presence or absence of InO^+ cationic sites over spent catalysts or over partially coked samples (taken out of the reactor after different duration of the catalytic run) was estimated by microbalance thermal analysis. The registered weight loss at different temperature regions served as a measure for the relative distribution of carbonaceous species removed in flowing Ar, and in air, analogous to the procedure described in [10]. In accordance with it and with the interpretations of Bibby et al. [18] and Pradhan et al. [19], three well established peaks of elimination of water (I), reaction intermediates and strongly adsorbed products (II) as well as more mobile carbonaceous deposits—"soft" coke (III) were detected in argon flow (Fig. 5). The strongly retained, more condensed compounds liberated upon air combustion are considered as "hard" coke (IV). In Fig. 5 the DTG profiles of the spent dealuminated HY(3.7) catalyst and its In modifications, are presented. In accordance with the catalytic results, for reaction time with 260 min duration, HY is still undergoing activation (Fig. 4B) and there is no "hard" coke accumulated on it after this long working period (Fig. 5A). A large amount of water (peak I), a very substantial quantity of adsorbed intermediates (most probably the so-called "chain carriers" and products trapped into the zeolite channels, peak II) as well as highly volatile coke precursors (peak III) are observed on it. In contrast, limited amount of H_2O (the lower the higher the In content) is detected on the In modifications, most probably because of the restricted pore void volume (Fig. 5B–D). The amount of the more loosely bound hydrocarbon compounds (peak II) and the carbonaceous species released last in Ar at about 800–810 K (peak III) are diminishing considerably with the increase of the concentration of InO^+ . They seem to be transformed to more condensed, most probably anthracenic and phenanthrenic compounds, formed through cyclization and hydride transfer [17] as the appearance of peak IV demonstrates upon introduction of air (Fig. 5B–D). These and other polycyclic aromatics as well as polyolefinic compounds are found to be the main coke constituents retained over HFAU and HFMI upon toluene disproportionation by means of various spectroscopic techniques [17,20].

Therefore, the parent and modified catalysts differ in the composition of the coke formed over them. The coke precursors on the H-forms consist of much higher amount of more volatile compounds, since on the In-containing samples it comprises more condensed deposits. The contribution of the introduced InO^+ cations to the process of transformation of the retained adsorbed species is obvious. As Fig. 6, curve B reveals, very substantial amount of "hard" coke is established still after 16 min reaction time over 0.43InY(3.7)

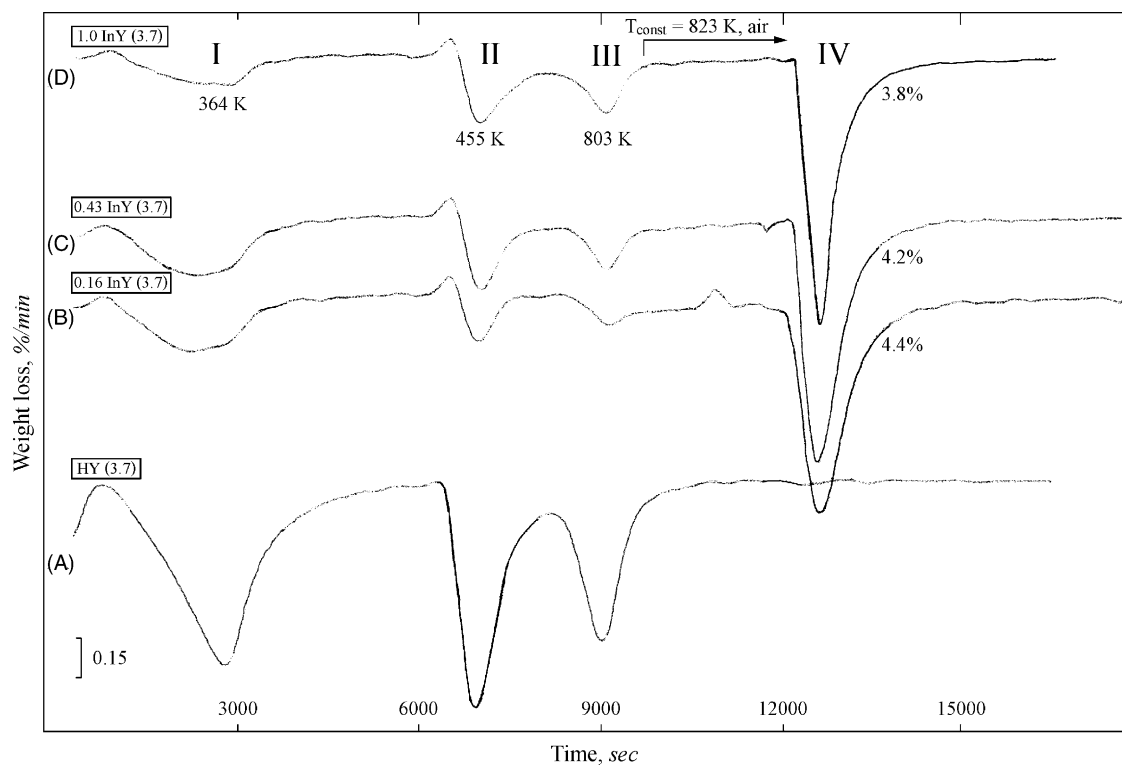


Fig. 5. DTG profiles of the spent (260 min TOS) catalysts: HY(3.7) (A), 0.16InY(3.7) (B), 0.43InY(3.7) (C) and 1.0InY(3.7) (D).

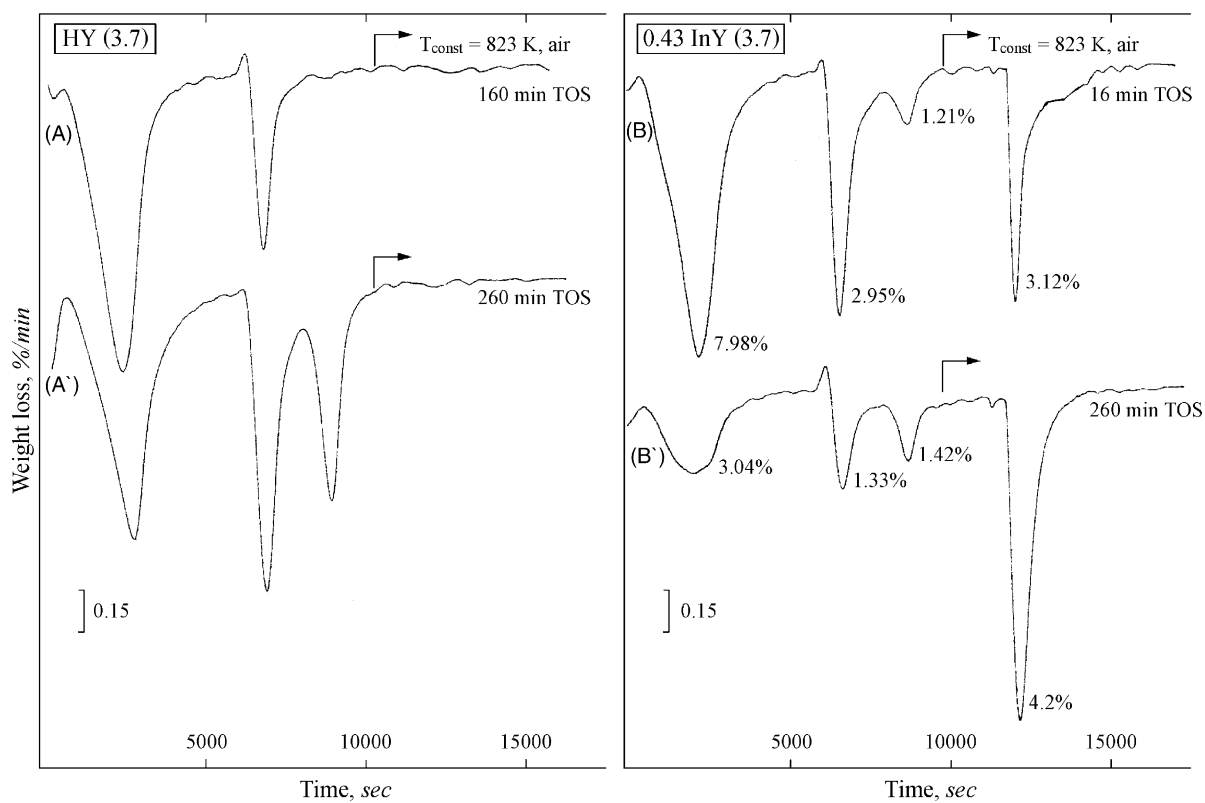


Fig. 6. DTG profiles of HY(3.7), 160 min TOS (A) and 260 min TOS (A') and 0.43InY(3.7), 16 min TOS (B) and 260 min TOS (B').

at which the degree of toluene conversion is practically the same as that attained over HY(3.7) after 260 min TOS (Fig. 4B). No indication for presence of “hard” coke is found on the latter catalyst neither after 160 min (Fig. 6A), nor after 260 min TOS (Fig. 6A’).

The variation of the TGA profiles indicate that the introduction of In strongly accelerates the formation of the necessary intermediates but also of “hard” coke in much shorter reaction time. The comparison of the amount of “hard” coke retained over 0.43InY(3.7) after 16 and 260 min TOS shows that 75% of it is formed still in the beginning of the run (Fig. 6B and B’). The remaining 25% are continuously accumulated within the next 4 h at the expense of the consumption–transformation of the weakly held intermediates. The rate of this transformation is determined by the amount of introduced In and reflects on the rate of deactivation. It can be supposed that the In connected Lewis sites contribute both to an accelerated biphenyl intermediates and oligomeric fragments formation, and to enhanced process of their condensation to coke deposits. In analogy to our observations Rhodes and Rudham have found that coke formation has been suppressed after extraction of non-framework, Lewis connected Al species from steam dealuminated Y zeolites [4]. They also suggest a route for coke formation upon toluene conversion starting from DPM and consider it as “catalytically active coke” participating in the reaction.

The continuous deactivation of the In containing catalysts results in inhibited rate of “chain carriers” formation (respectively reaction rate) as a result from the transfer of the “soft” coke to strongly retained polyaromatics (Fig. 5B–D and Fig. 6B and B’). This process plays, most probably, a major role also in determining the selectivity to xylenes. As it is seen from Fig. 4A’ and B’, an increase in the *p*-xylene production is detected after different reaction times, depending on the rate of deactivation (Fig. 4A and B) of the In exchanged catalysts.

4. Conclusion

Catalysts with large variation in the Brønsted to Lewis acid sites ratio have been obtained in order to study the contribution of the Lewis-connected InO⁺ cations to the reaction of toluene disproportionation over parent and dealuminated Y zeolites. The failure in preparation of proton devoided, fully InO⁺ exchanged catalysts did not permit an evaluation of the individual role of the Lewis acidity. The catalytic behavior of different modifications with prevailing proton or cationic function has been revealed. It is found that at predominant proton acidity the catalysts provide continuous activation period and slow or absence of any deactivation. The Lewis function manifests itself in enhancement of the initial activity, shortening or disappearance of the period of activation and acceleration of the catalysts aging. It is

suggested that InO⁺-connected Lewis acid sites contribute both to acceleration of the DPM intermediate formation (respectively the activity increase) and to an enhanced process of condensation of these intermediates, leading to intense catalysts’ decay. It is presumed that the process of deactivation of the In modified materials is determined by the rate of transfer of the more mobile carbonaceous deposits, “soft” coke to condensed polycyclic aromatics, “hard” coke, and depends on the amount of the introduced electron acceptor sites.

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