ACTIVITY AND SELECTIVITY OF Mg-Fe MIXED OXIDES IN THE ALDOL CONDENSATION OF FURFURAL

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The aim of this work has been to compare the activity and selectivity of Mg-Fe mixed oxides in the aldol condensation of furfural with that of previously studied Mg-Al mixed oxides. Mg-Fe mixed oxides were prepared by thermal pre-treatment of hydrotalcites with a Mg/Fe molar ratio from 1.1 to 7.6. Structural and textural properties of Mg-Fe mixed oxides were analysed by using of XRD and N_2-adsorption. It was found that Mg-Fe mixed oxides exhibited lower conversion of furfural in contrast to the Mg-Al mixed oxides, but being more selective to 4-(2-furyl)-3-buten-2-one (FAc). The difference in the conversion of furfural was relatively low among the Mg-Fe mixed oxides with the Mg/Fe molar ratio in the range of 1.1-5.5.

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Introduction

Aldol condensation of furfural with acetone (see Scheme 1) produces 4-(2-furyl)-4-hydroxybutan-2-one (FAc-OH), which subsequently reacts with 4-(2-furyl)-3-buten-2-one (FAc) and 1,4-pentandien-3-one-1,5-di2-furanyl (F2Ac) [1,2]. In recent studies, the aldol condensation is catalysed by using of homogeneous catalysts (e.g. NaOH). Nevertheless, the utilization of solid basic catalysts is attractive; mainly, due to its easy separation and re-utilization. Aldol condensation is a very important chemical reaction being able of transforming simple organic molecules into molecules with large amount of C atoms that are used in the biomass production. In addition, furfural can be obtained by acid hydrolysis of sugar cane bagasse [3].
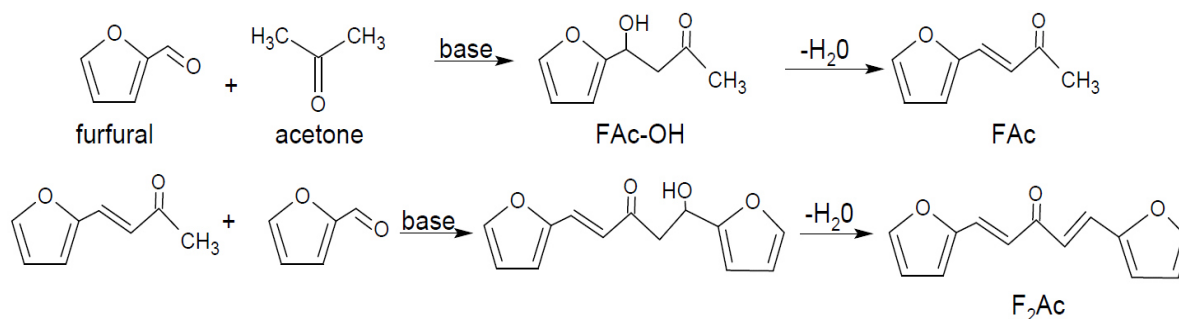
Scheme 1 Reaction scheme of aldol condensation of furfural

The Mg-Fe hydrotalcites have been applied such as adsorbents in the removal of pollutants from aqueous solutions [4,5]. Mg-Fe mixed oxides are attractive solid state catalysts with a potential applicability in basic reactions, e.g. in the trans-esterification of vegetable oil [6] and etherification of glycerol [7]. Mg-Fe mixed oxides could be prepared by thermal pre-treatment of hydrotalcite-like materials [8,9]. In general, more attention is focused on the analysis of structural, basic, textural, and catalytic properties of the Mg-Al mixed oxides that were intensively studied with respect to its utilization in transesterification [10], aldol and Knoevenagel condensations [11] or alkylation [12].

In this work, we focussed on the comparison of the catalytic behaviour of Mg-Fe mixed oxides in aldol condensation with the previously studied Mg-Al mixed oxides. These catalysts were prepared in a wide range of the Mg/Fe molar ratio (from 1.1 to 7.6) by thermal pre-treatment of the corresponding Mg-Fe hydrotalcites. This work is a continuation of our previous intensive study of the relationship between the structural/basic/textural properties and the catalytic behaviour of the Mg-Al mixed oxide based catalysts [13].

Experimental

Synthesis of Materials

The Mg-Fe hydrotalcites were synthesized by co-precipitation method at constant pH. The synthesis was carried out at 25 °C in 3 litre batch glass reactor equipped with a shaft stirrer. $Mg(NO_3)_2.6H_2O$ and $Fe(NO_3)_3.9H_2O$ were dissolved in distilled water and the amount of the individual salts corresponded to the Mg/Fe molar ratio selected; total concentration of metal ions being $1\ mol\ l^{-1}$. This solution was added at stirring (with flow rate of $7.5\ ml\ min^{-1}$) into 200 ml distilled water. The reaction mixture was intensively stirred (at 1400 rpm) and the basic solution (1.5 M KOH and 0.15 M K_2CO_3) simultaneously added in order to keep alkalinity in the range of pH 13 ± 0.1. The resulting suspension was left to age at 25 °C for 24 h. Then, the hydrotalcites formed were filtered off, washed thoroughly with distilled water, and dried at 80 °C for 24 h. The respective samples were denoted as Mg-Fe-HT-*X*, where *X* is the Mg/Fe molar ratio being experimentally determined as: 1.1, 2.3, 3.7, 5.5, and 7.6.

The Mg-Fe mixed oxides obtained by calcination of the corresponding hydrotalcites were grain into a particle size of 0.25-0.5 mm and calcined at 500 °C for 4 h in air flow. The corresponding Mg-Fe mixed oxides were denoted as Mg-Fe-*X*, where *X* is again the Mg/Fe molar ratio, experimentally determined as 1.1, 2.3, 3.7, 5.5, and 7.6.

Characterisation of the Catalysts

The chemical composition of as-prepared samples was determined using XRF analysis, recorded with an X-ray fluorescence spectrometer (model PW1404, Philips). The specific surface areas (S_{BET}) of the Mg-Fe mixed oxides were measured at the boiling point of the liquid nitrogen (–196 °C), determined by fitting the experimental data to the BET isotherm.

Powder X-ray diffraction (XRD) patterns were recorded with a diffractometer (model AXS D8-Advance, Bruker), when using the Cu Kα radiation ($\lambda = 0.154056$ nm) with a secondary graphite monochromator. The coherence length in the Mg-Fe mixed oxides was calculated from the width of periclase (220) diffraction line (observed at approx. $2\theta = 62.5°$) using the Scherrer's equation ($D = K\lambda/\beta\cos\theta$), where *D* means the coherence length (in nm) characterising the crystallite size of MgO-like phase, *K* the shape factor (value of $K = 0.9$ being used), λ wavelength of X-ray radiation, β is FWHM (in rad; full width at half maximum) value, and θ (in rad) is the diffraction angle [14].

Aldol Condensation

The reaction of interest between furfural and acetone was carried out in a 100 ml stirred batch reactor at the temperature of 50 °C. Prior to catalytic tests, the mixture of 39.5 g acetone (dried by a molecular sieve 3A) and 6.5 g furfural (with acetone-to-furfural molar ratio 10/1) was pre-heated to the reaction temperature of 50 °C. Afterwards, 2 g Mg-Fe mixed oxide (with grain of 0.25-0.5 mm) was added and the reaction taking place at 50 °C for 6 h, when the samples were being continually withdrawn from the reaction mixture after 5, 10, 20, 30, 40, 80, 120, 180, 240, 300 and 360 min during the whole experiment. The catalyst was isolated from the reaction mixture by filtration and the products analysed by GC. The gas chromatograph used (model 7890A, Agilent) was equipped with a flame ionization detector (FID), using a capillary column (HP 5 type; with 30 m/0.32 mm ID/0.25 μm).

Results and Discussion

Structure of Mg-Fe Hydrotalcites and Mg-Fe Mixed Oxides

Figure 1 shows the diffractograms of Mg-Fe hydrotalcites. The diffraction lines were observed at 11.6°, 23.2°, 34.1°, 38.2°, 59.9° and 60.9°; these lines being typical for hydrotalcites (with double-layered structure; see e.g. [15,16]). Table I
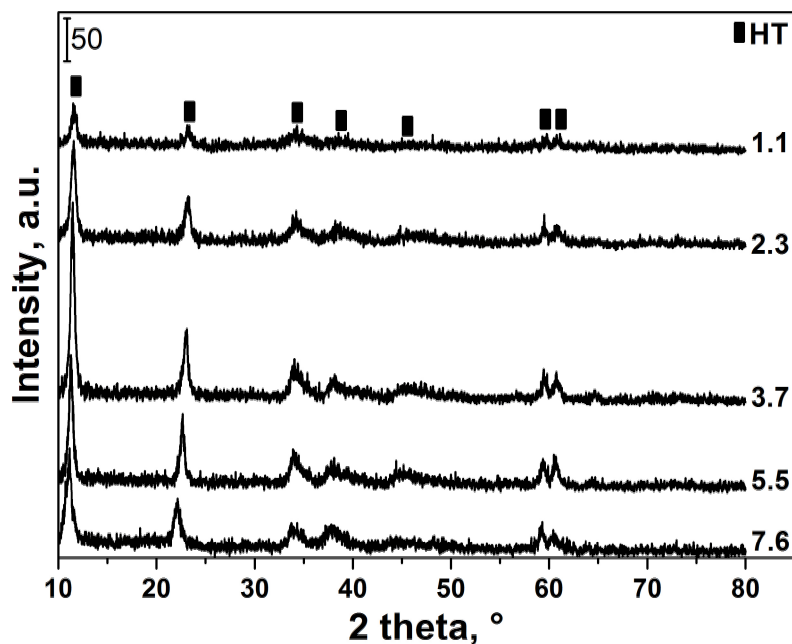

Fig. 1 Diffraction lines of Mg-Fe hydrotalcite-like precursors with different Mg/Fe molar ratio

gives the hydrotalcite lattice parameters a and c that were calculated based on d_{003} and d_{110} values originating from the diffraction lines at 11.6 and 59.9° (with $a = 2\,d_{110}$, $c = 3\,d_{003}$). The parameter a means the cation–cation distance in the brucite-like layer and parameter c then thickness of one brucite-like layer and one interlayer. Both parameters are in the range corresponding to that having been reported for the pure hydrotalcite phases [17,18]. While the values of the unit cell dimension (parameter a) were the same for all the oxides studied in the whole range of Mg-Fe mixed oxides, parameter c, influenced by the size of interlayer anion and the Fe^{3+}-Mg^{2+} cations, had slightly increased with the increasing Mg/Fe molar ratio.

Table I Survey of the Mg-Fe hydrotalcites with selected physical characteristics

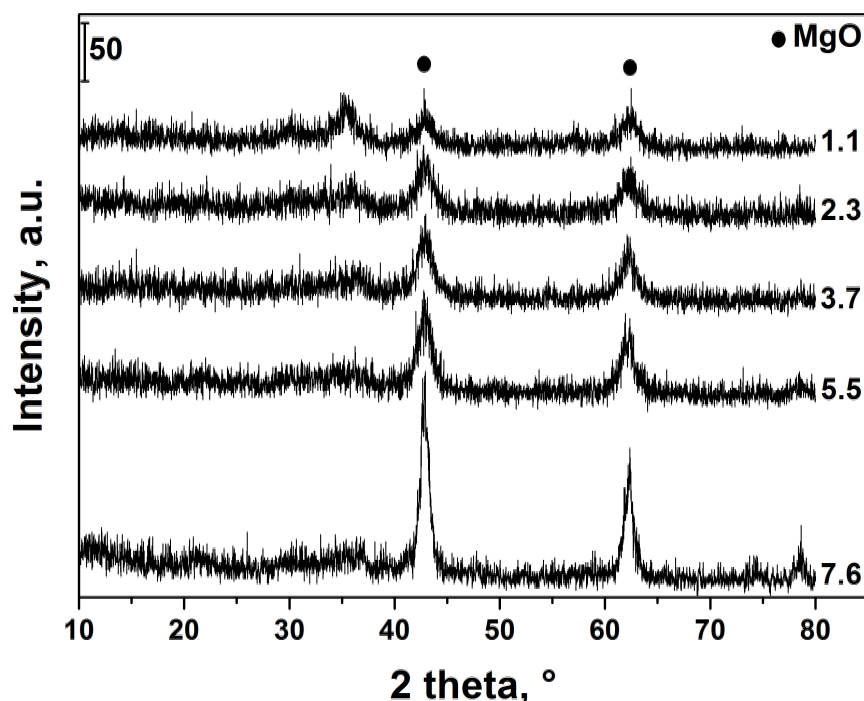|	d_{003} nm	d_{110} nm	a nm	c nm
Mg-Fe-1.1	0.76	0.155	0.31	2.28
Mg-Fe-2.3	0.766	0.155	0.31	2.298
Mg-Fe-3.7	0.773	0.156	0.312	2.319
Mg-Fe-5.5	0.784	0.156	0.312	2.352
Mg-Fe-7.6	0.795	0.156	0.312	2.385

Fig. 2   Diffraction lines of Mg-Fe mixed oxides with different Mg/Fe molar ratio

Figure 2 illustrates the diffractograms of Mg-Fe mixed oxides. There were observed intensive diffraction lines at 43.0° and 62.5° being typical for MgO-like phase or likely magnesia-iron solid solution in Mg-based mixed oxide materials [19,20]. Table II gives the crystallite size of MgO calculated from the diffraction line at 62.5° by using the Scherrer's formula. The crystalline size of MgO increased with the increasing Mg/Fe molar ratio (except for the Mg-Fe mixed oxide with Mg/Fe molar ratio 1.1). There also were low intensive diffraction lines at 30.2°, 35.5°, 43.0°, 57.2°, and 62.5° in the diffractograms of Mg-Fe mixed oxides with the low Mg/Fe molar ratio (1.1 and 2.3). These lines could be attributed to the $MgFe_2O_4$ (magnesioferrite) spinel structure [21-23].

Table II also contains the values of the specific surface area and the results of the elemental chemical analysis of the individual Mg-Fe mixed oxides. The specific surface area achieved its maxima for the Mg-Fe mixed oxide with Mg/Fe molar ratio 2.3-3.7.

Table II Survey of the Mg-Fe mixed oxides with selected physical characteristics

	Mg/Fe molar ratio	D(MgO) nm	S_{BET} $m^2\,g^{-1}$
Mg-Fe-1.1	1.1	5.8	81
Mg-Fe-2.3	2.3	4.9	126
Mg-Fe-3.7	3.7	4.9	127
Mg-Fe-5.5	5.5	6.1	113
Mg-Fe-7.6	7.6	7.7	104

Aldol Condensation of Furfural

Figure 3 shows of the conversion of furfural, the selectivity to FAc-OH, the selectivity to FAc; and the selectivity to F_2Ac; all these in dependence on time. It is clearly seen that, for all the samples, the conversion of furfural proceeded into the most pronounced stage with the increasing time of reaction. With such a pathway of conversion, the selectivity to FAc-OH decreased, whereas the selectivity to FAc and F_2Ac increased. The formation of these products is in agreement with the scheme for aldol condensation.

Figure 4 shows the dependence of the conversion of furfural on the Mg/Fe molar ratio (for 20, 80, 180 and 360 min). It should be stressed that the difference in the conversion of furfural was relatively low among Mg-Fe mixed oxides with the Mg/Fe molar ratio 1.1-5.5. For example, the furfural conversion was in the range of 13 and 15 % at a reaction time of 80 min for these Mg-Fe mixed oxides.
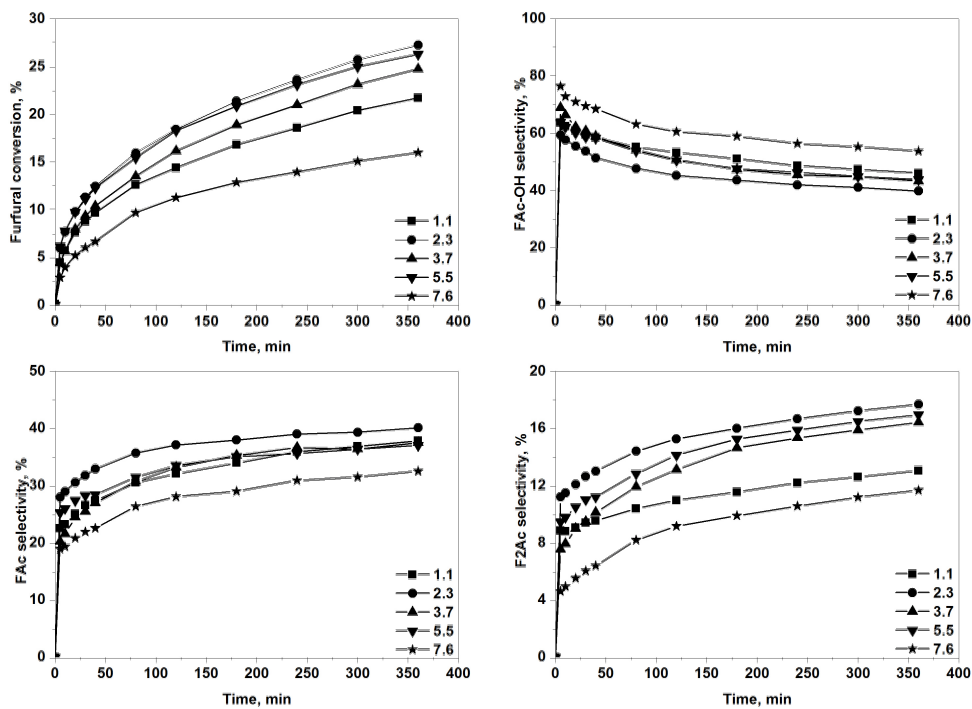
Fig. 3 The reaction-time dependence of the conversion of furfural with respect to the selectivity to FAc-OH, FAc, and F_2Ac for the Mg-Fe mixed oxides studied

Thus, it could be concluded that there was no clear dependence between the furfural conversion and the Mg/Fe molar ratio in the range of 1.1-5.5 being examined. On the other hand, the decrease in the furfural conversion was clearly observed for the Mg-Fe mixed oxides with the Mg/Fe molar ratio of 7.6.
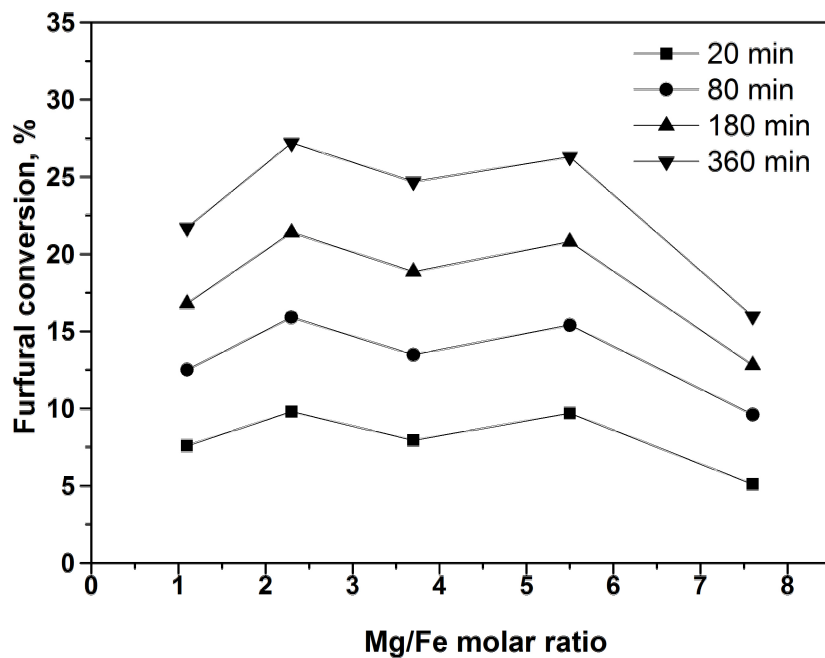

Fig. 4 Dependence of the conversion of furfural on the Mg/Fe molar ratio; reaction time: 20, 80, 180, and 360 min

Kocík J. *et al.*/Sci. Pap. Univ. Pardubice, Ser. A **22** (2016) 81–90

87

Comparison of the Activity/Selectivity of Mg-Fe Mixed Oxides with Mg-Al Catalysts

Firstly, it should be stressed that the Mg-Fe mixed oxides achieved lower values of the furfural conversion in contrast to the previously studied Mg-Al mixed oxides [13]. At the same reaction conditions, we had already reported on the conversion of furfural in the range of 80-100 % for the Mg-Al mixed oxides, having found a dependence on the Mg/Al molar ratio [13].

In contrast, the Mg-Fe mixed oxides achieved the conversion of furfural at 16-27 % depending on the Mg/Fe molar ratio (360 min, Figs 3 and 4). It is relatively surprising as a relatively high catalytic activity has been reported for the Mg-Fe mixed oxides in the trans-esterification of rapeseed oil [6]. It should also be emphasized that, at a reaction temperature of 50 °C, the Mg-Fe mixed oxides did achieve the same conversion of furfural (see Fig. 3) as that for the Mg-Al mixed oxides at 20 °C [13]. Nevertheless, at the same furfural conversion level, the catalytic action of the Mg-Fe mixed oxides was significantly more selective to 4-(2-furyl)-3-buten-2-one (FAc) than that of the Mg-Al mixed oxides (see Fig. 5).
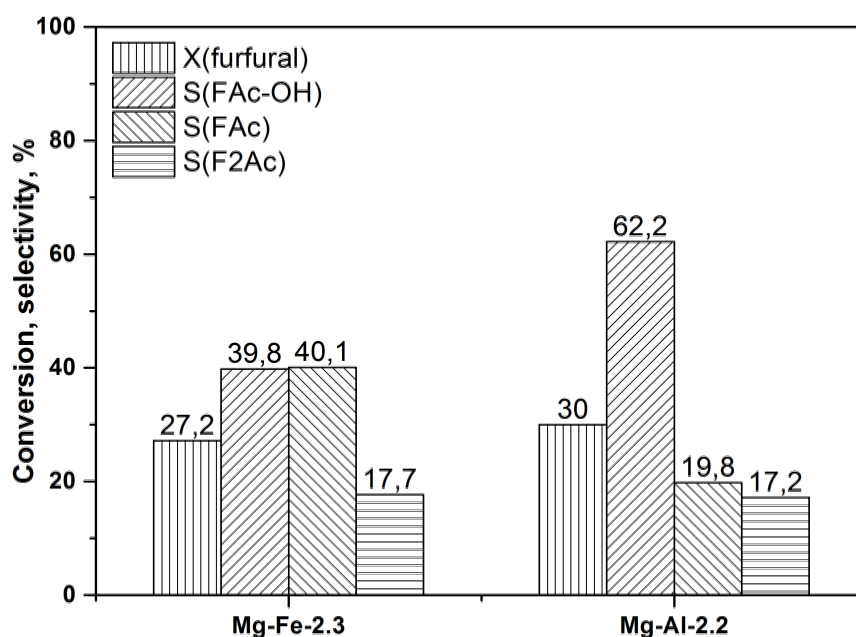

Fig. 5   Comparison of the conversion of furfural, the selectivity to FAc-OH, FAc, and F_2Ac obtained for the calcined catalysts of the Mg-Fe-2.3 (50 °C, reported here) and of Mg-Al-2.2 (20 °C, reported in [13]) type for 360 min

Secondly, there was no clear dependence of the furfural conversion on the Mg/Fe molar ratio (in the range of 1.1-5.5) for the Mg-Fe mixed oxides. This is in contrast to the cases, where the conversion of furfural was reported to be dependent on the Mg/Al molar ratio. For example, Hora *et al*. [13] reported that the conversion of furfural decreases with the increasing Mg/Al molar ratio. In

contrast, Summet *et al.* [24] reported on the increased conversion of propanal with the increasing Mg/Al molar ratio from 1.5 to 3.5 (i.e., aldol condensation of propanal to 2-methylpentenal). A similar trend was also reported by Pérez *et al.* [25] in a study on the condensation of benzaldehyde and phenylsulfonyl-acetonitrile, where the conversion level increased with the increasing Mg/Al molar ratio in the Mg-Al mixed oxides from 3.2 to 5.

Conclusion

The Mg-Fe mixed oxides were successfully prepared by thermal pre-treatment of Mg-Fe hydrotalcites being synthesized by the co-precipitation method. Mg-Fe mixed oxides were prepared in a wide range of the Mg/Fe molar ratio; namely, from 1.1 to 7.6. The Mg-Fe mixed oxides prepared have exhibited a significantly lower level of the conversion of furfural in contrast to the previously studied Mg-Al mixed oxides. The difference in this conversion was relatively low among the individual catalysts; in other words, there no evident dependence of the furfural conversion on the Mg/Fe molar ratio. Furfural was mainly converted to FAc-OH, and the respective selectivity decreased with the increasing conversion of furfural. In contrast, the selectivity towards both FAc and F_2Ac increased with the increasing conversion of furfural, but the resultant selectivity with respect to these components was lower in contrast to that for the FAc-OH.

Acknowledgment

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