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CATALYSIS

Catalytic Reactions Involving Sterically Separated Active Sites

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Abstract—The possibility of using mixtures of commercial catalysts bearing acid–base or redox sites for controlling the activity and selectivity of conversion of methanol into dimethyl ether, of these substances into desired hydrocarbons, and of low-temperature dehydroalkylation of benzene with propane was demonstrated.

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The development of processes for producing a source of hydrocarbons and motor fuels alternative to crude oil and based on natural gas (via syngas and methanol) and involvement of casinghead gas components (propane, butane) into such processes is a topical scientific and technical problem. The flowsheet of methanol conversion into fuels (MtSynfuels) includes steps of methanol conversion into dimethyl ether (MtDME) and olefin (MtO), and also of conversion of low-molecularmass olefins into motor fuels [1]. It is known that the MtSynfuels steps are accompanied by reactions of the intermediates and products formed both with the reactant and with each other. The drawback of the MtSynfuels implementation in which MtO in combined with the subsequent conversion of olefins into distillate (COD) is the presence of excess amounts of restricted aromatic hydrocarbons in the resulting fuel [1]. Low conversion of syngas into methanol in one pass over the catalyst also restricts the development of MtSynfuels. This drawback is eliminated by combining the methanol formation with its irreversible conversion into dimethyl ether (DME) in one reactor by contacting the syngas with appropriate mechanical mixtures of catalysts or with a polyfunctional catalyst exhibiting the required properties.

On the other hand, such passing from methanol to DME gives rise to the problem of passing from MtO to DMEtO and from MtSynfuels to DMEtSynfuels, and also of controlling the M/DME ratio, because methanol is also demanded as raw material for many other processes.

In cases when the product of one catalytic process (primary product) is the raw material for another process (final product), it becomes necessary to combine these reactions in a common reaction space. This result can be reached by using either mechanical mixtures of catalysts or polyfunctional catalysts combining the required catalytic properties. In contrast to polyfunctional catalysts, localization of active sites of different nature on separate components of a mechanical mixture of catalysts, conventionally termed spatially separated sites, can allow considerably simpler solution of the problem by choosing appropriate commercially available catalysts.

Mechanical mixtures of catalysts are considered by researchers, but mainly for comparison with polyfunctional catalysts [2–6]. The possibility of controlling the formation of final products or their distribution by replacing components of the mechanical mixture was not given due attention.

Here we consider the possibility of using mechanical mixtures of catalysts for controlled conversion of methanol and low-molecular-mass alkanes.

EXPERIMENTAL

Experiments were performed with mechanical catalyst mixtures (CMs) consisting of H forms of zeolites Y and TsVK (structural analog of ZSM-5) and of a metal oxide component. As metal oxide components we used



Fig. 1. Influence of the space velocity SV on the methanol converson on the P_2O_5/HY catalyst at (1) 260 and (2) 300°C. (*C*) Conversion.

aluminum-platinum-rhenium (APRC) and zirconiummagnesium catalysts prepared by the procedures described in [6, 7], respectively.

The Pt,ReO_x/Al₂O₃ catalyst was prepared by the adsorption procedure (a) [4]. Onto spherical γ -Al₂O₃ preliminarily calcined at 750°C, H₂PtCl₆ and NH₄ReO₇ were deposited from aqueous solutions by method (a). The samples were filtered, dried at 80 and 120°C, and then calcined at 750°C for 3 h. The amount of the deposited substances was determined from the difference between their concentrations in the initial and final solutions. The platinum and rhenium content of the ready catalyst was 0.3 and 0.5 wt %, respectively.

The Mg–Zr catalyst based on TsVK zeolite was prepared by successive impregnation with solutions of Zr and Mg nitrates, followed by evaporation, mixing with aluminum oxide, forming, and heat treatment at 120, 350, and 550°C for 4 h at each temperature. Catalyst composition, %: 2.5 Zr, 2.5 Mg/HTsVK, 25 Al₂O₃.

The H forms of the zeolites were prepared from the Na form of the commercial catalysts. The H forms of zeolites Y and TsVK (produced by the All-Russia Research Institute of Petroleum Processing) were prepared via ion exchange by threefold treatment of the initial zeolites with a 2 M NH₄Cl solution at 80°C, followed by washing to remove Cl⁻ ions and calcination at 350–450°C (4 h). The zeolites were formed with a binder, alumina gel (25 wt % Al₂O₃).

Some of the zeolite catalysts obtained were impregnated with an H_3PO_4 solution of preset concentration, which was followed by the above-described heat treatments. The phosphorus content of the samples was 5 wt % counting on P_2O_5 .

The starting reactants (methanol, *n*-butane, propane, benzene) were >99% pure.

The catalytic properties of CMs were studied in a flow-through reactor at 150-450 °C, atmospheric pressure, and feed space velocity of 1-10 h⁻¹ for liquid and 350-500 h⁻¹ for gas.

When performing experiments with a C_6H_6 : $C_3H_8 = 1$: 9 mixture, we used two methods of feeding the reactants: by bubbling and by feeding benzene in calculated amounts with a dosing pump into a vaporizer-mixer arranged before the reactor. Prior to experiments, the catalyst was treated with air at 400°C (1 h).

The reaction products were analyzed by chromatography. The yield of the reaction products was calculated in percents relative to the total amount of carbon atoms participating in the process.

RESULTS AND DISCUSSION

Dehydrative dimerization of methanol. The possible use of DME as environmentally clean energy source suggests sharp increase in the volume of its production. Combining the production of methanol with its dehydration into DME allows the syngas conversion in one pass over the catalyst to be increased from 15 (CH₃OH production) to almost 90% [8]. A mechanical mixture consisting of catalysts for methanol production from syngas and for its dehydration into DME is used for this purpose [9, 10]. Taking into account the acid nature of the catalysts for dehydration of alcohols into ethers, we used for methanol dehydration HY and HTsVK zeolitecontaining catalysts.

As seen from Table 1, the methanol conversion of HTsVK is accompanied by the formation of mainly hydrocarbon products, but the catalyst is unstable, and at 360°C in 30 min its activity decreases from 75.6 to 8%. The results of using the catalyst prepared from wide-pore zeolite Y also appeared to be unsatisfactory.

Despite the stability, the selectivity of this catalyst with respect to both DME and hydrocarbons appeared to be low. The positive results in methanol conversion are obtained with zeolite catalysts impregnated with phosphoric acid. As seen from Table 1, the HTsVK catalyst in this case becomes stable with respect to conversion of methanol into hydrocarbons, and it is possible to develop on the basis of zeolite Y a catalyst exhibiting high activity and selectivity in methanol dehydration into DME. As seen from Fig. 1, the Y-containing catalyst preserves its activity

Tima min	Reaction mixture composition, % C								
	CH ₄	$\sum C_{2^{+=}}$	$\sum C_{2^+}$	DME	CH ₃ OH				
	$HY + Al_2O_3$								
15	1.7	14.8	5.7	56.5	21.3				
120	1.6	16.5	4.5	55.8	21.6				
	$HTsVK + Al_2O_3$								
15	2.4	60.85	21.84	10.6	24.4				
120	_	-	_	7.4	92.0				
	5% P ₂ O ₅ /HY+Al ₂ O ₃								
120	2.6	0.25	0.23	95.7	1.25				
	5% P_2O_5 / HTsVK + Al_2O_3								
15	2.8	60.75	18.1	10.6	7.8				
120	2.5	60.8	21.6	10.8	4.3				

Table 1. Methanol conversion on zeolite-containing catalysts modified with H_3PO_4 ($T = 300^{\circ}C$, $SV = 4 h^{-1}$)

even at a space velocity (SV) exceeding 10 h⁻¹, i.e., it exhibits high productivity, which is very important not only for directly converting syngas into DME, but also for the controlling M/DME by simply varying the amount of the dehydrating catalyst loaded.

Our data show that not all the acid catalysts, even belonging to the same group (aluminosilicates), can be effective when synthesis of methanol and its dehydration into DME are combined in a common reaction space. It should also be noted that the use of catalysts based on structural analogs of ZSM-5 as the second component of mechanical mixture of catalysts, i.e., combination of the methanol production from syngas and its conversion into hydrocarbons, leads to deactivation of the first catalyst. Hence, the catalysts for the synthesis of the primary product in the mechanical mixture of the catalysts should not be susceptible to the negative action of final products, and the conversion of the primary product into the final product should be shifted toward the latter, as this takes place in the conversion of syngas into DME. Therefore, for efficient choice of components of the mechanical catalyst mixture for the subsequent step MtSynfuels or DMEtSynfuels, it is necessary to understand the factors governing formation of the primary product.

It follows from comparison of our results with published data [9, 10] that selective dehydration of methanol occurs on mesoporous aluminum oxide (specific surface area 220 m² g⁻¹, mean mesopore diameter 3–5 nm [10]) or wide-pore Y-type zeolites (micropore diameter 0.72 nm), whereas hydrocarbons are formed on ZSM-5 (0.55 nm) and narrower-pore zeolites of type SAPO-34 (0.39 nm) [11]. Hence, the yield of methanol conversion products depends not only on the acid properties of the catalyst, but also on its texture parameters.

Dehydrative dimerization of alcohol on Brønsted acid sites can be described by Scheme 1.

Scheme 1.



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Scheme 3.

$$\mathbf{I} + \mathbf{II} \longrightarrow \begin{bmatrix} \mathbf{CH}_{3} \\ \mathbf{O} & \cdots & \mathbf{CH}_{2} - \mathbf{OCH}_{3} \\ \mathbf{H} & \mathbf{H} \\ \mathbf{O} & \cdots & \mathbf{O} \\ \mathbf{Z}_{1} & \mathbf{Z}_{2} & \mathbf{Z}_{3} \end{bmatrix} \xrightarrow{-\mathbf{H}_{2}\mathbf{O}} \begin{bmatrix} \mathbf{CH}_{3} \\ \mathbf{O} - \mathbf{CH}_{2} \\ \mathbf{H} & \mathbf{CH}_{2} \\ \mathbf{O} - \cdots & \mathbf{H} \\ \mathbf{Z}_{3} \\ \mathbf{Z}_{1} \mathbf{Z}_{3} \mathbf{O} \end{bmatrix}$$
$$\longrightarrow \mathbf{CH}_{2} = \mathbf{CH}_{2} \mathbf{Z}_{1} \mathbf{Z}_{2} \mathbf{O} + \mathbf{Z}_{3} \mathbf{OH} \cdot \mathbf{HOCH}_{3}.$$

The cyclic intermediate formed in the process decomposes without formation of C–C bonds into DME and water molecules. In the systems containing wide-pore Y-type zeolite, the DME molecules formed are removed relatively readily, despite possible adsorption of DME molecules on base sites denoted in Scheme 2 as Z₂OZ₃:

However, mutual approach of such sites with Brønsted acid sites Z_1OH increases the probability of the

bond redistribution with the formation of a new cyclic state corresponding to participation of three methanol molecules in the process [12] or of a cyclic intermediate structurally corresponding to methoxyethane [13, 14]. Decomposition of this intermediate leads to the formation of the C–C bond of the primary hydrocarbon, ethylene:

In contrast to dehydrative dimerization of methanol, primary ethylene is formed from methanol molecules

Table 2. Distribution of conversion products of methanol and DME on 5% HTsVK and 5% $P_2O_5/HTsVK + 5\% P_2O_5/HY (1 : 1)$ (*T* = 375°C, SV = 350 h⁻¹, reactant : N₂ = 1 : 1 by volume)

	Content						
Products	CH ₃ OH	(CH ₃) ₂ O	CH ₃ OH	(CH ₃) ₂ O			
	5% P ₂ O ₅ ,	/HTsVK	5% P ₂ O ₅ /HTsVI	X + 5% P ₂ O ₅ /HY			
Methane	0.5	Traces	_	Traces			
Ethylene	14	11	24	12			
Ethane	2	0.5	1.0	0.5			
Propylene	34	21	40.2	23			
Propane	1.0	1.2	1.5	1.2			
DME	3.5	_	-	_			
$\sum C_{4=}$	13	9	14.2	8.5			
$\sum C_4$	4	18.2	9.6	16.5			
$\sum C_{5^+}$	10	19.0	7.0	18.5			
Benzene	0.8	0.8	Traces	1.0			
AHs	17.2	19.3	2.5	18.8			
	1						

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with the participation of two sites. The ethylene formation depends on the size parameters of the zeolite and can be classed with structurally sensitive reactions. It should be noted that, with a further decrease in the distance between the acid and base sites, i.e., in going from ZSM-5 to SAPO-17, SAPO-34, despite steric hindrance, Scheme 3 does not change essentially, and one hydroxy group of methanol molecule in ethylene production from DME is replaced by the hydroxy group of the water molecule.

Conversion of methanol and DME into hydrocarbons. The contact of DME and methanol with HTsVK catalyst modified with orthophosphoric acid leads, under equal other conditions, to different distribution of hydrocarbon products (Table 2).

Comparison of the products of DME conversion with those of methanol conversion on 5% P_2O_5 /HTsVK shows that, in the first case, hydrocarbons of higher molecular mass, ΣC_{5+} , and aromatic hydrocarbons (AHs), except benzene, are formed, i.e., in this case primary hydrocarbon intermediates undergo deeper oligomerization.

The products of methanol and DME conversion on P₂O₅/HTsVK differ essentially from those formed on contact of methanol and DME with a mechanical mixture consisting of phosphated HTsVK and HY. As follows from Table 2, in the presence of P_2O_5/HY the main products of methanol conversion are C2-C4 olefins whose yield reaches almost 80%. However, the DME transformations are not appreciably influenced by the presence of P₂O₅ in HY. The above-noted difference in the products of transformation of these substances may be due to different content of water vapor in the reaction medium in conversion of methanol and DME. Indeed, as seen from Fig. 2, introduction of an additional portion of water corresponding to the water amount released in methanol conversion makes the composition of DME and methanol conversion products closer.

The DME conversion on the mechanical mixture of phosphated zeolites under equal other conditions yields considerably lower amount of hydrocarbons containing more than four carbon atoms and especially of aromatic hydrocarbons. These data also show that, under the action of water and second zeolitic component, the conversion of both methanol and DME can be shifted toward MtO and DMEtO.

The observed distribution of methanol and DME conversion products (simultaneous occurrence of the oligomerization, disproportionation, alkylation, isomerization, etc.) is controlled by the reaction



Fig. 2. Effect of water vapor on the distribution of DME conversion products on (*1*, *2*) 5% $P_2O_5/HTsVK$ and (*3*) 5% $P_2O_5/HTsVK$ at T = 450°C, SV = 1 h⁻¹. (*Y*) Product yield. (a) C_2H_4 , (b) C_3H_6 , (c) ΣC_4H_{10} , (d) ΣC_{5+} , and (e) AHs.

conditions and catalysts, i.e., is kinetically controlled. The use of a mixture of acid catalysts leads to the predominant occurrence of MtO/DMEtO. However, owing to the presence of reactive intermediates formed in transformations of methanol into DME and primary ethylene, more efficient activation of low-molecular-mass hydrocarbons, e.g., propane and butane, is also possible. The conversion of methanol-butane mixtures on a mechanical mixture of catalysts with ZSM-5 zeolite as one of the components [4, 5] is a model for such transformations.

Preliminary experiments showed that individual *n*-butane underwent no transformations on $P_2O_5/HTsVK$ at temperatures of up to 400°C. In the temperature interval 400–450°C, the individual n-butane transforms into aromatic and C_1-C_4 hydrocarbons. The *n*- C_4H_{10} conversion does not exceed 10% in this case.

The catalyst Mg,ZrO₂/Al₂O₃ also exhibited low activity in conversion of individual *n*-butane in the temperature interval 350–450°C. The conversion of individual butane reaches 7%, with the product distribution varying from C_1 – C_5 to predominant formation of aromatic hydrocarbons.

Methanol on this catalyst in the same temperature interval without *n*-butane is converted to DME with up to 25-40% degree of conversion.

The results of conversion of the $CH_3OH : n-C_4H_{10} =$ 1 : 2 mixture on the mechanical catalyst mixture $P_2O_5/HTsVK + Mg,ZrO_2/Al_2O_3$ (1 : 1 by weight) are shown in Fig. 3. As can be seen, the conversion of the

T, °C	Conversion, %		Product yield, % C						
	C ₆ H ₆	C_3H_8	IPB	C_3H_6	<i>n</i> -PB	AHs	C ₁ -C ₂		
180	1	_	_	0	0	0	0		
200	5	_	0.3	0	0	0	0		
250	12	1.9	3.6	0.5	0.2	0	0		
300	34.2	6.3	9.0	2.2	0.4	Traces	0		
320	62.1	12.6	12.5	5.0	1.4	4.7	0		
350	41.3	17.2	6.4	11.2	0.7	5.2	0		
375	16.1	19.3	0.3	15.5	0.3	4.2	0		
400	7.9	7.9	0.1	6.3	Traces	2.3	Traces		
450	10.5	7.1	Traces	2.0	0	3.1	2.5		

Table 3. Influence of temperature on the conversion of the C_6H_6 : $C_3H_8 = 1$: 9 mixture (APRC + HY, SV = 500 h⁻¹)

methanol-butane mixture on the mechanical mixture of these catalysts is characterized by a synergistic effect. The *n*-butane conversion in the temperature interval $350-450^{\circ}$ C increases from 23 to almost 100%, and the distribution of the transformation products depending on the reaction conditions can be directed both toward selective formation of low-molecular-mass olefins and toward formation of aromatic compounds, including high-octane gasoline components. Considering this model reaction as an intermediate step in MtSynfuels (dehydration of intermediates with methanol and their



Fig. 3. Influence of temperature *T* on the yield *Y* of conversion products of CH₃OH : $C_4H_{10} = 1 : 1 \pmod{10}$ mixture on Zr,Mg/Al₂O₃ + HZSM-5 catalyst at SV = 500 h⁻¹. (*1*) Conversion, (*2*) C₁–C₃, (*3*) C₂–C₄, (*4*) C₅₊, (*5*) C₆H₆, and (*6*) AHs.

isomerization; etc.), we can note that the selective formation of the desired hydrocarbon products depends on the components of the mechanical mixture of the catalysts. Therefore, formulation of mechanical mixtures using catalysts with known properties can considerably facilitate solution of the problem.

The results of these studies concern problems related to the development of alternative hydrocarbon fuels, MtSynfuels/DMEtSynfuels [1]. Analysis of the results obtained and of published data suggests that it is appropriate to perform such process in steps: to implement MtO/DMEtO in the first step and then to subject the dried products to selective conversion into the distillate using mechanical mixtures of commercially available oligomerization and isomerization catalysts. Reactions in which the activation of hydrocarbons occurs via intermediate states are possible in such cases. The reaction of benzene with propane is among such reactions.

Low-temperature dehydroalkylation of benzene with propane and dehydrogenation of propane. The reaction of propane with benzene occurs on a mechanical catalyst mixture (MCM) whose components are unreduced APRC (analog of catalyst for reforming of straight-run naphthas) and the H form of the zeolite. These catalysts bear spatially separated redox and acid-base sites.

Studies of both individual and joint transformations of benzene and propane at temperatures of up to 450°C on the H forms of zeolites Y and TsVK show that these zeolites do not activate any transformations of

Zeolite	Conversion, %		Product yield, %		Conversion, %		Product yield, %			
	C_6H_6	C_3H_8	IPB	C_3H_8	AHs	C_6H_6	C_3H_6	IPB	C ₃ H ₆	AHs
	320°C				375°C					
Y	62.1	12.6	12.5	5.0	6.1	0.3	15.5	0.3	15.5	4.5
TsVK	43.7	16.0	8.6	8.4	4.5	1.5	22.5	1.5	22.5	4.7

Table 4. Effect of zeolitic component on the conversion of C_6H_6 and C_3H_8 and yield of conversion products of the C_6H_6 : $C_3H_8 = 1 : 9$ mixture on APRC + zeolite, SV = 500 h⁻¹

the reactants. The conversion of propane on APRC and mechanical mixtures of APRC with one of the H forms of the zeolites occurs similarly, and at $300-400^{\circ}$ C small amounts of C₂H₄ and C₄H₈ (propylene metathesis products) and also of hydrogen are formed, suggesting the propane dehydrogenation.

Addition of small amounts (e.g., 10 mol %) of benzene to propane leads to the propane activation and formation of hydrogen, whose yield corresponds to the molar conversion of propane. As seen from Table 3, even at temperatures as low as 180-200°C, benzene and propane react on the mechanical mixture of the catalysts to form isopropylbenzene (IPB). The temperature elevation influences the conversion of the reactants ambiguously: Up to 375°C, the propane conversion grows monotonically, and at higher temperatures it decreases; the benzene conversion increases as the temperature is increased to 320°C, decreases in the interval 320-400°C, and then increases again, but in this case methane and ethane appear in the reaction products instead of hydrogen. Such transformations of C₆H₆ : C₃H₈ are similar to those described in [3, 4]; therefore, hereinafter we will consider only the transformations of this mixture at temperatures lower than 400°C.

Depending on temperature, the distribution of C_6H_6 : C_3H_8 transformation products is characterized by changes in the yields of IPB, *n*-propylbenzene (*n*-PB), sum of other aromatic hydrocarbons, and propylene. The yield of IPB and AHs correlates with the temperature dependence of the benzene conversion, and the propylene yield sharply increases in the interval 320–375°C, when the benzene conversion decreases.

The start and progress of the reaction are preceded by the period in which the catalyst reaches the operation activity level (Fig. 4). Individual treatment of the zeolite components of MCM with ammonia leads to inhibition of the C_6H_6 : C_3H_8 mixture conversion but does not affect the conversion of propane into C_2H_4 and C_4H_{10} , suggesting that acid-base sites are required for the process to occur. Hence, presumably, activation of the catalytic system is associated with the formation of redox sites on APRC.

The temperature dependence of the IPB and propylene formation (Table 3) in transformations of the C_6H_6 : $C_3H_8 = 1$: 9 mixture on MCM suggests the competition of two processes: formation of products of low-temperature dehydroalkylation of benzene with propane and dealkylation of IPB, i.e., formation of the propane dehydrogenation product. The absence of C_1-C_2 hydrocarbons suggests that the AH formation occurs via IPB isomerization. The hydrogen release in these transformation reflects the whole set of the above reactions and independently characterizes the reactivity of the C_6H_6 : C_3H_8 mixture in contact with MCM.

Figure 5 shows the curves describing the rate of hydrogen evolution in conversion of the benzene–propane mixture on MCM subjected to regeneration treatment with air. These results show that the hydrogen formation is preceded by the period when the catalysts reach the operation activity. In the first minutes of the experiment,



Fig. 4. (1) C_3H_8 conversion K and yield Y of (2) IPB and (3) C_3H_6 as functions of time τ . $T = 225^{\circ}C$, $C_3H_8 : C_3H_6 = 9 : 1$.

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Fig. 5. Rate of hydrogen evolution V as a function of time τ of contact of the C₆H₆ : C₃H₈ = 1 : 9 mixture. T = 250°C, SV = 500 h⁻¹. (1) APRC + HZSM-5 and (2) APRC + HY.

neither products of conversion of the C_6H_6 : C_3H_8 mixture nor hydrogen are formed. However, carbon dioxide and water molecules are formed in this period of contact of C_6H_6 : C_3H_8 with CM. The formation of these molecules sharply decreases by the 5th–7th minute of the experiment and virtually ceases by the 15th–20th minute. These periods of the experiment are characteristic of the onset of hydrogen detection and attainment of the maximal rate of its evolution (Fig. 5).

The activation of the catalyst mixture is associated exclusively with the reaction of propane with APRC, and the formation of carbon dioxide and water is due to partial reduction of the metal component of this catalyst mixture [15].

The results of experiments with other zeolitic components showed that, on replacement of zeolite Y by, e.g., HTsVK the relationships of the conversion of the C_6H_6 : C_3H_8 mixture on MCM in the temperature interval 200-400°C do not change. The benzene and propane conversions and the yields of the transformation products of the C_6H_6 : $C_3H_8 = 1$: 9 mixture in relation to the type of the H-zeolite component of CM at temperatures corresponding to the maximal yields of IPB (320°C) and propylene (375°C) are given in Table 4. As can be seen, the propane conversion increases in going from HY to HTsVK irrespective of the extent to which benzene is involved in the process. The propylene yield varies in the same order. Table 4 shows that formation of the DHA and DH products depends on the kind of the zeolitic component.

Therefore, the use of modified zeolites or other objects containing acid–base sites as support can improve

DHA of benzene or direct the process toward increasing propylene yield.

Returning to the consideration of the role of benzene in the process, we can assume that it acts not only as reactant but also as agent transferring protons from the acid component of the catalytic system to redox sites of APRC. Hence, probably, the occurrence of transformations in such mixtures depends on the time of the existence of the intermediate benzonium ions and thus on the distance between the redox and acid–base sites. Therefore, for the conversion of C_6H_6 : C_3H_8 mixtures, it seems more efficient to use polyfunctional catalysts whose phase composition corresponds to MCM. Nevertheless, our results demonstrate the possibility of improving the fuel composition when performing MtSynfuels/DMESynfuels or producing propylene (MtP process) on spatially separated active sites.

CONCLUSIONS

(1) The use of a mechanical mixture of catalysts bearing spatially separated active sites of different nature allows reactions occurring via not only stable but also unstable intermediates to be combined in a common reaction space.

(2) The possibility of using mechanical catalyst mixtures for increasing the conversion of primary products into desired final products and for controlling the product composition was demonstrated by the example of methanol transformations (MtDME, MtO, MtSynfuels) and of DMEtO and DMEtSynfuels processes.

(3) Implementation of the processes on spatially separated active sites opens prospects for using commercially available catalysts as components of mechanical catalyst mixtures.

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