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Vapor-Phase Condensation of Formaldehyde and Acetaldehyde into Acrolein over Zeolites

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The vapor-phase condensation of formaldehyde and acetaldehyde into acrolein was investigated. Zeolite catalysts; e.g. Y-faujasite, mordenite, ZSM-5, and volcanic tuff have been tested in this aldol reaction. The best results were obtained when modified volcanic tuff was used. The catalytic activity seems to depend on the balance between acidic and basic properties. © 1994 Academic Press, Inc.

INTRODUCTION

Acrolein is synthesized successfully via propylene oxidation (1–6). Nevertheless, a major disadvantage of the process is that propylene oxidation is hindered by acrolein formation. The aldol condensation of acetetaldehyde with formaldehyde, commonly called the "Tollence Reaction" (7), is a convenient alternative for obtaining acrolein.

Both liquid and vapor phase aldol condensations of carbonylic compounds are well known to be acid-catalyzed processes which may involve approximately the same mechanisms (8, 9). Recently, the vapor-phase processes became increasingly investigated thanks to the use of zeolitic catalysts (10–14). The main feature of these processes is that the formation of bulky condensates can be avoided and, consequently, improved selectivities can be obtained.

Zeolitic catalysts can exhibit acidic or basic catalytic properties according to their preparation procedures (7–9, 15). These properties can be easily modified by ion-exchange, impregnation, dealumination, etc. It is of interest to elucidate the dependence of the acid–base properties on the nature of the catalyst. In this context, we have investigated the behavior of various types of zeolite catalysts, namely Y-faujasite, mordenite, ZSM-5, and the natural zeolitic material volcanic tuff in the vapor-phase condensation of acetaldehyde with formaldehyde.

EXPERIMENTAL

Catalyst Preparation and Characterization

The volcanic tuff (Mîrsid deposit Romania) used as raw material contains about 60–62% clinoptilolite, 11.95% Al_2O_3, 0.40% Na_2O, 2.80% K_2O, 3.35% CaO, 0.70% MgO, and 0.86% Fe_2O_3. The loss on calcination reached 11.40% at 773 K. The specific surface area is 47 $m^2\,g^{-1}$ and the ion-exchange capacity is ca. 0.4–1.70 meq g^{-1} when hydrated. Samples of natural tuff with particle size of about 0.25–0.43 mm were previously ion-exchanged into the monocationic sodium form. The catalysts were prepared by ion-exchange with 0.1–0.2 *M* solutions of the respective metal nitrates during 3 × 8 h at 343 K. The exchange degree was about 40–60%. Other catalysts based on volcanic tuff were prepared via hydrothermal treatments. Thus, the native tuff was impregnated for 2 h at 333 K with 2 *M* aqueous HCl. X-ray diffraction investigation indicated that the resulting crystalline phase contains mainly clinoptilolite with illite traces. The alkaline treatment of the native tuff gave rise to crystalline catalysts consisting of analcime with small amounts of clinoptilolite.

Other samples of native tuff were modified by impregnation with magnesium acetate. When a loading degree of 4.04% was reached, the resulting catalysts were filtered, washed, and calcined at 823 K.

Mordenite catalyst was obtained by hydrothermal crystallization of an amorphous alumina–silica gel(Si/Al = 10). The H^+ form of mordenite was obtained by acid treatment (16). HY catalysts were prepared by ion-exchanging NaY (LZ-Y52, Ventron product) with 0.1 *M* aqueous NH_4NO_3 and consecutive thermal deammoniation at 773 K in air flow. HZSM-5 (Si/Al = 64.2) was obtained as above (17). These zeolites, without binder, have been pressed, crushed, and sieved.

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Reactants and TPD Procedure

Formaldehyde (Merck reagent) was used as aqueous solution containing 37% HCHO and stabilized with 12% methanol. For temperature-programmed desorption experiments (TPD) the gaseous formaldehyde was obtained by the controlled decomposition of paraformaldehyde. Acetaldehyde (Fluka reagent) was a puriss. p.a. grade reagent. The acidity measurements have been carried out by thermoprogrammed desorption of ammonia at a heating rate of 17 K/min, in the temperature range 373–823 K using nitrogen as carrier gas. TPD experiments were also performed for acetaldehyde.

Condensation Reactions

The condensation reactions were run in a pulse type microreactor containing 20 mg of catalyst with particle size 0.25–0.43 mm. This allowed us to obtain a ca. 2 × 5 mm cylindrical fixed bed of catalyst which was found to be optimal for avoiding diffusion-controlled phenomena in the condensation experiments. Each catalyst was previously activated at 823 K under air flow. The microreactor was coupled to a gas chromatograph. Two columns were used: Carbowax 10 M/Chromosorb and Porapak N. Samples of 0.3 μl of the reaction mixture were injected under nitrogen flow.

RESULTS

TPD of Reactants

A series of experiments of temperature-programmed desorption of formaldehyde and acetaldehyde over various zeolites have been performed and some results are shown in Fig. 1. TPD profiles show the general shape of the desorption process whatever the nature of the adsorbed species may be. One can observe that both acetaldehyde and formaldehyde are adsorbed in the same way on the volcanic tuff. Acetaldehyde is strongly retained on very acidic catalysts such as H-mordenite (HM), and the self-condensation of this reactant can occur on the catalyst surface. Note that the profile of acetaldehyde desorption from HM presents the same shape as that of ammonia.

Another aspect is that acetaldehyde and/or its derivatives are progressively released as the temperature is increased. It results from these observations that a selective aldol condensation requires a certain distribution of the acid–base sites. The latter can modify not only the catalytic activity but also the product distribution.

Conversion to Acrolein

An obvious choice for correlating the modification procedure and, subsequently, the catalytic activity is the conversion of acetaldehyde. Results presented in Table 1 show clearly that the selectivity to acrolein formation is affected when the catalyst acidity is increased. One can observe that the volcanic tuff exhibits the highest selectivity for acrolein formation.

Influence of Na Content

Generally, the catalytic activity and the selectivity are strongly dependent on the type of catalyst and its acid–base properties. Thus, for the Na^+ form of the zeolites, NaZSM-5 is the most active and selective catalyst. Among the H^+ form catalysts, HM is the most active, but the most selective is HY. HZSM-5 catalyst has approximately the same behavior as HY. Comparatively, it appears that the Na^+ forms of the zeolites are more selective than the H^+ ones.

In order to establish the influence of the Na^+/H^+ ratio on the activity and selectivity, some samples of Y faujasite with various Na^+/H^+ ratios were prepared and tested in the aldol condensation. The results are presented in Fig.

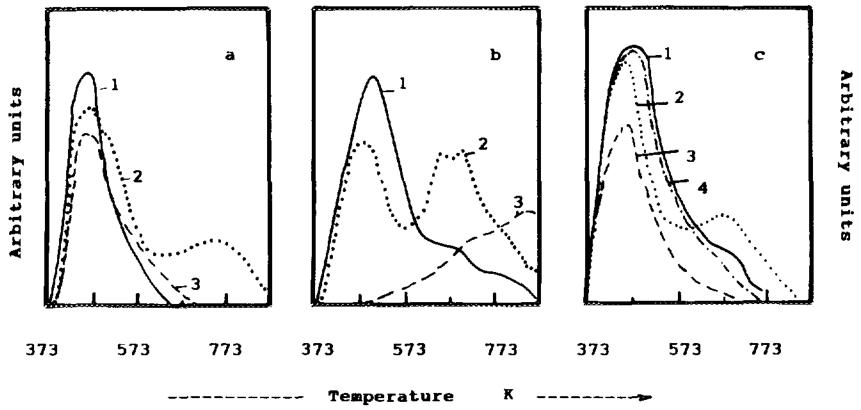


FIG. 1. Rates of desorption of formaldehyde (a), acetaldehyde (b), and ammonia (c). Heating rate: 17 K/min. 1, native tuff; 2, H-mordenite; 3, NaY; 4, MgO/tuff.

TABLE 1

Acetaldehyde Conversion to the Condensation Products

Catalyst	Conversion of acetaldehyde (%)		Acrolein/crotonaldehyde mole ratio
	Acrolein	Crotonaldehyde	
NaY	8.99	10.42	0.86
NaM	7.75	6.68	1.16
NaZSM-5	26.32	14.80	1.77
NaH(48)Y	16.04	55.31	0.29
NaH(65)Y	8.21	34.12	0.24
HM	2.90	51.92	0.05
HZSM-5	3.07	27.07	0.11
HY	3.58	28.98	0.12
Native tuff	22.52	4.45	5.06

Note. Mole ratio formaldehyde/acetaldehyde = 1.1, reaction temperature = 548 K.

2. As the Na^+ ions are replaced by H^+ ions, the conversion of acetaldehyde to crotonaldehyde is greater than that to acrolein, reaching a maximal value at about 50% degree of ion-exchange. Thereafter the conversion to crotonaldehyde decreases as the H^+ content is increased.

Taking into account the above results, the volcanic tuff appears to be the best catalyst for conversion to acrolein.

Influence of Tuff Treatment

Due to the complex composition of the volcanic tuff, attempts were made to improve the catalytic performance by applying various chemical treatments. Thus, by exhaustive ion-exchange, it was transformed into the sodium form. Further, various catalysts were prepared by ion-exchange with aqueous metal nitrates. After activation, these catalysts were tested in the aldol condensation, and the results are shown in Table 2.

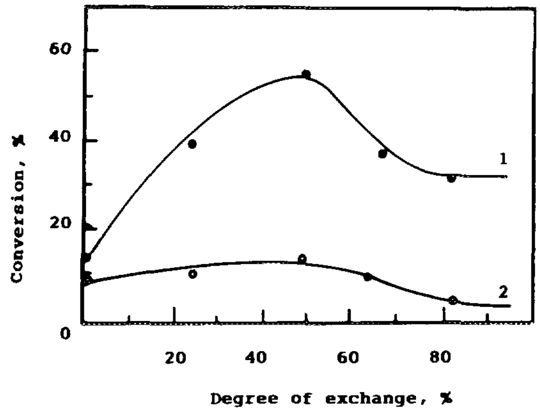


FIG. 2. Acetaldehyde conversion versus the ion-exchange degree of Y-faujasite. (1) Conversion to crotonaldehyde and (2) conversion to acrolein. T = 548 K, pulse number = 1.

One can observe that the ion-exchanged volcanic tuff exhibits higher selectivities than those obtained by the synthetic zeolites. In addition, it was also found that the Group II cations confer to the catalyst better selectivities than the Group I cations. The best selectivity has been obtained when the Na^+ cations are replaced by Mg^{2+}. Comparable selectivities are obtained with Cd^{2+} and Zn^{2+}. These results suggest that the influence of the cation nature is strongly related to that of the ionic radius. Thus, for the Group I cations, the selectivity decreases as the ionic radius is increased.

The impregnation of the volcanic tuff with a NaOH solution gave rise to a catalyst designated C_{16A}. This catalyst exhibited a catalytic activity similar to that of the native volcanic tuff (Table 3). Ammonium-treated tuff (C_{16B}) was obtained by ion-exchange with 1 *N* NH_4OH. In this case, the catalytic activity is relatively low, as shown also in Fig. 4. Simultaneously, a significant coking process is revealed on this catalyst.

Another modification of the native tuff consisted in acid treatment with HCl to give catalyst C_{19}. The impregnation of the volcanic tuff with a 2 *N* HCl solution leads to an increase of the 'SiO_2' content up to 80.5% and a decrease of the 'Al_2O_3' content to 8.20 wt.%. Simultaneously, cations such as Ca^{2+}, Mg^{2+}, K^+, Na^+, and Fe^{3+} (from Fe_2O_3) are totally removed. The resulting treated material (sample C_{19}) was tested in the same conditions as previously, and it was found that its catalytic activity is smaller than that of the native tuff but higher than that of C_{16B}, as illustrated in Table 3.

TABLE 2

Influence of the Nature of the Cation in the Volcanic Tuff on the Acetaldehyde Conversion to Acrolein

Cation	Degree of exchange (%)	Acetaldehyde conversion (%)		Acrolein/crotonaldehyde mole ratio
		Acrolein	Crotonaldehyde	
La^+	62	10.83	4.86	2.22
Na^+	—	12.68	6.78	1.87
K^+	58	11.06	5.65	1.95
Cs^+	47	7.40	4.35	1.70
Mg^{2+}	63	23.21	4.96	4.68
Ca^{2+}	54	11.01	5.99	1.84
Sr^{2+}	55	9.41	6.12	1.53
Zn^{2+}	49	15.49	4.31	3.59
Cd^{2+}	52	16.61	4.55	3.65
H^+	89	14.85	6.94	2.14

Note. Operating conditions: T = 623 K, pulse number = 1.

TABLE 3

Catalysts Based on Tuff Treatments

Catalyst	Identification	Procedure for tuff treatment	Conversion mol%[a]
C_{16A}	Alkali-treated tuff	Impregnation in aqueous NaOH at 333 K	39–41
C_{16B}	Ammonium-exchanged tuff	Ion-exchange with 1 *M* aqueous NH_4OH and calcination under air stream at 823 K	19–20
C_{19}	Acid-treated tuff	Impregnation in 2*M* aqueous HCl during 2 h at 333 K	28–29
MgO/tuff	Magnesia deposited over tuff	Impregnation in magnesium acetate aqueous solution and calcination at 823 K	50–51

[a] These conversion values are related to acetaldehyde and were estimated at T = 623 K and a pulse number = 1.

Deposition of 4% magnesium oxide on the volcanic tuff gave rise to the highest catalytic activity (ca. 50–51%). Ai (7) has provided evidence that the incorporation of an alkaline earth oxide such as MgO enhances significantly the activity of SiO_2.

Effect of Temperature and Pulse Number

The effect of temperature on the catalytic properties of the volcanic tuff catalyst was further investigated. In a first step, the analysis of the reaction products shows that acrolein is selectively formed in the presence of the volcanic tuff within a large range of temperatures as illustrated by Fig. 3 (curves 1–4). It was also found that crotonaldehyde formation takes place only for reaction temperatures lower than 623 K (curve 5). For instance, the acrolein/crotonaldehyde mole ratio is 11.2 : 1 at 523 K, but the crotonaldehyde proportion decreases as the temperature is increased. This product becomes chromatographically undetectable when the temperature is raised to 623 K. This could be explained partly by the possible consumption of crotonaldehyde in the coking process. If one does not take into account its relatively fast deactivation (as shown in Fig. 4), the volcanic tuff exhibits appreciable catalytic performance, since the acetaldehyde conversion to acrolein reaches values of about 40 mol %.

Besides the effect of the reaction temperature, the performance of each catalyst is strongly dependent on the number of pulses. An increase of the reaction temperature improves the conversion, whereas an increase of the pulse

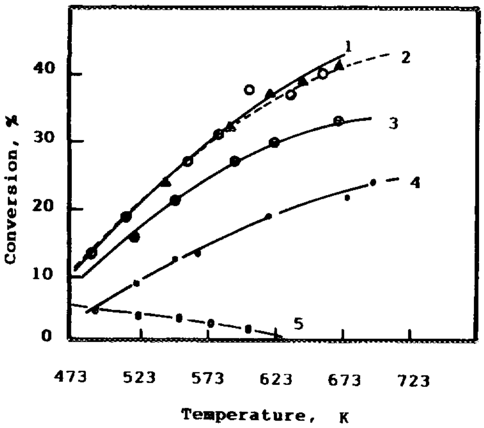


FIG. 3. Effect of temperature on the formation of acrolein (curves 1–4) and crotonaldehyde (curve 5). (1) Native volcanic tuff (untreated), (2) C_{16A} catalyst, (3) C_{19} catalyst, (4) C_{16B} catalyst, and (5) native volcanic tuff. Pulse numbers = 1 to 10; volcanic tuff: native tuff; C_{16A}: alkali-treated tuff; C_{16B}: ammonium-treated tuff; C_{19}: acid-treated tuff.

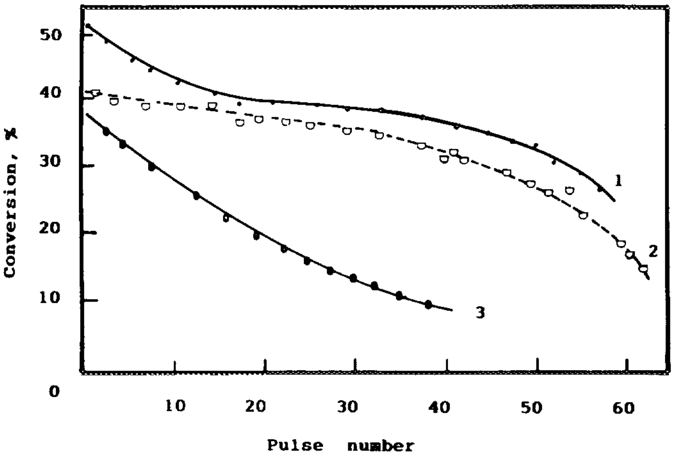


FIG. 4. Effect of the pulse number on acetaldehyde conversion. (1) MgO/tuff, (2) C_{16A}, and (3) Native volcanic tuff (untreated). T = 623 K.

number leads to a decay of the catalytic activity (Figs. 3 and 4).

One can observe from Fig. 4 that, in all cases, the pulse number affects the catalytic activity of the native tuff and, to a lesser extent, that of the modified tuff. For instance, after 10 and 30 pulses, the volcanic tuff presents an activity loss of about 25 and 70%, respectively, whereas on MgO/tuff catalysts the activity loss is smaller than 25%, and after 40 pulses the catalytic activity was practically constant. The catalytic activity of C_{16A} catalyst is less affected by the increase of the pulse number than those of the other catalysts. In fact, after 40 pulses, the activity loss is about 5–10% for C_{16A} catalyst.

It is well known that a good catalyst lifetime is due more to its chemical and thermal stability than to coke formation because coke removal can be easily performed by repetitive regenerations. This suggests that the lifetime of the treated tuff is longer than that of the native tuff, and one may conclude that tuff modification improves the stability of the catalyst.

Effect of the Mole Ratio of Reactants

Another aspect studied was the influence of the ratio of the reactants on the conversion of acetaldehyde. As can be observed from Fig. 5, measurements carried out at 673 K in the presence of the volcanic tuff show that conversion into acrolein is favoured by a formaldehyde excess. The conversion rises as the formaldehyde/acetaldehyde mole ratio is increased. This is in agreement with the experiments performed by Ai (18) over phosphate catalysts where a direct dependence was found between the conversion and this parameter, although the selectivity is scarcely influenced. In the present case, the increase is quite slow; this could be explained by the decrease of the partial pressure of the reactants due to the increase of the water content in the feed. On alkaline treatment (C_{16A}), the volcanic tuff exhibits more significant activities. Additional experiments carried out at 523 K allow us to attribute the increase of H_2 and CO formation to formaldehyde decomposition at high temperatures. In this case, an increase of the conversion of acetaldehyde into acrolein is also observed when the formaldehyde/acetaldehyde ratio is increased. An acetaldehyde excess does not have a favourable effect upon the conversion (Fig. 5).

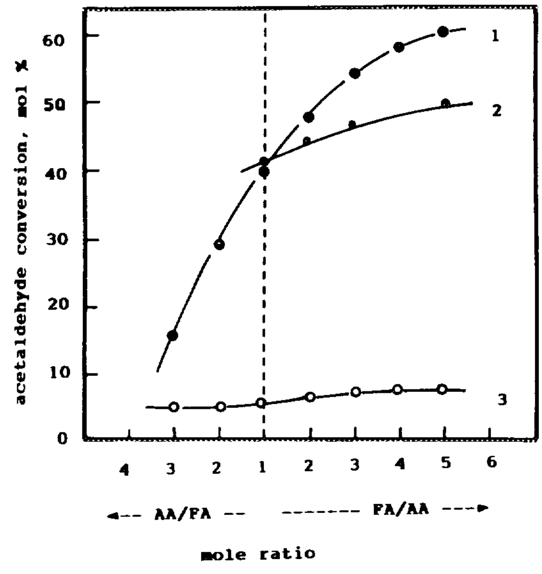


FIG. 5. Dependence of acetaldehyde conversion to acrolein on the mole ratio of reactants. (1) C_{16A} catalyst at 673 K, (2) native tuff at 673 K, and (3) C_{16A} catalyst at 523 K. Total pressure in reactor = 1 atm; pulse number = 1; AA/FA: acetaldehyde/formaldehyde mole ratio; FA/AA: formaldehyde/acetaldehyde mole ratio.

It is well known that the main disadvantage of such an aldol condensation process is its low selectivity with respect to side reactions. Acetaldehyde can condense with itself, leading to crotonaldehyde formation. Consequently, this could explain the fact that at low temperatures the native tuff favours the formation of small amount of crotonaldehyde.

DISCUSSION

The first stage of acetaldehyde condensation with formaldehyde leads to the formation of a hydroxy-aldehyde or an aldol according to the following scheme:

$$CH_3CHO + HCHO \xrightarrow{cat.} HO\text{-}CH_2\text{-}CH_2\text{-}CHO. \quad [1]$$

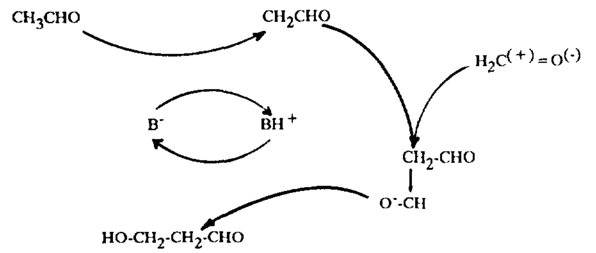
Water removal to form acrolein occurs as follows:

$$HO\text{-}CH_2\text{-}CH_2\text{-}CHO \xrightarrow{cat.} CH{=}CH\text{-}CHO + H_2O. \quad [2]$$

The selectivity of the condensation process is strongly influenced by the nature of the catalyst and the operating conditions, especially the reaction temperature. According to the parameters chosen, the selectivity can be greatly affected by the appearance of side reactions such as the further condensation of the reaction products, the self-condensation of acetaldehyde, and the Cannizzaro reaction.

Referring to the condensation mechanisms, one can assume that the reaction intermediates are carbanion species on solid base catalyst (Scheme 1) or enol ones on solid acid catalysts (Scheme 2). Water elimination occurs both via acid and base catalysis.

As already pointed out, the native volcanic tuff presents significant activities and selectivities by comparison to the solid base catalysts. For the latter, the maximal conversion of acetaldehyde varies between 5 and 57% according to the catalyst used. It must be emphasized that



SCHEME 1

an increase of temperature improves acetaldehyde conversion, which is apparently not in agreement with the expectations of thermodynamic equilibrium, i.e., 90% at 600 K and 86% at 800 K, but this is not significant since acetaldehyde conversion does not reach the equilibrium value. It is also interesting to observe that using the volcanic tuff, the amount of crotonaldehyde decreases as the temperature is increased and, again, this is not in agreement with the thermodynamic expectations according to which the theoretical maximum yields are about 49% at 600 K and 68% at 800 K.

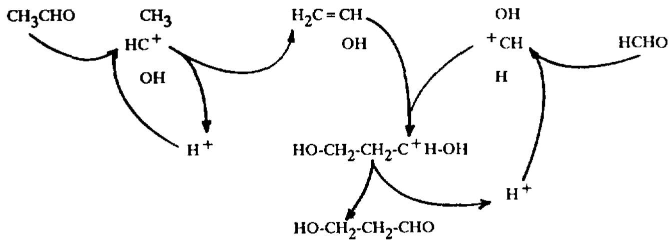
Acrolein yield does not rise so much as the formaldehyde/acetaldehyde mole ratio is increased; this is probably due to the influence of water content in the feed mixture. This is in agreement with the thermodynamic calculations made by Malinowski *et al.* (11) according to which the theoretical acrolein yield decreases in the presence of water from 79 to 77% when the temperature varies between 500 and 800 K. In the same temperature range, crotonaldehyde yield varies reversely, i.e., from 25 to 39%.

The details of tuff modification also contain significant information and should correlate with the physicochemical properties of the catalyst surface. As indicated by the experimental data, the catalytic properties of volcanic tuff can be improved by applying various treatments. The high performance obtained using MgO/volcanic tuff could be attributed, to some extent, to a decrease in the proportion of macropores and an increase in the catalyst basicity. The acidity measurements performed by TPD of ammonia indicate the following distribution of acid sites: 3.39×10^{19} acidic sites/g for the C_{16A} catalyst obtained by the alkaline treatment of the volcanic tuff, 9.35×10^{19} acidic sites/g for the native tuff, and 5.98×10^{20} acidic sites/g for the acid treated tuff. Consequently, if the acidity of catalysts varies such that

$$C_{16A} > \text{volcanic tuff} > C_{16B},$$

then the catalytic activity varies reversely as

$$C_{16A} \cong \text{volcanic tuff} > C_{16B}.$$



SCHEME 2

On basic catalysts (7), it was assumed that MgO acts directly on SiO_2 by generating acidic sites which may also serve to enhance the reaction. On acidic catalysts, it is well known that acrolein formation is due to Brønsted-type acid centers (15). Over phosphate catalysts, one generally assumes that the activity and the selectivity could be governed by the balance of acidic and basic properties (19); i.e., strong basic properties promote secondary reactions whereas a pronounced decrease of these basic properties affects the activity. The same remarks could be applied to the present case.

The acid treatment of the volcanic tuff gives rise to a clinoptilotite-rich material. Consequently, one may expect an improvement of the catalytic performance. Nevertheless, the conversion does not seem to be enhanced by a pronounced acidity (C_{16B}). The selectivity increases by such a treatment. On the other hand, the alkali-treated tuff leads to an analcime-rich material. The latter has the same activity as that of the volcanic tuff but an improved selectivity and a higher stability to coking.

To sum up, one can conclude that suitable modifications of the volcanic tuff can yield valuable catalysts for the vapor-phase condensation of acetaldehyde and formaldehyde to produce acrolein. Moreover, the experimental data reveal that good achievement in acrolein synthesis needs judicious choice of a catalyst. Such a catalyst should have a significant catalytic activity, but it must also have adequate acidity and porosity which can limit the secondary reaction. In this way one can obtain very active catalysts with improved selectivity for acrolein formation.

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