

New horizons in catalysis using modified and unmodified pentasil zeolites

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Abstract - Know-how obtained from petrochemical processes on the catalytical properties of pentasil zeolites is being used for selective organic syntheses in the chemistry of intermediates. The isomerization properties are demonstrated by doublebond migrations in olefins with carbonyl groups and by the aldehyde/ketone rearrangement. The dehydration properties are used in the conversion of aldehydes to 1,3-dienes, in aldol condensation reactions and for the preparation of dicarboxylic acid nitriles from acids and ammonia. Therefore this paper concentrates on hydrocarbons with carbonyl groups.

INTRODUCTION

The advance of zeolites as catalysts started at the beginning of the 1960s when cracking catalysts based on amorphous aluminosilicates were replaced by faujasite-type zeolites, which gave higher conversion rates and large yields of a higher octane gasoline (ref. 1 - 4). Metal doped Y zeolites have also replaced amorphous systems as bifunctional hydrocracking catalysts (ref. 4 - 7). In the 1970s, the outstanding achievement in zeolite chemistry was the discovery of ZSM 5 (ref. 8), the first representative of the pentasil zeolite family (ref. 9, 10), and the use of these as highly acidic, extremely shape-selective and heat-stable catalysts. The use of pentasil zeolites in petrochemistry and mineral oil processing was marked by work at Mobil Oil Corp. (ref. 11, 20): selectoforming (ref. 12), olefin oligomerization (ref. 14), dewaxing (ref. 4, 15, 16) and the MTG (= methanol to gasoline) process (ref. 4, 17) have established themselves as industrial processes alongside cracking and hydrocracking. They will probably soon be joined by dehydrocyclization of ethane, propane or LPG to aromatics (ref. 13, 18, 19) and, somewhat further into the future, the MTO (= methanol to olefins) process (ref. 4, 21). What all these processes have in common is a wide product spectrum. Selective reactions, leading to one main product, such as the Mobil-Badger process for the alkylation of aromatics (ref. 4, 22) and the para-selective xylene isomerization (ref. 4, 23), disproportionation (ref. 23, 25) or alkylation of monosubstituted aromatics (ref. 26) are practiced in petrochemistry.

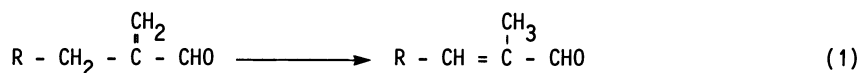
The potential regarding acidity and selectivity of faujasite-zeolites as catalysts for the organic synthesis of compounds with functional groups has been investigated (ref. 27 - 29). The major obstacle to industrial use up to now has been the rapid deactivation of these catalysts. The pentasil zeolites and their numerous modifications in number and strength of the acid sites, in isomorphous substitution (ref. 30) and in metal doping present opportunities of introducing such reactions successfully to industry; experience gained from zeolite-catalyzed processes in petrochemistry could be a helpful guide here. In the last 3 years, for example, work on the chemistry of intermediates has been published in which pentasil zeolites have been used successfully for doublebond and skeleton isomerization (ref. 31 - 34), dehydrations (ref. 35, 36, 40), addition reactions (ref. 37 - 39) and substitutions (ref. 41 - 46). BASF considers it as her special task to use pentasil zeolites in the chemistry of intermediates for such reactions. Part of that research will be shown in this paper in which carbonyl compounds are chosen as examples.

DOUBLEBOND ISOMERIZATION

It is known (ref. 48, 49) that alumo-zeolites can be used for doublebond isomerization in linear olefins without functional groups. Boron-zeolites can also be used, with the advantage that the selectivity is not reduced by skeleton isomerization or oligomerization (ref. 50 - 52). What effect do pentasil zeolites have on olefins with functional groups such as aldehyde or acetoxy?

Isomerization of 2-alkylacroleins to 2-methyl-2-alkenals

In the isomerization shown in Eq. 1, the terminal doublebond in the 2-alkyl-acroleins is converted to the internal doublebond in the 2-methyl-2-alkenals; skeleton isomerization or reactions of the aldehyde group don't occur.



R = alkyl, aryl or aralkyl

It is known that palladium carrier catalysts poisoned by sulfur catalyze this type of reaction in the presence of H₂ (ref. 53). The basic disadvantage is that significant amounts of the starting material are hydrogenated. The results with CaCl₂ as catalyst (ref. 54) are also unsatisfactory. A further possibility exists via 2-alkyl-acroleindialkylhydrazones, dialkylhydrazones and their hydrolysis (ref. 55) (three steps!). Until now, this reaction has always proved unsuitable for industry because of inadequate activity and selectivity or because of the complicated reaction sequence.

We have been able to show (ref. 56) that 2-ethylacrolein which is easily accessible from n-butyraldehyde and formaldehyde (ref. 57) can be converted to trans-2-methyl-butenal (tiglaldehyde) with a high yield using boron zeolites (Table 1).

TABLE 1. 2-ethyl-acrolein to tiglaldehyde at 400 °C (ref. 56)

catalyst	boron-zeolite ^a			
	^b	^b	3,2 % La ^c	7,2 % Ce ^c
doped with	1	2	2	2
WHSV h ⁻¹	48	15	22	20
conversion %	64	78	70	82
selectivity %				

^a SiO₂/B₂O₃ = 47, prepared in 1.6-diaminohexane (ref. 47).

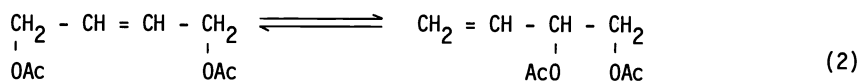
^b Pure, i.e., extruded without binder.

^c Doping by impregnation.

The Ce-doped catalyst thus exhibits better performance for this reaction than the systems known hitherto.

Allyl rearrangement of diacetoxybutenes

If the olefin has a functional acetoxy group, the pentasil zeolites not only isomerize the doublebond, but they cause a rearrangement by means of simultaneous functional group migrations (ref. 58), such as in the reversible allyl rearrangement of diacetoxybutenes (Eq. 2).



OAc = OCOCH₃

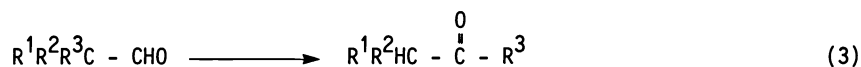
A mixture of 92 % trans and 6 % cis 1,4-diacetoxy-2-butene reacts, with a conversion of 52 % and selectivity of 55 %, to 3,4-diacetoxy-1-butene in the presence of the boron-zeolite (SiO₂/B₂O₃ = 47, according to ref. 47) at 300 °C and WHSV = 3 h⁻¹. A conversion rate of 56 % and a selectivity of 66 % is obtained under comparable reaction conditions using the alumo-zeolite (SiO₂/Al₂O₃ = 34, according to ref. 47). The conversion is reversible since 1,4-diacetoxy-2-butene is obtained from 3,4-diacetoxybutene using the boron-zeolite. At 200 °C and WHSV = 6 h⁻¹, 25 % of the 3,4-isomer give an 80 % selectivity of 1,4 product.

Hitherto, this type of allyl rearrangement has been carried out in the liquid phase on SeO₂ (ref. 59) or Pt and Pd halides, respectively in the presence of O₂ (ref. 60, 61). Use of pentasil-type zeolites and carrying out the conversion in the gas phase thus offers an alternative to homogeneously catalyzed liquid phase reactions.

SKELETON ISOMERIZATION

The allyl rearrangement of diacetoxybutenes already shows that skeleton isomerization of hydrocarbons with carbonyl groups is possible in the presence of pentasil zeolites without reaction of the carbonyl function.

The aldehyde ketone rearrangement shown in Eq. 3 is a further example of this.



Preparation of ketones from aldehydes would be an attractive route, as the latter are easily accessible via oxo synthesis, for example. This type of isomerization is known, eg. with tin-, molybdenum- and copper-containing mixed oxide catalysts (ref. 62) or using cerium oxide on alumina (ref. 63). The disadvantage of these processes is the low selectivity obtained with satisfactory yields and that steam is needed in order to get high selectivity and long life time. Because of this, unsymmetric, substituted ketones are generally prepared in industry by the condensation of various organic acids followed by decarboxylation (ref. 64). The unavoidable formation of symmetrically substituted ketones and carbon dioxide are disadvantages in this process.

It has now been found at BASF that ketones can be obtained advantageously by isomerization of aldehydes using pentasil zeolites (ref. 65). A plus point of that method is that the addition of steam is not necessary. The results are summarized in Table 2. The question here is of the priority of the migrating group. Surprisingly, the methyl group migrates if phenyl-, benzyl- and methyl-groups are present. This could be caused by the high shape selectivity of the pentasil zeolites; in the Beckmann rearrangement of ketoximes on HY zeolites, migration of the phenyl group (95 %) is favored ahead of the methyl group (5 %) (ref. 27).

The iron-zeolite is more active than the boron-zeolite, as may be seen in the case of the conversion of 2-phenyl-propanal (Table 2). This tendency is found eg. in the conversion of methanol to olefins, too, (ref. 80, 81). The iron-zeolite formed into extrudates with boehmite as a binder is less appropriate than the pure zeolite catalysts (Table 2). Using the alumo-zeolite ZSM 5 only low selectivity is obtained at high conversion rate even when steam is used as shown by Celanese (ref. 66).

TABLE 2. Aldehyde - ketone - rearrangement (ref. 65)

Feed	Zeolite	Condit. ^d	Product	Conv.	Selec.
2-Methyl-propanal	boron-a	400 °C 2 h ⁻¹	Butan-2-one	42 %	90 %
Pival-aldehyde	boron-a	360 °C 2 h ⁻¹	3-Methyl-butane-2-one	92 %	85 % ^e
2-Phenyl-propanal	boron-a	400 °C 0,8 h ⁻¹	1-Phenyl-propan-2-one	63 %	97 %
2-Phenyl-propanal	iron-b	400 °C 2 h ⁻¹	1-Phenyl-propan-2-one	98 %	95 %
2-Phenyl-propanal	iron-c	400 °C 2 h ⁻¹	1-Phenyl-propan-2-one	100 %	87 %
3-Phenyl-2-methyl-propanal	boron-a	400 °C 2 h ⁻¹	4-Phenyl-butane-2-one	59 %	85 %

^a SiO₂/B₂O₃ = 47, prepared in 1.6-diaminohexane (ref. 47), without binder.

^b SiO₂/Fe₂O₃ = 18, prepared in 1.6-diaminohexane (ref. 47), without binder.

^c Extruded with boehmite as a binder in the ratio 60 : 40 wt.-%.

^d Under isothermic conditions in a tube reactor; WHSV h⁻¹ = g feed/g catalyst and hour.

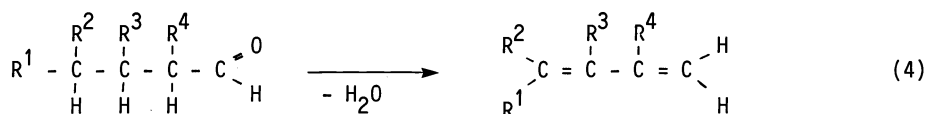
^e Plus 12 % isoprene.

DEHYDRATION REACTIONS

The dehydration properties of pentasil zeolites have been clearly demonstrated up to now by the industrially and scientifically interesting MTG and MTO processes (ref. 4, 11, 20).

Dehydration of aldehydes to 1,3-dienes

The aldehyde ketone rearrangement has its limitations if the aldehydes possess α -, β - and γ -hydrogen. In this case the kinetically favored dehydration to 1,3-dienes occurs. The enolization takes place rather than the alkyl migration presumably because the enol can react irreversibly to form the diene via the allyl isomers by 1,4-elimination of water.



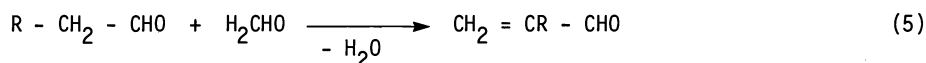
The preparation of dienes from aldehydes by simple dehydration is useful because the aldehydes are easily accessible via oxo synthesis, for example. Catalysts such as acids, eg. phosphoric acid (ref. 67) or borophosphates (ref. 68 - 70), are used, as Monsanto and Goodyear have been able to show at the same time as our studies. The addition of steam is a particular disadvantage of these processes.

At BASF, it has been found (ref. 71) that this disadvantage can be avoided by catalytical dehydration according to Eq. 4 using pentasil zeolites. The formation of isoprene from pivalaldehyde (cf. Sec. 2) has already pointed to the possibility of this reaction. At 400 °C and WHSV = 2 h⁻¹, isoprene with up to 95 % selectivity at a conversion rate of 51 % is obtained using the pure boron-zeolite from 2-methylbutanal (R¹ = R² = R³ = H, R⁴ = CH₃). 2-Methyl-1,3-pentadiene is formed from 2-methylpentanal (21 % conversion, 92 % selectivity) and methylenecyclohexene or its doublebond isomerization products are obtained from cyclohexylaldehyde (86 % conversion, 96 % selectivity), again under comparable conditions. Alumo-zeolites are less suitable for this aldehyde dehydration as aromatics are formed in larger amounts.

Aldol condensations

The aldol condensation is a further dehydration reaction of carbonyl-containing hydrocarbons and is generally carried out with bases as catalysts, but can also be carried out with acids. The aldol condensation of acetone over acidic alumo-zeolites gives mesitylene oxide, isobutene, phorones, mesitylene and alkylphenols (ref. 72 - 76). A detailed investigation by P. Jacobs (ref. 75) showed that ZSM 5, contaminated with iron oxide, converted acetone selectively to 2,4-dimethylphenol.

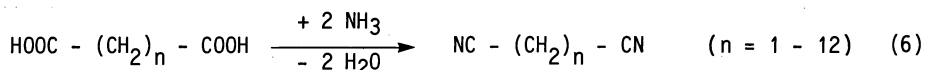
The preparation of α , β -unsaturated aldehydes from formaldehyde and aldehydes of the formula RCH₂CHO (R = H, alkyl, aryl, aralkyl, cycloalkyl or alkylaryl) according to Eq. 5 succeeds with high selectivity using Amoco boron-zeolite HAMS-1 B (ref. 77).



For example, a 1 : 1 molar mixture of propionaldehyde and formaldehyde forms methacrolein with 98 % selectivity at 300 °C and τ = 1.7 sec. with HAMS-1 B (extruded with alumina, 50 % : 50 % by weight). The propanal conversion rate here is 57 %. Aldol condensations with formaldehyde can thus be carried out highly selectively using boron zeolites.

Preparation of aliphatic dinitriles

Aliphatic dinitriles, such as adipodinitrile, are prepared from dicarboxylic acids and ammonia (Eq. 6) on a large scale using fluidized and fixed bed processes in the gas phase with heterogeneous catalysts. Selectivity-reducing cyclization to cyclopentanone and cyanocyclopentanone occurs in this reaction using conventional catalysts (ref. 78, 79).



This type of side reaction can be drastically reduced if the boron-zeolite is used which is charged with 5.6 wt.-% Na and 7.6 wt.-% P, as the comparison with conventional catalysts based on SiO₂ shows (Table 3). The transition state selectivity of the zeolite catalyst, which does not allow cyclization, is clearly responsible for this. This example also shows the interrelationship between dehydration property and shape selectivity of the pentasil zeolites.

TABLE 3. Adipodinitrile out of adipic acid^a

Catalyst	Na/P-B-zeolite ^b	Na/P-SiO ₂
Adipodinitrile	94.0 % (mol/mol)	83.4 % (mol/mol)
Cyanovaleric acid	0.7 % "	3.0 % "
Cyanovaleramide	2.8 % "	0.6 % "
useful products	97.5 % "	87.0 % "
Cyanocyclopentanoneimine	0.5 % "	2.4 % "
Cyclopentanone	0.9 % "	4.3 % "

^a Fluidized bed reactor, 400 °C, 200 g adipic acid / 500 g catalyst, 400 l (S.T.P.)/g NH₃.

^b SiO₂/B₂O₃ = 47, prepared in 1,6-diaminohexane (ref. 47); 0.06 - 0.3 mm.

CONCLUSIONS

These selected examples are intended to illustrate the opportunities given by shape-selective, acidic pentasil zeolites:

1. Numerous scientifically interesting organic reactions which, until now, have not been successful industrially because the catalysts employed have not been sufficiently active, selective and/or stable can now be successfully introduced commercially.
2. If environmental or technical problems occur during the separation, work-up or recycling of homogeneous catalysts, the change of homogeneous to heterogeneous catalysis is desirable.
3. Existing processes can be improved by simple replacement of the conventional heterogeneous catalyst.

The pentasil zeolites, therefore, make a significant contribution to the reduction of raw material and energy costs and to environmental protection. Zeolite chemistry for selective organic synthesis of intermediates and of compounds with functional groups is just beginning. New horizons are appearing.

Acknowledgement

The presented results were obtained in co-operation with BASF colleagues. The author thank them for the team-work. He feels specially indebted to Dr. F. Merger, Dr. R. Fischer and Dr. H. Lendle.

Patent rights have been applied for in respect of the results disclosed in this paper.

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