

Letter

Synthesis of acetal (1,1-diethoxyethane) from ethanol and acetaldehyde over acidic catalysts

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Abstract

Various acidic catalysts (zeolitic and amorphous FCC catalysts, mordenite, montmorillonite, and sulfonic ion exchange resin) were tested for the synthesis of acetal from ethanol and acetaldehyde, at 4 and 20°C and atmospheric pressure in batch stirred reactors. All the catalysts were active, but the exchange resin showed a much better performance than the other catalysts, since it quickly reached equilibrium ethanol conversion values. The resin was also tested under different pressures and catalyst to reactants ratios. Clear relationships between the catalyst activity, the amount of acidity and the physical properties of the catalysts were not apparent. A possible reaction mechanism suggests that protonic acid sites are necessary. Water, a reaction product, seems to have an inhibitory effect on the reaction rate. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

1,1-Diethoxyethane (acetal) and water are produced by the acid-catalyzed addition of 2 moles of ethanol and one of acetaldehyde. Acetal has been used as a solvent, as an intermediate in chemical synthesis for the protection of the carbonyl group in ketones and aldehydes, and in the fragrance industry [1]. Interestingly, it can be blended with diesel fuels, and recent patents claim that it can be used as an additive, which

would keep or increase the cetane number of the fuel [2] and help in the combustion of the resulting mixtures [3]. The possibility of using renewable resources (e.g., ethanol obtained from sugar cane or other vegetal sources) is very attractive in order to substitute fossil sources.

The synthesis of acetal is typically conducted under conditions of homogeneous catalysis, with strong liquid inorganic acids like sulfuric and phosphoric acids as the catalysts [4]. Since the disadvantages of using liquid inorganic acids are obvious, specially from the environmental standpoint, heterogeneous catalysts are more desirable; however, there is an almost complete lack of previous works on these issues [5], and only

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Table 1
Properties of the catalysts

Catalyst	Description	Surface area (m ² g ⁻¹)	Pore volume (ml g ⁻¹)	Acidity (meq g ⁻¹)
A15	Polystyrene-polydivinylbenzene sulfonic resin, Rohm and Haas	45	0.360	4.7 ^a
K10	Acid-treated montmorillonite, Aldrich	345 ^b	0.564 ^b	0.273 ^c
M	Mordenite, Norton	436	0.210	0.649
MAA	Acid treated montmorillonite, natural	235 ^b	0.262 ^b	0.640 ^c
R	Zeolite FCC catalyst, Fresh BR1160, Engelhard, UCS: 24.72Å	342	0.259	0.540
S	Zeolite FCC catalyst, Isoplus 1000, Engelhard, UCS: 24.40Å	336	n.a.	0.474
T	Amorphous FCC catalyst, HA-HPV, Ketjen 25% Al ₂ O ₃	454	0.688	0.382
U	Amorphous FCC catalyst, LA-LPV, Ketjen 12% Al ₂ O ₃	559	0.642	0.350
W	Equilibrium zeolitic FCC catalyst, BR1160, Engelhard, UCS: 24.31Å	175	0.213	0.065
X	Equilibrium zeolitic FCC catalyst, Octavision, FCC S.A., UCS: 24.24Å	151	0.120	0.160

^a H⁺ miliequivalent g⁻¹.

^b From [5].

^c From [10].

a few patents were published that mention the utilization of ionic exchange resins and zeolites [6]. Then, it is necessary to search for active, selective and stable solid acid catalysts that could be used for the acetal synthesis. It is the objective of this work to report the performance of solid acid catalysts of various types, from commercial, natural and laboratory sources, in the synthesis of acetal. The relationship between catalyst activity and properties is also investigated.

2. Experimental

Different types of acidic catalysts were used. They included (a) commercial catalysts for the process of catalytic cracking of hydrocarbons (FCC), amorphous and with zeolite components, either fresh or equilibrated from running refineries; (b) montmorillonites, a sulfuric acid-treated, natural sample from the province of San Juan, Argentina, and a commercial sample; (c) commercial Amberlyst15-wet polystyrene-polydivinylbenzene sulfonic resin; and (d) zeolite mordenite. The catalysts' properties are summarized in Table 1.

The catalysts were characterized by nitrogen adsorption at -196°C to assess catalyst physical properties, and by ammonia temperature-programmed desorption to determine catalyst acidity [7]. The number of proton acid sites in resin A15 was evaluated by means of conventional exchange-titration. The unit cell sizes of FCC catalysts were determined following ASTM D-3942-85 technique.

The catalytic performances of the various catalysts were evaluated by means of experiments with reactant ethanol (Cicarelli, >99.5%) and acetaldehyde (Merck, >99%) following the stoichiometric relationship. All the experiments were conducted in a 10 ml microreactor maintained at 4°C and atmospheric pressure under stirring in a refrigerated bath. Products were analyzed by gas chromatography. All the catalysts were used after drying at 100°C; particularly catalyst A15 was also tested as received in its 'wet' form.

3. Results and discussion

It was shown from exploratory tests that room temperature and atmospheric pressure were convenient conditions under which all the catalysts were active and selectivity was close to 100% in most of the cases; only minor amounts of an acetaldehyde trimer compound were detected. However, the particular catalytic behaviors differed, as can be observed in Fig. 1. In effect, flat activity profiles as a function of reaction time were observed for most of the catalyst samples, although catalyst A15 reached conversion values that can be considered to be at the equilibrium under those conditions. The other catalysts defined two levels of activity: an intermediate level (montmorillonites), with conversions approaching equilibrium values, and a low level (zeolitic and amorphous FCC catalysts, mordenite). Then, a coarse ranking of performances can be established to be A15 > montmorillonites > zeolitic and amorphous FCC catalysts, mordenite.

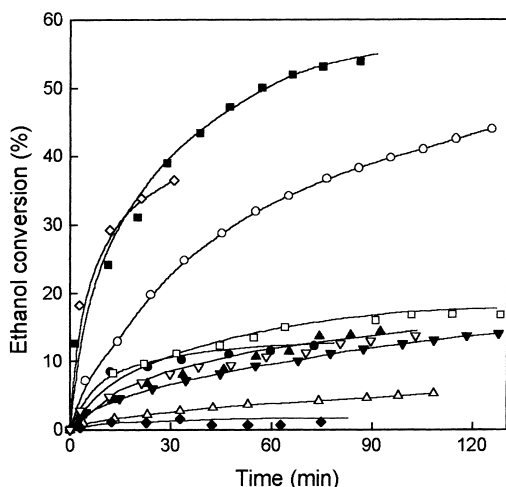


Fig. 1. Ethanol conversion as a function of reaction time for catalysts A15, K10, MAA, U, M, S, R, W, X and T. Catalyst to reactants ratio: 8.33 g/100 ml. T : 4°C. Symbols: (■) A15, (◇) K10, (○) MAA, (●) U, (□) M, (▲) S, (▽) R, (▼) W, (△) X, (◆) T.

It has to be considered, however, that zeolitic FCC catalysts are not bulk but compound materials in which the zeolite Y component is diluted supported on a matrix. Another fact that could be also influencing the observed behaviors of these catalysts, is the particular status of the zeolite on them, as shown by the corresponding unit cell size (refer to Table 1). In effect, they change from 24.72 Å in catalyst R to 24.24 Å in catalyst X, thus comprising a wide range of intrinsic acid site activities.

If the numbers of acid sites are considered, then a clear relationship can not be established with the observed activities, although comparisons have to be performed carefully due to differences that are inherent to the various types of catalysts used. However, if two catalysts of the same type are considered, such as equilibrium commercial FCC catalysts X and W that contain zeolite Y, then catalyst W with an amount of acid sites lower than that of catalyst X, showed a better performance. A similar comparison can be established between fresh commercial FCC catalysts R and S, with different amounts of acid sites and very similar performances. The comparison between samples T and U (amorphous FCC catalysts), with very similar acidities, also indicates that they perform differently, because sample U showed a significantly better conversion profile.

Other important catalyst properties, like specific surface area and pore volume, and even the structure of the pore system seem not to be limiting. In effect, among the catalysts tested, those which are compound, like the zeolitic FCC catalysts, contained different amounts of Y zeolite (pore openings of 7.4 Å, channels interconnecting supercages of about 13 Å in diameter). The other zeolite tested, mordenite, has pore openings of about 6.5 Å. The interlaminar spacing d_{001} in the acid-treated montmorillonites used was 13 Å, which is similar to that of natural montmorillonites [5]. All the other catalysts have pore sizes well above those of these zeolite and montmorillonite catalysts. The molecular size of reactants and products, then, allows to expect that the various pore systems can accommodate them easily and, consequently, no shape selectivity effect or diffusional restrictions at the pore level are to be expected.

Additional experiments with different reactant to catalyst ratios performed on catalyst A15 allowed to observe that, as expected, the lower the ratio, the faster the evolution of the conversion versus time profiles towards the equilibrium values. The effect of pressure was moderate, differences being subtle between 1 and 5 bar, and somewhat more noticeable at 10 bar, in the sense of increasing the observed equilibrium conversion (results not shown).

Water, which is one of the reaction products, may play an adverse role in this equilibrium reaction, particularly if it is adsorbed on the catalyst surface. Evidences were gathered in comparing experiments with catalyst A15, in its pre-wetted standard form and after drying it at 100°C. In effect, as shown in Fig. 2, the production of acetal on the dried catalyst was significantly faster than on the wet sample, where water was already present before the chemical reaction. Moreover, long-term experiments showed that, as expected, the equilibrium conversion is lower on the pre-wetted sample.

The role of the acid property in the catalysts could be rationalized in view of a proposed reaction mechanism. Accepting that the basic concepts from the reaction in homogenous media [8,9] can be extended to this situation, the protonation of the oxygen atom in the acetaldehyde's carbonyl group by an acidic site from the catalytic surface can be considered as the initial step that enables a subsequent nucleophilic attack by an alcohol molecule; then, the loss of a proton from

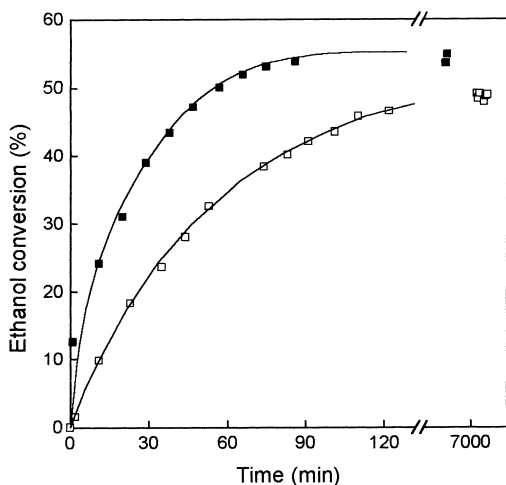


Fig. 2. Ethanol conversion as a function of reaction time for catalyst A15. Effect of water. Catalyst to reactants ratio: 8.33 g/100 ml. T : 4°C. Symbols: (■) dry, (□) pre-wetted.

this intermediate species (protonated hemiacetal) back to the catalyst surface, or to the reaction media if water is present, would allow the desorption of the hemiacetal. In turn, this compound could be additionally protonated in the OH group by the catalyst; then, by losing water, an oxonium ion would be formed that can suffer a new nucleophilic attack by the alcohol. The loss of a proton from this surface intermediate would finally yield acetal. In describing the formation of a tetrahedral carbon atom in the hemiacetal intermediate, however, the nucleophilic addition by the alcohol molecules to the carbonyl group as a first step followed by protonation, or the concerted nucleophilic attack — protonation, could be considered less feasible alternatives [8].

It is inherent to this description that protonic acid sites play a key role. Then, the higher acid strength in the resin catalyst with only Bronsted-type sites, as compared to the other materials, could be associated in conjunction with this mechanism to explain its better performance.

4. Conclusions

The synthesis of acetal from ethanol and acetaldehyde can be accomplished selectively in the liquid phase under mild conditions by using acidic catalysts

of various types, including commercial FCC catalysts, zeolites, sulfonic ion exchange resins, and natural montmorillonites. While all the catalysts tested are active for the reaction, the resin with which it was possible to achieve conversions at the equilibrium values of about 50% at 20°C, showed the best performance. Clear relationships between activity and the amount of acidity, or the physical properties of the catalysts, were not observed. A reaction mechanism can be conceived based on protonic sites that involves successive proton additions by the catalyst that favor the subsequent nucleophilic attacks by the alcohol and lead to intermediate hemiacetal and finally acetal. Water adsorbed on the catalyst may play an inhibitory effect.

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