

Kinetics of furfuryl alcohol hydroxymethylation with aqueous formaldehyde over a highly dealuminated H-mordenite

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Abstract

Hydroxymethylation of furfuryl alcohol with aqueous formaldehyde, yielding selectively 2,5-bis(hydroxymethyl)furan, has been carried out at 338 K in the presence of a highly dealuminated H-form mordenite. Kinetic analysis of the experimental results allows to propose an original kinetic law involving two types of catalytic sites. According to furfuryl alcohol concentration, there is competition, or not, upon these two types of sites. © 1998 Elsevier Science B.V. All rights reserved.

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1. Introduction

Reactions of furan and its derivatives with formaldehyde have received little attention because Friedel–Crafts alkylation of furans usually leads to complicated reaction mixtures due to the high reactivity of these heterocycles [1]. In fact, oligomers, resinification of furan compounds and other decomposition products are obtained upon heating and in presence of an acidic catalyst [2].

One of the valuable products in the furan series is 2,5-bis(hydroxymethyl)furan (BHMF), useful as intermediate in the synthesis of drugs [3], crown compounds [4], and polymers [5]. It

is generally produced either by reduction of 5-hydroxymethylfurfural, or by furfuryl alcohol condensation with formaldehyde.

In spite of high yields (90–96%), 5-hydroxymethylfurfural reduction processes (with sodium amalgam [6] or hydrogen over Cu–Cr catalyst [7] are limited because of the not readily available starting material (HMF).

Single step BHMF synthesis by hydroxymethylation of the easily available furfuryl alcohol by formaldehyde requires mildly acidic conditions. Thus, 2,5-bis(hydroxymethyl)furan can be obtained in yields of 75–80% with acetic acid as solvent and catalyst [8]. On the contrary, furfuryl alcohol hydroxymethylation with aqueous formaldehyde, in the presence of weakly carboxylic ion-exchange resins in their H⁺ form [9], has not led to such high yields (only 25–30% in isolated pure product after 120 h reaction

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time). Moreover, with strong acid solids, condensation and polymerisation products are generally obtained.

Our interest in the use of zeolites in liquid phase reactions led us to substitute zeolites for cation-exchange resins which do not have high reactivity and selectivity in furfuryl alcohol hydroxymethylation.

HY zeolites are generally considered to be inactive in aqueous solutions. Because of their high hydrophilic character, water covers the surface of those catalysts and prevents adsorption of organic materials. High-silica zeolites, such as dealuminated mordenites, are known to be hydrophobic. Chen [10] showed further that their degree of hydrophobicity depends upon the $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio and found that dealuminated mordenites with an $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio higher than 80 adsorb little or no water. These highly siliceous zeolites are truly hydrophobic and are expected to have a high activity as solid acid catalysts in aqueous solution.

In the present work, we have studied furfuryl alcohol hydroxymethylation reaction with aqueous formaldehyde solution (formalin) in the presence of an acidic and hydrophobic H-mordenite as catalyst (HMOR 100 with a molar $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio of 200). Reaction is carried out in liquid phase under mild conditions (338 K). The present paper deals, more specially, with kinetic results obtained in this reaction in order to understand reaction mechanisms in the presence of hydrophobic zeolites.

2. Experimental

Furfuryl alcohol was distilled before use; formalin (37% aqueous formaldehyde) was from Aldrich and used as such. The catalyst, H-MOR 100, was a highly dealuminated mordenite in a protonic form, supplied by Zeocat.

Reaction was carried out in a glass reactor using 37% aqueous formaldehyde (6 ml), at 338 K, in the presence of 250 mg of dealuminated mordenite. The resulting suspension was mag-

netically stirred at 338 K during 0.5 h before adding furfuryl alcohol (from 0.06 to 1 ml). Samples were withdrawn periodically and analyzed by high performance liquid chromatography (HPLC), using a Shimadzu pump LC-6A with a 0.5 ml min^{-1} constant flow, a Shimadzu UV spectrophotometer SPD-6A detector at 230 nm and controlled by a PC with a software package (ICS). A Kromasil C18 column (15 cm, $5 \mu\text{m}$) was used and the mobile phase was acetonitrile/water (30/70 by volume).

3. Results and discussion

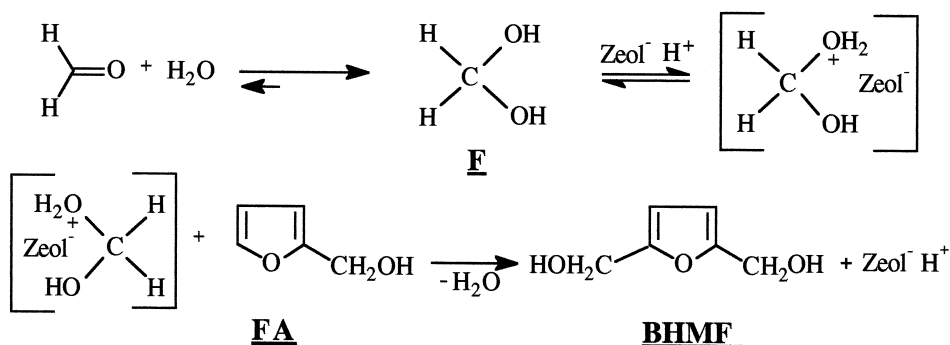
3.1. Reaction scheme

The first step of all the mechanisms observed for Friedel–Crafts electrophilic substitutions involves a fast protonation of one of the two reagents, followed in a subsequent step by the nucleophilic attack of the other [11]. In our case, there is, first, protonation of formol in his hydrate form (more than 99.99% in water) on the zeolite protonic sites and then, electrophilic attack of the protonated hydrate on the 5-position of the furan ring (Scheme 1).

The H-MOR 100 zeolite presents a very high activity in this reaction as illustrated in Fig. 1. At a 0.12 M furfuryl alcohol concentration, both high conversion (70%) and high BHMF selectivity (95%) are observed after a very short reaction time (180 s). Thus, in spite of the aqueous medium, this hydrophobic zeolite is a very efficient catalyst.

3.2. Weisz modulus

For this kinetic study, it is important to make sure that the reaction is not diffusion limited, under our experimental conditions. External diffusion limitations from bulk solution to catalyst surface were excluded by a vigorous stirring of the suspension. Internal diffusion limitations can also be excluded because of the weak value of



Scheme 1. Proposed mechanism of furfuryl alcohol hydroxymethylation with aqueous formaldehyde over zeolites.

the Weisz modulus [12], calculated according to Eq. (1):

$$\theta = (r * \rho * a^2) / C * D_{\text{eff}} \quad (1)$$

in which r is the reaction rate ($\text{mol s}^{-1} \text{g}^{-1}$), ρ the catalyst particle density (g cm^{-3}), C the concentration of the reagent (mol cm^{-3}), a the particle radius (cm) and D_{eff} the effective diffusion coefficient ($\text{cm}^2 \text{s}^{-1}$).

Taking $r = 3.6 \times 10^{-5} \text{ mol s}^{-1} \text{g}^{-1}$, $\rho = 0.8 \text{ g cm}^{-3}$, $a = 6 \times 10^{-4} \text{ cm}$, $C = 0.12 \times 10^{-3} \text{ mol cm}^{-3}$, $D_{\text{eff}} = 10^{-6} \text{ cm}^2 \text{s}^{-1}$ (which appears reasonable for reactants in liquid phase) [12], this leads to $\theta = 9 \times 10^{-2}$. This value, much smaller than 1, allows to conclude that intracrystalline diffusion is not the rate limiting step in this reaction.

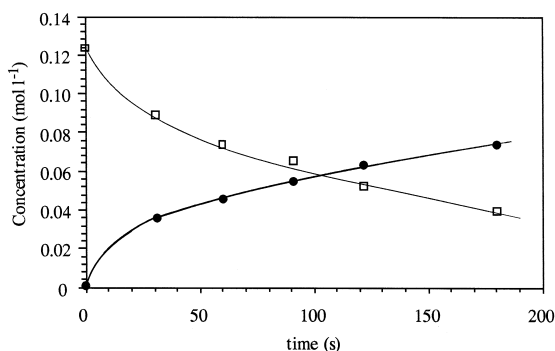


Fig. 1. Concentration of furfuryl alcohol (FA) (□) and 2,5-bis(hydroxymethyl)furan (BHMF) (●) vs. reaction time over H-MOR 100 (0.25 g) at 65°C.

3.3. Kinetic law

In order to gain further understanding of the reaction mechanism, we have measured initial rates at different initial concentrations of furfuryl alcohol while the concentration of formol is kept constant and vice versa, using H-MOR 100 as catalyst. Figs. 2 and 3 show the initial reaction rate evolution with the initial concentration of furfuryl alcohol (FA) and formol hydrate (F), respectively.

As can be seen from Fig. 2, the initial rate increases, reaches a maximum when the furfuryl alcohol concentration is about 0.12 M and then decreases drastically, demonstrating self-poisoning of this reaction (inhibition) at high furfuryl

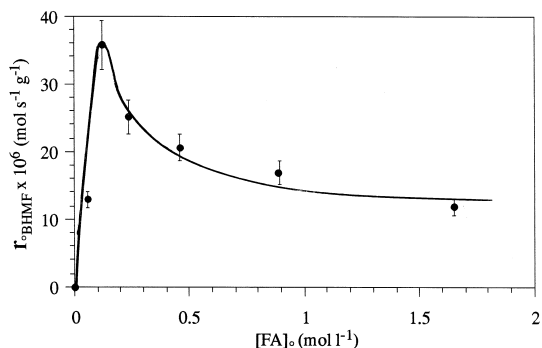


Fig. 2. Initial rates of BHMF formation from furfuryl alcohol: formol mixtures as a function of initial concentration of furfuryl alcohol, with formol concentration kept constant ($11.44 \leq [F] \leq 13.22$, the formol concentration slightly varies because of the dilution of formalin by the furfuryl alcohol).

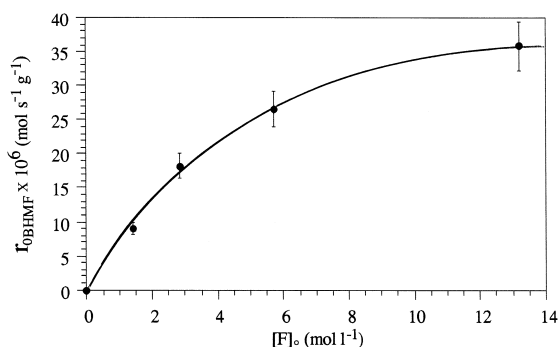


Fig. 3. Initial rates of BHMf formation from furfuryl alcohol: formol mixtures as a function of initial concentration of formol, with furfuryl alcohol concentration kept constant (0.1 M).

alcohol concentrations. On the contrary, Fig. 3 illustrates saturation kinetics wherein the rate of BHMf formation first increases with the formol concentration and then becomes constant at higher formol concentration.

This behaviour might indicate a Langmuir–Hinshelwood type mechanism, with a competitive adsorption of the two reactants, leading to an inhibiting effect at high furfuryl alcohol concentrations. This would require both reacting species to be adsorbed competitively on equivalent sites on the surface (protonic sites). However, such an approach is unable to describe the formol concentration effect (which presents a plateau and not a maximum, Fig. 3). Moreover, it is obvious that such an assumption would lead to erroneous conclusions (on one hand, attack of the electrophile on a positive charged substrate and on the other hand, the unlikely neighbourhood of two protonic sites (adjacent sites) in the case of high dealuminated mordenites). This problem is overcome when two types of sites are considered: one of which is the protonic site (H^+) and the other the hydrophobic surface ($\equiv Si-O-Si \equiv$).

Thus, the reaction is assumed to proceed between a formol hydrate molecule adsorbed on a protonic site (leading to the electrophilic species) and a furfuryl alcohol molecule adsorbed by hydrophobic interactions on the siliceous surface of the catalyst.

At low concentrations, furfuryl alcohol is only adsorbed on the hydrophobic surface following a Langmuir adsorption type:

$$[FA]_{\text{ads}} = \frac{K[FA]}{1 + K[FA]}$$

where K (equilibrium constant of the furfuryl alcohol adsorption/desorption) represents the furfuryl alcohol adsorption affinity for the hydrophobic surface.

At high concentration, furfuryl alcohol is adsorbed on both hydrophobic surface and protonic sites, inhibiting the reaction. Under these conditions, furfuryl alcohol competes with formol hydrate for the protonic site adsorption, so:

$$\theta_F = \frac{\lambda_F[F]}{\lambda_F[F] + \lambda_{FA}[FA] + \lambda_W[\text{water}] + \lambda_P[\text{products}]}$$

with: λ_{FA} : furfuryl alcohol adsorption coefficient on protonic site; λ_F : formol hydrate adsorption coefficient on protonic site; λ_W : water adsorption coefficient on protonic site; λ_P : products adsorption coefficient on protonic site; $[FA]$: furfuryl alcohol concentration; $[F]$: formol hydrate concentration; $[\text{water}]$: water concentration; $[\text{products}]$: products concentration. The initial rate of the process is then given by the following equation:

$$r_0 = k\theta_F[FA]_{\text{ads}}$$

Taking into account that in formalin, the water concentration is twice the formol's (or formol hydrate concentration), and assuming that the adsorption coefficients of water and formol hydrate are similar ($\lambda_W = \lambda_F$), the initial rate equation takes then the following form (the products concentration being negligible):

$$r_0 = k \frac{\lambda_F[F]_0 \cdot K[FA]_0}{(\lambda_{FA}[FA]_0 + 3\lambda_F[F]_0)(1 + K[FA]_0)} \quad (2)$$

This rate law, which is a modified Langmuir–Hinshelwood scheme, accounts satisfactorily for the experimentally observed kinetics.

• At low furfuryl alcohol concentrations, the rate equation is reduced to $k'[FA]_0$ which agrees

with the first-order observed under these experimental conditions.

- At furfuryl alcohol concentrations higher than 0.12 M, adsorbed furfuryl alcohol molecules saturate the catalyst surface, and the term $(\lambda_{FA}[FA]_0 + 3\lambda_F[F]_0)$ becomes dominant in the denominator of Eq. (2) (the order in furfuryl alcohol becomes negative). The furfuryl alcohol molecules prevent the adsorption of formol and therefore the reaction is inhibited.

- At a furfuryl alcohol concentration close to 0.12 M, for which the initial rate is maximum and the order relative to furfuryl alcohol is probably close to zero, furfuryl alcohol molecules are assumed to be preferentially adsorbed on the whole hydrophobic surface but not yet on the protonic sites. Consequently, formol hydrate molecules can be adsorbed on the free protonic sites leading to a fast and selective reaction with furfuryl alcohol molecules adsorbed in the near neighbourhood.

These assumptions are consistent with the addition order effect of the two reactants observed in exploratory experiments. In fact, it has been found that the BHMF selectivity was strongly dependent on this addition order. In the case of high furfuryl alcohol concentrations (1 ml for a concentration of 1.65 M for example), this selectivity is higher when furfuryl alcohol is introduced at last. On the contrary, no effect is observed when furfuryl alcohol concentration is about 0.12 M. These data are in good agreement with those reported in literature by different authors [13,14].

3.4. Activation energy

The influence of the temperature on the reaction has been investigated within the temperature range from 313 and 338 K. The Arrhenius plots are shown in Fig. 4 for three different initial concentrations of furfuryl alcohol (0.12, 0.24 and 0.46 M).

- At concentration near of 0.12 M, for which the initial rate is maximum, the observed activa-

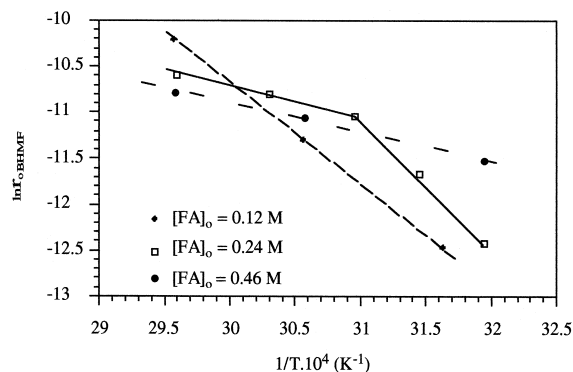


Fig. 4. Arrhenius plot for hydroxymethylation of furfuryl alcohol on highly dealuminated H-mordenite.

tion energy is the true activation energy of the reaction ($E_a = 92 \text{ kJ mol}^{-1}$).

- At 0.46 M, the reaction becomes -1 order in furfuryl alcohol and consequently, the observed activation energy is an apparent energy ($E_{app} = 21 \text{ kJ mol}^{-1}$).

- At a concentration of 0.24 M, the situation is intermediate and the Arrhenius plot shows a curvature (broken line).

These results well illustrate the effect of temperature and/or concentration on reaction order with respect to furfuryl alcohol which depends on the catalyst surface coverage.

4. Conclusion

In summary, we assume that the surface reaction takes place between the formol hydrate adsorbed on Brönsted sites and furfuryl alcohol adsorbed on the hydrophobic framework of dealuminated mordenites. However, the furfuryl alcohol molecules can also be adsorbed on acidic sites competitively with formol hydrate, leading to an inhibition of the reaction for high furfuryl alcohol concentrations. The consequence of this behavior is that there is a maximum rate at an optimum furfuryl alcohol concentration. The kinetic law presented in this paper is a ‘variante’ of the classical Langmuir–Hinshelwood scheme and agrees well with the experimentally measured kinetic rates.

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