

SELECTIVITY CHANGES OF ACETONE TRANSFORMATION OVER ZSM-5 ZEOLITES WITH DIFFERENT ACIDO-BASIC PROPERTIES

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Acetone transformation catalyzed by HZSM-5 and NaZSM-5 zeolites and by zeolites modified with basic oxides was studied in an integral reactor at a temperature of 350°C. Modification of acido-basic properties of ZSM-5 zeolites resulted both in the total conversion changes and in the essential changes in the product composition. Isobutene was found to be the main product over HZSM-5 zeolites exhibiting low activity, while aromatics prevailed when high conversion level was attained. Classical condensation of acetone yielding mesityloxy and phorones was observed over NaZSM-5 zeolites impregnated with CaO and ZnO.

The search of new sources for industrially important compounds has resulted in increased interest in acetone conversion. This interest arose primarily from the feasibility of its production from natural materials using biofermentation processes. Acetone can be transformed into a variety of compounds¹ depending on the nature of the catalyst. The most common reaction is aldol condensation to mesityloxy, phorones, and mesitylene carried out using oxide catalysts exhibiting basic properties²⁻⁵. Over acidic oxides, the reaction path is more complex, so that aromatics can be obtained as the dominating products. Recently it has been shown⁶⁻¹¹ that acidic zeolites are particularly effective catalysts for this transformation, because of their selectivity for isobutene formation.

The purpose of this contribution is to compare the catalytic activity and product selectivity of acid and sodium forms of ZSM-5 zeolites with those of ZSM-5 impregnated or mixed with basic oxides (CaO, ZnO, Fe₂O₃) and Ca(OH)₂.CaCO₃ in acetone transformation.

EXPERIMENTAL

Catalysts. ZSM-5(1) and ZSM-5(2) zeolites with Si/Al ratios of 13.6 and 600, respectively, were synthesized in the Research Institute of Oil and Hydrocarbon Gases (Czechoslovakia), according to the refs^{12,13}. Organic templates were removed from zeolites in a dry oxygen stream at 550°C for 5 hours. For the ZSM-5(1) zeolite the formation of Na form was confirmed by the absence of the band of the bridging hydroxyl groups vibrating at 3 611 cm⁻¹ in the infrared

spectrum of this sample. The acidic forms of the zeolites were prepared by acid exchange of Na forms with 0.5 HNO₃.

Impregnation of NaZSM-5(2) with CaO, ZnO and Fe₂O₃ was carried out by adding aqueous solutions of the appropriate nitrates to the dry zeolite. Nitrates were then decomposed in an oxygen stream at 550°C (5 hours). 3 Ca(OH)₂ · 2 CaCO₃ was supplied by Merck. This compound was simply mixed with HZSM-5(1) and HZSM-5(2) zeolites. The crystallinity of all these catalysts was verified on the basis of infrared spectra of the skeletal vibrations. The catalyst compositions are listed in Table I.

Kinetic runs were performed in glass fixed bed reactor. A mixture of 70 vol. % of acetone vapours and 30 vol. % of He was fed into the reactor at a temperature of 350°C at atmospheric pressure. Weight hour space velocity (WHSV) and weight of catalyst were in the range 0.7--10.0 h⁻¹ and 0.5--1.5 g, respectively. Samples were activated in a N₂ or O₂ stream at 350 or 450°C (indicated in Table I) for 2 hours. After activation the catalyst was purged with helium at the reaction temperature until the gas was free of N₂ or O₂.

Analyses. The gaseous products were analyzed by on-line TCD gas chromatograph using glass column 3 mm i.d., 2.5 m long, packed with octane/Porasil for hydrocarbon analysis and Porapak Q-S for analysis of CO, CO₂, H₂O and acetone. After passing through the valve system of the chromatograph the reactor effluent was condensed in a trap at 0°C. The liquid, trapped 5--10 minutes before and after each dose of the products formed to chromatograph was separately analyzed using FID chromatograph and a glass column packed with 10% OV-17 on Chromaton N. This procedure enables to refine the analysis of aromatic hydrocarbons and higher ketones.

In the case of the determination of the amount of carbonaceous deposits, the reaction was stopped after desired time interval, then the catalyst was purged with dry helium at the reaction temperature for 0.5 hour. The remaining carbonaceous residue, coke, was determined gravimetrically by combustion with oxygen at 700°C for 2 hours.

TABLE I
Characteristics of the catalysts investigated

Sample	M, wt. % ^a	Preparation	Activation temperature, °C
HZSM-5(1)	—	pure	450
NaZSM-5(1)	—	pure	450
HZSM-5(2)	—	pure	450
NaZSM-5(2)	—	pure	450
Fe ₂ O ₃ .NaZSM-5(2)	10.0	impregnated	450 ^b
CaO.NaZSM-5(2)	10.0	impregnated	450
ZnO.NaZSM-5(2)	10.0	impregnated	450
3Ca(OH) ₂ ·2CaCO ₃ .HZSM-5(1)	8.5	mixed	350
3Ca(OH) ₂ ·2CaCO ₃ .HZSM-5(2)	8.5	mixed	350
3Ca(OH) ₂ ·2CaCO ₃	46.0	pure	350

^a M cation (Fe, Ca, Zn); ^b activated in O₂ stream, all other catalysts in N₂ stream.

RESULTS

The activities and selectivities observed for the individual catalysts in acetone transformation are summarized in Table II.

TABLE II
Conversion and selectivities in acetone transformation over catalyst studied

	HZSM-5(1)		HZSM-5(2)		HZSM-5(1) + 3 Ca(OH) ₂ ·2 CaCO ₃		HZSM-5(2) + 3 Ca(OH) ₂ ·2 CaCO ₃	
	0.7	5.0	0.7	5.0	0.7	5.0	0.7	5.0
WHSV, h ⁻¹	0.7	5.0	0.7	5.0	0.7	5.0	0.7	5.0
Time, min	60	300	60	300	60	300	60	300
$g_{\text{acet}}/g_{\text{catal}}$	0.7	25	0.7	25	0.7	25	0.7	25
$g_{\text{coke}}/g_{\text{catal}}$, %	— ^a	10.7	— ^a	5.7	— ^a	7.5	— ^a	13.8
Conversion, wt. %	100.0	4.7	8.7	2.3	100.0	5.2	69.0	3.0
Selectivity, wt. %								
O-compounds	1.4	2.6	8.5	6.4	1.4	11.4	4.4	20.4
aliphatics	17.3	50.4	87.3	85.2	11.7	27.1	19.5	65.8
aromatics	80.4	47.1	4.4	7.9	86.6	60.6	75.4	12.7
CO	0.5	1.0	3.9	1.5	0.4	1.1	1.4	2.6
CO ₂	0.9	0.5	3.8	2.3	1.2	1.3	2.3	4.4
Mesityloxide	—	—	0.2	2.6	—	1.5	0.2	1.0
Isophorone	—	—	0.6	—	—	7.5	0.5	12.4
Acetic acid	—	1.1	—	—	—	—	—	—
C ₁	0.8	1.9	2.9	1.3	0.1	1.0	0.2	2.0
C ₂	3.4	2.3	7.8	4.6	0.4	2.9	0.5	4.8
C ₃	8.1	—	—	—	6.3	—	0.6	—
C ₂ ⁼	—	0.7	0.8	1.4	0.1	0.8	2.2	1.3
C ₄	4.3	—	—	—	3.9	—	1.3	—
iC ₄ ⁼	—	45.5	75.8	77.6	—	22.4	12.6	57.7
C ₅	0.7	—	—	—	0.9	—	2.1	—
Naphthenes	—	—	—	—	—	1.0	1.6	—
Benzene	3.7	4.0	0.2	2.1	7.4	0.5	3.9	traces
Toluene	15.4	3.2	0.3	0.6	26.8	8.8	3.3	1.1
<i>p,m</i> -Xylene	38.9	15.3	0.7	0.7	24.7	13.4	15.4	0.7
<i>o</i> -Xylene	11.0	0.1	0.1	0.1	12.7	5.3	2.8	0.1
1,3,5 TMB	3.6	7.9	1.0	0.8	7.2	9.8	24.5	2.2
1,2,4 TMB	7.8	5.4	1.9	3.2	5.6	12.8	14.0	3.7
1,2,3 TMB	—	—	—	—	0.6	0.8	0.2	—
A ₁₀ ^b	—	6.4	0.2	0.4	1.0	8.4	7.8	3.3
A ₁₀ ^{+ b}	—	4.8	—	—	0.9	0.8	3.5	1.6

^a Not determined; ^b A means aromatics.

ZSM-5 zeolites with highly different Si/Al ratios (see Table I) were used in both the acidic (H) and sodium forms. HZSM-5(1) contains 1.15 mmol g^{-1} and HZSM-5(2) $0.025 \text{ mmol g}^{-1}$ (of the dry sample) of strongly acidic bridging hydroxyl

TABLE II
(Continued)

3 Ca(OH) ₂ .2 CaCO ₃		Fe ₂ O ₃ .NaZSM-5(2)		CaO.NaZSM-5(2)	ZnO.NaZSM-5(2)
0.7	5.0	0.7	5.0	5.0	5.0
60	300	60	300	300	300
0.7	25	0.7	25	25	25
— ^a	— ^a	— ^a	0.5	0.1	0.8
10.1	5.1	29.5	3.1	5.1	4.1
68.1	77.8	11.4	11.2	66.7	57.4
5.1	10.6	74.3	83.7	7.1	13.6
26.8	11.5	9.4	4.0	26.2	29.1
2.5	4.6	1.0	1.3	3.8	2.1
0.4	0.9	9.6	6.7	2.2	3.5
57.0	25.7	0.2	3.1	54.8	47.7
8.2	46.6	0.4	0.2	5.9	4.1
—	—	—	—	—	—
0.8	1.4	0.7	1.9	1.0	1.6
0.9	1.9	1.6	4.5	2.4	3.8
—	—	—	—	—	—
0.4	0.8	0.8	1.2	0.9	1.4
—	—	—	—	—	—
3.0	6.5	71.2	76.1	2.8	6.8
—	—	—	—	—	—
—	—	4.4	0.7	—	—
0.2	0.2	2.3	0.5	1.6	2.6
17.8	7.9	0.4	1.4	17.0	16.4
0.6	0.3	1.2	0.5	0.1	2.9
0.5	0.1	0.1	0.1	—	0.5
2.4	2.1	1.5	0.2	5.2	3.5
1.2	0.1	3.3	1.0	0.7	1.2
0.3	—	0.1	—	—	—
3.8	0.8	0.5	0.3	1.6	2.0
—	—	—	—	—	—

groups while their sodium forms contain primarily only nonacidic SiOH groups located on the outer surface and structural imperfections so that these samples can be considered as neutral ones. As should be expected from the differences in acidic properties, the catalytic activity and product composition varied in a rather broad range. Besides that, conversion of acetone over HZSM-5 zeolites was dependent on the WHSV which affects the rate of the activity decrease. The time-on-stream dependence of acetone conversion over HZSM-5(1), together with the variation in the selectivities, are given in Fig. 1. These data indicate that the higher the space velocity, the shorter is the period necessary for attaining the steady state represented here by the deactivated catalyst with coke deposit (Table II) causing a very low acetone conversion. As the deactivation occurred with nearly all the samples used, the catalytic properties of individual catalysts are here characterized with the activity and product distribution at the relatively low coking level and high conversion (i.e. after 1 hour time-on-stream with WHSV 0.7 h^{-1}) and at the steady state (represented here with values obtained after 5 hours time-on-stream with WHSV 5.0 h^{-1}). In addition, when steady state is once attained the formation of isobutene prevails in products irrespective of the contact time $(\text{WHSV})^{-1}$ and, consequently, the preceding period of higher activity.

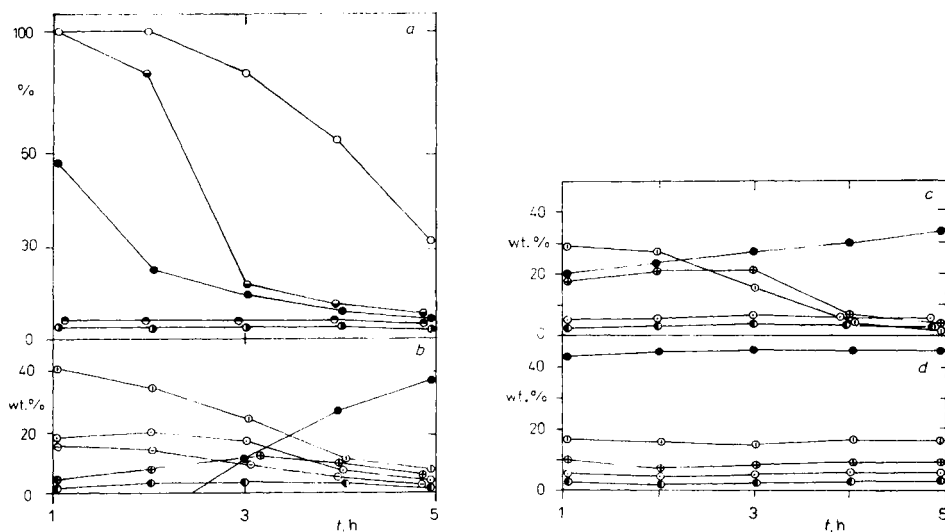


FIG. 1

Time dependence of conversions (a) and selectivities (b - d) over HZSM-5(1) zeolite. a For different WHSV (h^{-1}): \circ 0.7, \bullet 1.24, \bullet 2.5, \bullet 5.0, \bullet 10.0; b WHSV 0.7 h^{-1} , c WHSV 2.5 h^{-1} , d WHSV 10.0 h^{-1} : \bullet isobutene, \bullet CO + CO₂, \circ C₁-C₄, \circ toluene, \circ p,m-xylene, \circ mesitylene

It should be noted here, that the activity of all catalysts examined varied between 2 and 5.5% at the steady state (Table II).

In contrast to HZSM-5(1), where after 1 hour of the reaction at WHSV 0.7 h^{-1} all of the acetone fed was transformed into the products, the activity of HZSM-5(2) was low (9%) and both sodium forms were nearly inactive ($\text{NaZSM-5(1)} < 0.5\%$, $\text{NaZSM-5(2)} < 0.8\%$). Over the OH-rich HZSM-5(1) zeolite aromatic hydrocarbons dominated in the products, while the HZSM-5(2) zeolite with a very small amount of acidic hydroxyls catalysed predominantly the formation of isobutene. This zeolite exhibited the highest selectivity for isobutene among all catalysts studied.

At the steady state, after 5 h time-on-stream at WHSV 5.0 h^{-1} , the activity of both HZSM-5(1) and HZSM-5(2) were very low but the amount of carbonaceous residue formed in the case of the former zeolite was twice higher than that in the latter one. The number of HZSM-5(2) zeolite bridging SiOHAl hydroxyls was too small for the detection of these groups using infrared spectroscopic technique (i.r.). With HZSM-5(1) zeolite, however, the i.r. spectra easily revealed that carbonaceous deposits displays catalytically active bridging hydroxyl groups remaining only at about of 10% of their original number. Coked HZSM-5(1) zeolite yielded mainly isobutene together with aromatic hydrocarbons, HZSM-5(2), as was mentioned above, exhibited higher selectivity for isobutene.

The $\text{Ca(OH)}_2 \cdot \text{CaCO}_3$ sample can be considered as a representative of basic catalysts and, consequently, catalysed the transformation of acetone preferably to the oxygen-containing organic compounds, among them mesityloxide was found to dominate at the beginning of the reaction (1 hour, WHSV 0.7 h^{-1}), while isophorone was more abundant after a prolonged run (5 hours, WHSV 5.0 h^{-1}); see Table II. NaZSM-5(2) impregnated with both CaO and ZrO exhibited also features typical for basic oxides which were again manifested by the rather high selectivity for oxygen-containing organic compounds (mesityloxide always dominated here in products). The activity of the examined impregnated systems was rather low even at the beginning of the reaction (1 hour, WHSV 0.7 h^{-1}) but it was still considerably higher than the activity of the pure support. In contrast to the basic catalysts mentioned above the behaviour of $\text{Fe}_2\text{O}_3 \cdot \text{NaZSM-5(2)}$ was very similar to that of the acid form of support with typical selectivity for isobutene; the cause of it remains still unclear.

When the acidic hydroxyl-rich sample HZSM-5(1) was mixed with basic $\text{Ca(OH)}_2 \cdot \text{CaCO}_3$, the conversion and products distribution were very near to that of the pure acidic component at the beginning of the reaction (1 hour, WHSV 0.7 h^{-1}), while more aromatic hydrocarbons, namely trimethylbenzenes, and more mesityloxide appeared in the products at the steady state. The selectivity for isobutene was, consequently, appreciably lower than in the case of pure HZSM-5(1). Mixing of the less acidic HZSM-5(2) zeolite with a basic component resulted in the decrease in the selectivity for isobutene. In pronounced contrast to the original HZSM-5(2)

zeolite, the activity of catalyst was found to be substantially improved after 1 hour of the reaction at WHSV 0.7 h^{-1} when also aromatics (with considerable portion of trimethylbenzenes) highly prevailed among the products.

DISCUSSION

A scheme of the probable main pathways for acetone transformation is depicted in Fig. 2, although the reaction itself is evidently more complex. The aldol condensation is known to be catalysed both by acids⁷ and bases² yielding products in the sequence: acetone – diacetonol – mesityloxyde – phorone, isophorone – trimethylbenzenes. As far as the examined catalysts are concerned, this sequence was indeed observed in the case of basic solids, i.e. $\text{Ca}(\text{OH})_2 \cdot \text{CaCO}_3$, $\text{CaO} \cdot \text{NaZSM-5}(2)$ and $\text{ZnO} \cdot \text{NaZSM-5}(2)$, while with pure HZSM-5 zeolites, which contain

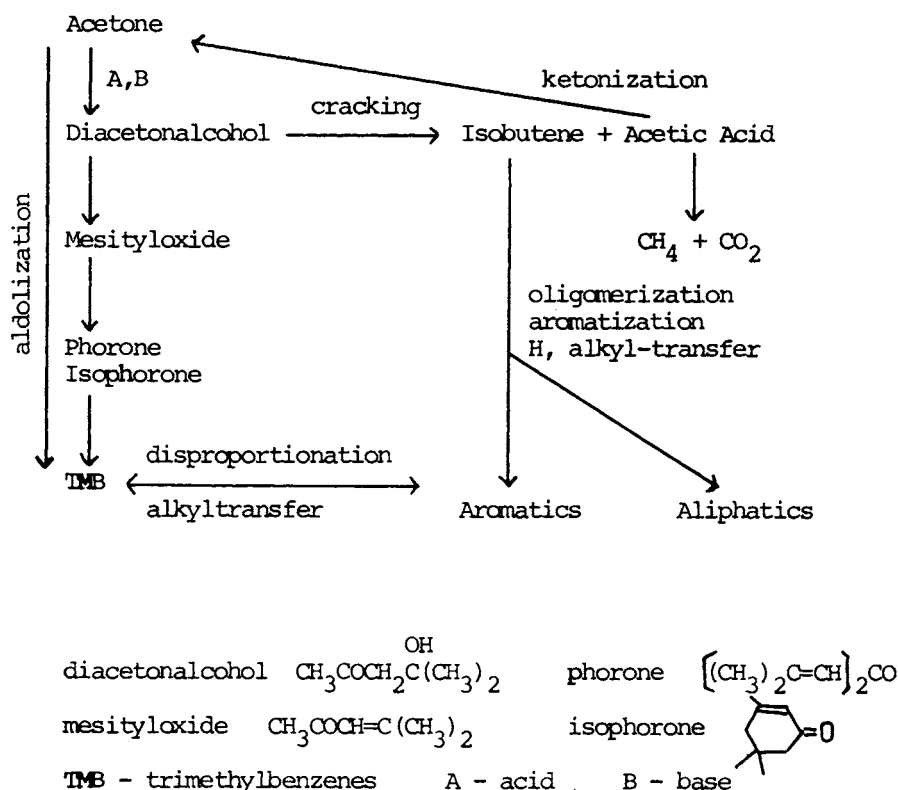


FIG. 2
Main reaction pathways of acetone transformation

strongly acidic bridging hydroxyls, the aliphatics and C_6-C_8 aromatics are the dominating components of the products. The appearance of these hydrocarbons can be taken as an evidence of the occurrence of further subsequent reactions—cracking, oligomerization, aromatization, H and alkyl-transfer, disproportionation etc.

Chang⁷ supposes that isobutene together with acetic acid is formed on acid zeolites via the cracking of diacetonolcohol. He explains the small amount of acetic acid found in the products by a decarboxylation reaction resulting in the hydrocarbon formation which proceeds presumably via "ketonization". According to Kurganova¹⁴, isobutene can also be formed from the non-dehydrated product of the reaction of three acetone molecules; this suggestion has recently been supported by the finding⁸ that the appearance of butene is accompanied by the formation of surface unsaturated cyclic ketones. In the present work diacetonolcohol as reaction intermediate was detected neither over acidic zeolites nor over basic catalysts where it was readily dehydrated to mesityloxide.

Generally, here there are two factors which could account for the changes in the activity and selectivity of HZSM-5 zeolites: the contact time and the properties of the catalyst. At the very beginning of the each reaction run over HZSM-5(1), the 100% of acetone was converted to products where practically no isobutene was found. This occurred in the whole range of contact times used. The relevant points are not shown in Fig. 1, because the complete analysis could not be performed in such a very short time, so that we were not able to follow rigorously possible differences in the composition of aromatic hydrocarbons and other aliphatics in dependence on the contact time. Nevertheless, HZSM-5(2) zeolite, containing much less bridging hydroxyl groups was at the beginning of the catalytic run at the identical conditions less active than HZSM-5(1) and yielded high portion of isobutene in products. Isobutene always dominated in the products of acetone transformation over both HZSM-5 zeolites at steady state conversion when the number of accessible active sites had been reduced by coking. These observations allow us to deduce for the range of contact times examined that the high number of strongly acidic hydroxyls in HZSM-5 is responsible for the high overall acetone conversion and for enhancement of such reactions as oligomerization of unsaturated hydrocarbons, H- and alkyl-transfer, aromatization etc. resulting in the formation of C_6-C_8 aromatics, saturated hydrocarbons and coke. High selectivity for isobutene appears only on zeolites with low number of bridging hydroxyls and, therefore, at low zeolite activity. This low activity can be achieved using either the zeolites with low content of Al in the lattice or coked zeolites.

Considering the typical features of acidic and basic catalysts discussed above, the behaviour of their mixtures can be brought about as follows: the action of strongly acidic HZSM-5(1) is apparently decisive on fresh catalysts while the basic component, $Ca(OH)_2 \cdot CaCO_3$, becomes more important after the catalyst deactivation and coking.

The latter conclusion can be drawn from the appearance of isophorone in products at the steady state. When the number of acidic hydroxyls on zeolitic component is low (HZSM-5(2)) then the effect of the basic component of the catalyst is pronounced already with the fresh catalyst, when it seems to be reflected in the appreciably high selectivity for trimethylbenzenes. The formation of these bulky compounds indicate also that they are formed outside the narrow channels of the zeolite structure (the diameter of these channels is about 0.55 nm).

CONCLUSION

Variation of acido-basic properties of HZSM-5 zeolites resulted both in the appreciable changes of total conversion, and also in essential changes in product composition and distribution:

i) The transformation of acetone over HZSM-5 zeolites is an acidic-catalyzed reaction consisting of aldolization and cracking and is accompanied with further parallel and subsequent reactions yielding aromatic and aliphatic hydrocarbons. High selectivity for isobutene is achieved over catalysts with low activity which contain appropriate small numbers of strongly acidic SiOHAl groups on the zeolite skeleton. This number can be attained by reduction of the Al atoms in the skeleton of original zeolite or by the formation of coke in the zeolite during the reaction.

ii) Non-acidic Na forms of ZSM-5 zeolites are inactive but, when they are impregnated with basic CaO and ZnO, acetone is transformed with low conversion yield but high selectivity to mesityloxide. Similarly, mesityloxide and isophorone were found to be the dominant products in the acetone transformation catalyzed by basic $\text{Ca}(\text{OH})_2 \cdot \text{CaCO}_3$.

iii) The net effect of the mixing of acidic HZSM-5 zeolites with basic $\text{Ca}(\text{OH})_2 \cdot \text{CaCO}_3$ depends above all on the properties of acidic component. The addition of the basic component does not improve the selectivity for isobutene and does not considerably decrease the coking.

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