

INFLUENCE OF WATER ON ACTIVITY, SELECTIVITY AND DEACTIVATION OF ZEOLITES IN ACETONE TRANSFORMATION

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Dedicated to late Academician Eduard Hála.

The suppression of the deactivation of acid forms of zeolites in acetone transformation was studied by adding water vapours to the feed. Both conversion of acetone and yield of isobutene increased remarkably. Water prevents the substitution of bridging hydroxyls for coke species and limits the aldolization steps, which are decisive for catalyst deactivation.

Increasing attention has been recently paid to the transformation of acetone catalyzed by various forms of zeolites¹⁻⁶. Isobutene was found to be the main product over all zeolites studied in the temperature range of 300–350°C. Selective formation of isobutene was, however, strongly connected with low catalytic activity and was attained only after the coking of the catalysts⁶.

The purpose of this work was to suppress the deactivation of zeolites by adding water vapour into the acetone feed. We tried also to explain changes in conversions and selectivities to isobutene occurring with and without water in the feed.

EXPERIMENTAL

The ZSM-5a and ZSM-5b zeolites with Si/Al ratios of 13.6 and 600, respectively, were synthesized in the Research Institute of Oil and Hydrocarbon Gases, Bratislava (Czechoslovakia), as well as erionite (Si/Al = 3.17). Acidic forms of these zeolites were prepared by ion exchange of Na forms with 0.5M HNO₃. A physical mixture of 3 Ca(OH)₂·2 CaCO₃ with HZSM-5b zeolite was prepared. The crystallinity of these catalysts was checked by the infrared spectra of the skeletal vibrations using a FT-IR Nicolet MX-1E spectrometer.

The reaction runs were carried out in an integral glass fixed-bed reactor at temperatures of 300 and 350°C at atmospheric pressure. Mixture of 35 vol. % of acetone in helium or mixtures of acetone, water and helium (the ratios of partial pressures are indicated in Table I) were fed into the reactor. The weight hour space velocity (WHSV) used was 5.0 h⁻¹ and the amount of catalyst was 1.0 g. Samples were activated in an oxygen stream at 450°C for two hours. After the activation the catalyst was purged with helium at the reaction temperature until the effluent gas was free from oxygen.

TABLE I

Conversions and selectivities of acetone transformation with and without water in the feed (WHSV 5.0 h⁻¹, time 300 min, steady state conversion)

Conditions and products	HZSM-5a								HZSM-5b		Erionite		Ca(OH) ₂ -CaCO ₃ -HZSM-5b	
	—	1.4	—	0.6	1	1.4	2.0	2.5	—	1.4	—	1.4	—	1.4
<i>p_w</i> / <i>p_{ac}</i>	—	1.4	—	0.6	1	1.4	2.0	2.5	—	1.4	—	1.4	—	1.4
Temperature, °C	300	300	350	350	350	350	350	350	350	350	350	350	350	350
Conversion, %	2.4	9.2	4.7	15.8	17.2	18.8	23.1	28.5	2.3	10.0	2.0	6.0	3.0	6.5
Selectivity, wt. %														
CO	1.8	0.7	1.0	0.4	0.7	0.5	0.7	1.0	1.5	1.2	2.5	1.3	2.6	1.9
CO ₂	1.3	0.6	0.5	0.6	0.9	0.5	0.9	1.0	2.3	0.9	2.5	1.8	4.4	4.8
Mesityloxyde	—	0.9	—	0.4	—	0.5	—	0.5	2.6	—	17.5	2.5	1.0	—
Phorone	—	0.3	—	0.3	—	2.3	—	0.3	—	—	—	0.7	—	—
Isophorone	—	—	—	—	—	—	—	—	—	—	0.9	—	—	—
Acetic acid	—	—	1.1	2.4	3.1	3.7	1.6	3.1	—	—	—	—	—	—
C ₁	1.3	0.6	1.9	0.4	0.6	0.5	0.7	0.9	1.3	0.9	1.4	1.4	2.0	1.4
C ₂	3.6	1.6	2.3	0.9	1.6	1.0	1.1	1.8	4.6	2.3	4.7	2.4	4.8	3.6
C ₃ =	1.3	0.9	0.7	0.5	0.8	0.5	1.0	3.0	1.4	1.0	1.5	1.8	1.3	1.7
i-C ₄ =	67.2	80.3	45.5	83.7	78.6	67.2	66.2	62.1	77.6	77.7	81.6	79.0	57.7	75.2
C ₄	—	—	—	—	—	—	0.7	—	—	1.4	—	—	—	—
C ₆ —C ₈	—	—	—	—	—	—	—	—	—	0.8	—	—	—	1.2
Benzene	0.3	0.3	4.0	2.1	2.1	3.8	3.2	3.3	2.1	0.3	1.2	1.1	0.1	1.0
Toluene	1.9	0.5	3.2	0.6	2.1	5.8	2.6	0.9	0.6	0.9	6.8	1.7	1.1	1.6
<i>p,m</i> -Xylenes	9.7	2.4	15.3	1.4	2.3	2.1	4.7	3.5	0.7	4.7	0.1	0.5	0.7	3.5
<i>o</i> -Xylene	1.1	0.1	0.1	0.2	—	0.3	0.3	0.2	0.1	0.2	—	0.1	0.1	0.4
1,3,5-TMB ^a	4.0	2.8	7.9	1.8	1.9	2.6	4.6	5.1	0.8	2.8	7.9	3.0	2.2	1.0
1,2,4-TMB ^a	3.2	5.2	5.4	3.2	3.0	3.0	7.0	6.6	3.2	3.7	0.9	0.7	3.7	1.7
1,2,3-TMB ^a	—	0.4	—	0.3	—	—	—	0.3	—	0.3	—	0.3	—	—
A ₁₀ ^b	3.1	1.6	6.4	0.5	1.4	2.1	3.4	3.6	0.4	1.0	—	1.6	3.3	0.9
A ₁₀₊ ^b	—	0.7	4.8	0.4	0.7	—	1.0	2.7	—	—	—	—	1.6	—

^a TMB trimethylbenzene; ^b A aromatic hydrocarbons.

The gaseous products were analyzed by an on-line gas chromatograph with a TCD, using glass columns of 3 mm i.d., 2.5 m long, packed with octane/Porasil for hydrocarbon analysis and Porapak QS for the analysis of CO, CO₂, H₂O and acetone. The reactor effluent passing through a valving system of the chromatograph was then condensed at 0°C. The trapped liquid condensation products (acetone, aromatics, aldol condensation products) were then analyzed using a gas chromatograph with a FID and glass column packed with 10% OV-17 on Chromaton N.

RESULTS AND DISCUSSION

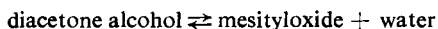
The steady state conversions and selectivities for all catalysts studied in acetone transformation are given in Table I. According to the data, one can assume that the addition of water vapour into the feed influenced the reaction in several ways. The catalytic activity of the zeolites studied increased in all cases whereas the selectivity for isobutene either increased or remained on a similar level. These trends resulted in an improvement of the isobutene yield⁷.

Together with the increased catalytic activity a lower amount of coke deposits was produced⁸. Therefore, the life of catalysts was prolonged, too. Also infrared measurements proved that about 30% of the original amount of strong acidic bridging hydroxyl groups in the case of HZSM-5a was preserved⁸, while in the case when only acetone was passed over the catalyst, about 10% of these hydroxyls able to catalyze the reaction remained.

In Fig. 1 the relationship between water and acetone partial pressure ratios and catalytic activity or isobutene yield for HZSM-5a is shown. With the increasing ratio of water to acetone the conversion of acetone increased and the isobutene yield slightly increased as well. However, the selectivity for isobutene was a little diminished. The amount of aromatic compounds rose simultaneously. The production of oxygen containing compounds was strongly limited, especially in comparison with the acetone reaction over pure erionite and Ca(OH)₂.CaCO₃. HZSM-5b when only acetone as a reactant was used. Time dependence of acetone conversion for HZSM-5a zeolite and various water acetone partial pressure ratio is given in Fig. 2.

Chang and coworkers^{1,2} reported that the mechanism of acetone transformation starts via a reaction of two acetone molecules resulting in diacetone alcohol formation. The suggested reaction pathway can then proceed either by decomposition of the diacetone alcohol (4-hydroxy-4-methyl-2-pentanone) formed to isobutene and acetic acid or by the dehydration of diacetone alcohol to mesityloxide. Recently, it has been found that also mesityloxide can be converted to isobutene⁹, however, the rate of coke formation is much higher than with acetone. It seems to us that the latter possibility represents the most important step of deactivation of acid forms of zeolites. As it will be reported elsewhere⁸, the mechanism of isobutene transformation, catalyzed with acid forms of zeolites, proceeds via the commonly assumed carbocationic steps. The decrease of catalytic activity of the HZSM-5a zeolite is practically negligible and is uncomparable with very rapid activity decrease in the

case of acetone transformation. Similar results have been found also for diethyl ketone. Therefore, it can be inferred that the products of isobutene transformation practically do not contribute to the deactivation of HZSM-5a zeolite. On the other hand, Nováková and coworkers⁴ have already reported the formation of isobutene by the decomposition of higher condensation products of acetone reaction. The rest of this molecule then remains strongly bound to the surface in the form of a not fully saturated (possibly cyclic) ketone⁸ which substitutes a bridging hydroxyl group. Addition of water to the feed influences the equilibrium



and shifts it to the left side. Owing to the limits of mesityloxyde formation, diacetone alcohol is preferentially cracked to isobutene and the catalytic activity increases. The amount of acetic acid found does not correspond to that of isobutene but acetic acid can subsequently react by a bimolecular "ketonization" reaction¹⁰ back to acetone or be also cracked. It is apparent that the actual reaction mechanism of acetone transformation is much more complex and complicated. For example Kurganova and coworkers¹¹ suggested the formation of isobutene also via cracking of the non-dehydrated condensation product of three acetone molecules.

Formation of aromatic hydrocarbons increases with decreasing the acetone/water ratio in the feed and with accordingly decreasing selectivity to isobutene. Water

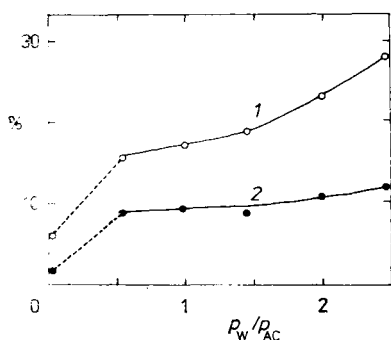


FIG. 1

Relationships between 1 catalytic activity of HZSM-5a or 2 yields of isobutene and the partial pressure ratios water/acetone (WHSV = 5.0 h⁻¹, time 300 min, 25 g acetone per 1 g catalyst)

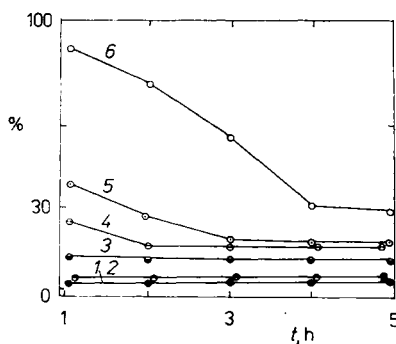


FIG. 2

Time dependence of acetone conversion for HZSM-5a and different partial pressure ratios water/acetone (WHSV = 5.0 h⁻¹, 1 g catalyst, 300°C: 1 acetone, 2 $p_W/p_{AC} = 1.43$, 350°C: 3 acetone, 4 $p_W/p_{AC} = 0.7$, 5 $p_W/p_{AC} = 1$, 6 $p_W/p_{AC} = 2.5$)

molecules can act as supporter of hydrogen transfer and enhance subsequent reactions of isobutene resulting in the formation of aromatics.

It can be concluded that the addition of water vapour to the feed suppresses the substitution of acid bridging hydroxyls of zeolite catalysts for the unreactive coke species which causes a remarkable improvement of the steady state conversions (2–6 times). Simultaneously the yield of isobutene formed increases, too. Apparently water prevents the dehydration of diacetone alcohol and further aldolization steps, so that cracking to isobutene is favoured. It could be suggested that the formation of aldol condensation products of acetone is decisive for the deactivation of acid catalysts. The increase of the catalytic activity of acid forms of zeolites can be, therefore, obtained by preventing the formation of condensation products.

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