

Ultrasound Assisted Air Oxidation of Trans-Anethole over V-BEA Zeolite Catalyst

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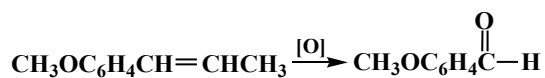
The catalytic oxidation of trans-anethole (1-methoxy-4-[(E)-prop-1-enyl]benzene) with air oxygen in the presence of deeply dealuminated V-SiBEA zeolites ($v_{\text{Si}}/v_{\text{Al}} = 1480$) containing 0.9 and 2.2% V, and by ultrasound assisted (100–300 W, 25 kHz) at temperatures of 353–408 K has been studied. V-SiBEA zeolites were prepared according to the method of Prof. S. Dzwigaj. The thermocatalytic oxidation with oxygen of air leads to non-selective conversion of trans-anethole mainly into products of isomerization – cis-anethole, oxidation to ketone – 1-(4-methoxyphenyl)propan-2-one; and also very small amounts of 1-methoxy-4-propylbenzene, 1-(4-methoxyphenyl)propan-1-one, 4-methoxybenzaldehyde and two unidentified compounds are formed. By catalytic oxidation of trans-anethole with air oxygen on V-SiBEA zeolites in the presence of ultrasound, the trans-anethole is oxidized mainly to the desired 4-methoxybenzaldehyde with a selectivity of 80% at a conversion of 79.2% at 408 K and a small extent to ketones: $\text{C}_{10}\text{H}_{12}\text{O}_2$, 1-(4-methoxyphenyl)propan-2-one and $\text{C}_{10}\text{H}_{10}\text{O}_3$, 1-(4-methoxyphenyl)propane-1,2-dione. The oxidation reaction products were analyzed using GC/MS. © 2025 Bull. Georg. Natl. Acad. Sci.

trans-anethole, oxidation, vanadium-containing BEA zeolite, ultrasound-promoted reaction

Trans-anethole, $\text{C}_{10}\text{H}_{12}\text{O}$, is a terpenoid and belongs to the group of phenyl ethers and is a phenylpropanoid. The chemical activity of trans-anethole molecules is due to the presence of methoxy and prop-1-en-1-yl functional groups in their molecules. Due to the double bond contained in the prop-1-en-1-yl group, two isomers exist: cis (Z) and trans- (E) anethole. Both isomers are present in natural compounds, with the trans-isomer being predominant. Trans-anethole is widely found in plant essential oils – fennel oil (30–90%), anise oil (80–99%), star anise oil (87%), and other herbs [1, 2].

Due to the low content (1–4.5%) of essential oils in essential oil plants, the main industrial method for the preparation of anethole is its chemical synthesis by various methods [1, 3]. Trans-anethole is widely used, including as a raw material for the preparation of 4-methoxybenzaldehyde (i.e. para-anisaldehyde), $\text{C}_8\text{H}_8\text{O}_2$ [1, 3–5]. These methods were based on catalytic oxidation of trans-anethole with different oxidants

(air O₂, O₃, H₂O₂) and irradiations (VIS [6, 7], UV [8, 9], MW [10]), in the presence of different homogeneous or heterogeneous acid catalysts according to the reaction scheme:



4-Methoxybenzaldehyde has a wide range of applications in science and technology. It is used as an intermediate in organic synthesis, in pharmaceuticals to produce bilitrast and betazin, in electroplating to impart luster to products, as a dye to detect UV-inactive substances by thin layer chromatography, as a fragrance ingredient to produce fragrant anisyl acetate, as a flavoring agent in perfume compositions, food essences and in the production of soaps, as a triplet sensitizer to catalyze photochemical intermolecular atom transfer radical addition (ATRA) of haloalkanes to olefins.

In industry, 4-methoxybenzaldehyde is obtained at 50°C by oxidation of essential oils containing trans-anethole, for example star anise oil, in the presence of oxidizing agents: ozone, potassium permanganate, chromium mixture (mixture of Na₂Cr₂O₇ and H₂SO₄), [1, 3-5, 11]. The latter, a strong, cheap, but environmentally harmful oxidizer, is often used, the yield of 4-methoxybenzaldehyde is low – 65% [11].

A convenient and economical method is proposed in [12-14]; in a mixture of trans-anethole and water-ethyl acetate solvent, para-anisaldehyde is directly synthesized by ozonolysis using a one-pot synthesis method with a relatively high yield of 82.7% with a purity of 99.5% at room temperature. “Compared with the traditional ozonolysis process, with the presence of water, ozonolysis of trans-anethole results in the direct formation of anisaldehyde at room temperature and avoids the isolation or decomposition of ozonide” [14].

At the lead dioxide anode, during the electrochemical oxidation of trans-anethole in the form of a suspension in aqueous sodium sulfate solution, mainly para-anisaldehyde and anisic acid are formed with current yields of 52% and 33.9%, respectively, at 20°C [15]; other by-products are also formed. To improve the process, electrochemical oxidation was performed in an aqueous-alcoholic medium. The para-anisaldehyde yield increased to 80%, but the process is inefficient in terms of charge consumption [16].

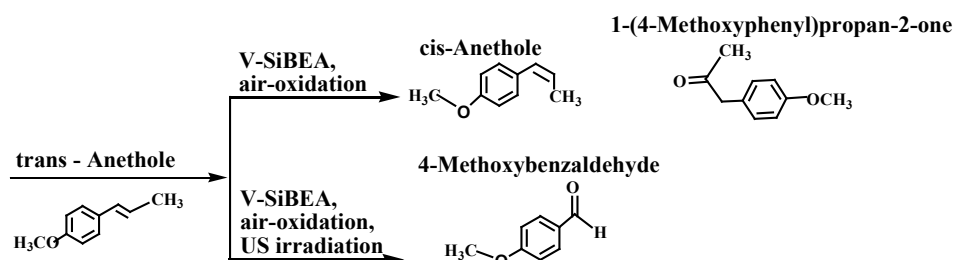
The photochemical oxidation of trans-anethole with hydrogen peroxide [6] and molecular oxygen [7] proceeds non-selectively with the formation of an epoxy derivative and a diol, respectively, besides 4-methylbenzaldehyde.

Hydrogen peroxide is an inexpensive, environmentally safe, and powerful oxidizing agent. It forms peroxo complexes with transition metals that catalyze the oxidation reactions of alcohols to ketones, unsaturated hydrocarbons to epoxides, and aldehydes to acids [17, 18]. In particular, these are peroxovanadium(IV) complexes containing aromatic carboxylate ligands, such as the oxovanadium(IV) phthalate complex [19] and the diperoxyorthovanadate ion VO(O₂)₂[–] formed from FeVO₄ and H₂O₂ using hydrogen peroxide [20-22]. In these homogeneous systems, which are strong oxidizing agents, para-anisaldehyde was synthesized under mild conditions with high selectivity and 100% conversion by oxidation of trans-anethole.

Oxidation of trans-anethole with hydrogen peroxide in a solution of ethyl alcohol under the influence of a catalyst – peracetic acid and microwaves (24-300 Watts) gave a yield of anisaldehyde of 74-94% [10].

On zeolite catalysts, trans-anethole conversion has been little investigated; in [8, 9] it was shown that when trans-anethole is converted on microporous acidic dealuminated zeolite HY at 30-90°C or UV-visible irradiation, parallel reactions of dimerization of trans-anethole and its isomerization to cis-anethole occur.

The present study describes the thermocatalytic oxidation of trans-anethole in the presence of a vanadium-containing BEA-type zeolite and by ultrasound. The choice of vanadium-containing zeolite and ultrasound is due to the large surface area and porosity of zeolites [23, 24], the high reducing potential of vanadium with an oxidation state of +5 [25], and the property of ultrasound in solutions to induce acoustic cavitation – a specific activation in which mechanical activation destroys intermolecular attractive forces in the liquid phase [26]. During the thermocatalytic conversion of trans-anethole, the isomerization reaction to cis-anethole occurs predominantly, and to a lesser extent, oxidation with the formation of aldehydes (including 4-methoxybenzaldehyde) and ketones. Under the combined action of the V-SiBEA catalyst and ultrasound, trans-anethole is mainly converted to the desired 4-methoxybenzaldehyde, Scheme.



Scheme. The main products of the oxidation of trans-Anethole with air on the V-SiBEA zeolite catalyst and using ultrasound irradiation.

Experimental

Chemicals. The following substances were used: trans-Anethole (1-Methoxy-4-[(*E*)-prop-1-enyl]benzene, 99%, Sigma-Aldrich, USA); NH_4VO_3 (99.8%, Carl Roth, Germany); Ethanol (99.9%, HPLC, Carl Roth, Germany), Acetone (HPLC Plus $\geq 99.0\%$, Sigma-Aldrich, USA); HNO_3 (65%, Russia).

Catalyst preparation. The starting material for the preparation of catalysts was synthetic zeolite of BEA type in ammonium form- NH_4BEA ("Zeolyst International", USA, bath CP 814C, $\text{SiO}_2/\text{Al}_2\text{O}_3 = 38$ molar ratio, $\text{Na}_2\text{O} - 0.05\%$, specific surface $710 \text{ m}^2/\text{g}$).

Vanadium-loaded BEA zeolite catalysts V-SiBEA with different vanadium contents were prepared according to the methods of Prof. S. Dzwigaj, which are described in detail in [27-29]. In particular, to prepare acid-dealuminated SiBEA zeolites (with Si/Al molar ratio equal to 1480), 350 ml of 65% HNO_3 solution was added to the starting zeolite NH_4BEA (4 g) and the resulting suspension was boiled for 4 h at 353 K [28]. Vanadium was introduced into SiBEA by its interaction with 25 ml of 1.9×10^{-2} and $7 \times 10^{-2} \text{ M}$ NH_4VO_3 solutions at pH 2.5 of the suspension without stirring for 72 h at 296 K. After centrifugation, the samples were washed with distilled water and dried at 353 K [27, 29-34]. The resulting samples of V-SiBEA (I) and V-SiBEA (II) contained 0.9 and 2.2% vanadium, respectively.

Characterization of the catalysts. The partial chemical composition of the catalysts was determined by X-ray fluorescence analysis (Spectro Scout ED XRF Elemental Analyzers Spectro Ametec, Germany). The crystalline phases of the zeolite catalysts were identified by X-ray powder diffraction analysis (DRON-4 with $\text{Cu-K}\alpha$, $\lambda = 0.15406 \text{ nm}$; 40 kV, 16 mA, in the range $2\theta = 5 - 50^\circ$ at a scan rate of $2^\circ/\text{min}$).

Trans-anethole oxidation reaction procedure. The solvent-free catalytic oxidation reaction of trans-anethole was carried out in a 20 ml three-necked glass flask with a branch pipe for the supply of oxidizing air, a thermometer, a reflux condenser and a magnetic stirrer with temperature control (MSKh-300), at atmospheric pressure and temperatures of 353-408 K. 0.05-0.15 g of catalyst powder, 2-5 ml (0.0134-0.0336 mol) of trans-anethole, then the oxidant – air (0.2 mol/h), purified from CO₂ and wetted were added to the flask; the reaction time was 1.5-2 h. The ultrasound-assisted reactions were carried out in a hybrid reactor (UMR-300B, Japan) under the same conditions under direct sonication using an ultrasonic probe system.

The reaction mixture was irradiated with ultrasound of different power (100-300 W, 25 kHz). Prior to the experiments, the zeolite catalysts were activated in an air stream and then in argon at 400°C for 4 h. The catalyst was separated from the final reaction products by centrifugation. The reaction product contained two immiscible layers – a lower aqueous layer and an upper organic layer. According to their separate analysis, the presence of an insignificant portion of organic substances in the lower aqueous layer was shown; therefore, the organic substances were separated from the final reaction product with acetone and then analyzed using GC/MS.

Reaction products analysis. GC-MS analysis (Agilent Technologies, 5890B/5977A, USA) of the trans-anethole oxidation reaction products was performed in the EI mode, 70 eV, capillary column HP-5ms, Ultra Inert, 30 m × 0.32 mm × 0.25 μm, helium (1.0 mL/min) as carrier gas, acetone as solvent; analyses were performed in program mode: hold at 80°C for 5 min, ramp to 230°C at 30°/min, hold at 230°C for 10 min. The Identification of the compounds was performed by comparing the spectra with the NIST 2014 library. The amounts of trans-Anethole and 4-methoxybenzaldehyde were determined from their calibration curves. The content of the reaction products was compared in terms of GC-MS area%.

Results and Discussion

Powder XRD patterns. Powder X-ray diffraction (XRD) patterns of all the catalysts studied contain characteristic diffraction lines, mainly corresponding to BEA-type zeolites [35], Fig. 1.

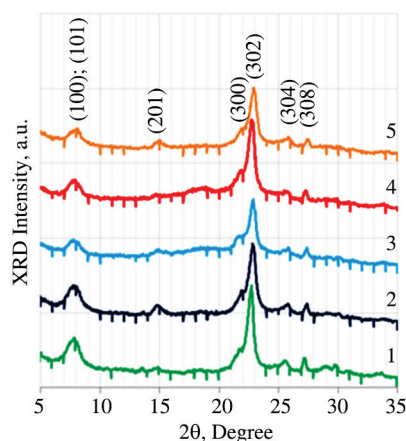


Fig. 1. Powder XRD patterns of the starting zeolites 1 – NH₄BEA, 2 – acid-dealuminated zeolite SiBEA. V-zeolite catalysts: 3 – V-SiBEA (I) and 5-VSiBEA (II); V-zeolite catalyst after catalytic conversion: 4 – V-SiBEA (I).

The distance d_{302} value for the initial NH₄BEA was 3.909 Å, which decreases upon acid dealumination of the NH₄BEA zeolite and is 3.883 Å for SiBEA, Fig. 1; upon contact with a solution of NH₄VO₃ in the formed V-SiBEA (I) and V-SiBEA (II), the d_{302} value increases to 3.892 Å, which indicates the introduction of vanadium into the framework of the BEA zeolite and is in agreement with literature data [29, 30, 32, 36].

It is noteworthy that the diffraction pattern for V-SiBEA (I) and V-SiBEA (II), used in the oxidation reaction at 353-408 K and under its sonication conditions (100-300 W), is identical to that of fresh V-SiBEA (I) and V-SiBEA (II) zeolites, and no destruction of the zeolite crystalline structure is observed, Fig. 1.

Catalytic activity. In the study of oxidation of trans-anethole, the dependence of catalyst activity (trans-anethole conversion (C), selectivity (S), and yield of 4-methoxybenzaldehyde (Y) on its mass (0.05-0.15 g), temperature (353, 383, and 408 K), and ultrasonic power (100, 200, 300 W, 25 kHz) was investigated. Optimal conditions for the oxidation reaction of trans-anethole were selected: 0.12 g catalyst, molar ratio of trans-anethole/air – 1/10, ultrasonic power 200 W. In blank experiments it was shown that when trans-anethole was exposed to temperatures (353-408 K) without the use of a catalyst and ultrasound in an air stream, the thermal conversion of trans-anethole was insignificant – 3-4%. The qualitative composition of the products of the trans-anethole oxidation reaction in the presence of V-SiBEA zeolite catalysts at temperatures of 353-408 K was the same, Fig. 2, Table 1.

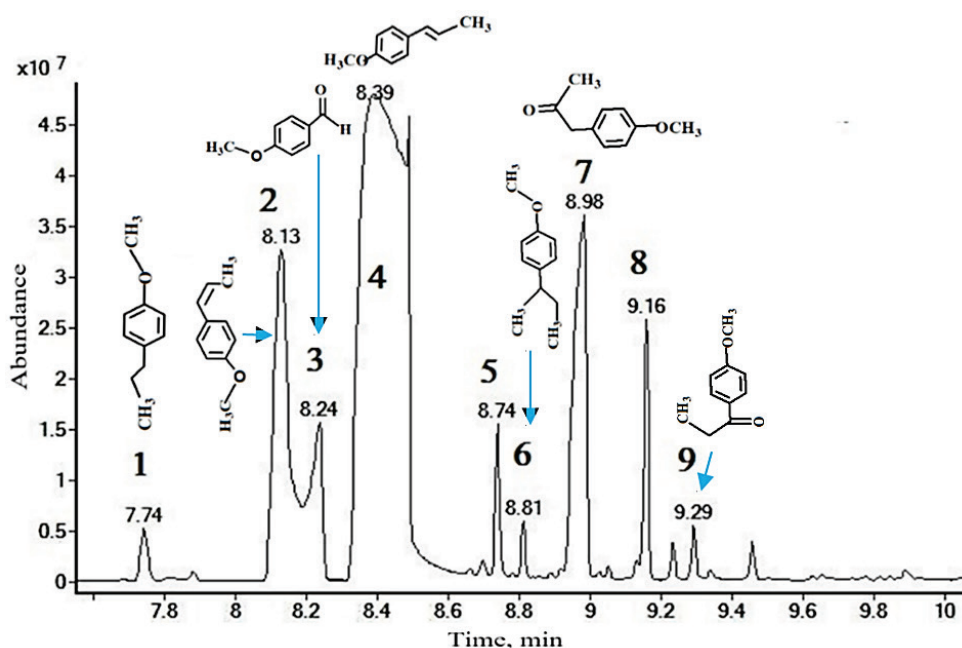


Fig. 2. GC/MS Chromatogram and structures of the starting trans-anethole (0.0134 mole) **4** and products (**1-3**, **5-9**) of its catalytic oxidation in a flow of pure air (molar ratio 1/10) over 0.12 g V-SiBEA (I) at 353 K, run time-2 h. **1** – 1-Methoxy-4-propylbenzene, $C_{10}H_{14}O$, **2** – 1-Methoxy-4-[(Z)-prop-1-enyl]benzene (i.e. cis-Anethole), $C_{10}H_{12}O$, **3** – 4-Methoxybenzaldehyde (i.e. para-Anisaldehyde), $C_8H_8O_2$, **4** – 1-Methoxy-4-[(E)-prop-1-enyl]benzene (i.e. trans-Anethole), $C_{10}H_{12}O$, **5** – not identified, **6** – Benzene,1-methoxy-4-(1-methylpropyl)-, $C_{11}H_{16}O$, **7** – 1-(4-Methoxyphenyl)propan-2-one (i.e.4-Methoxyphenylacetone), $C_{10}H_{12}O_2$, **8** – not identified, **9** – 1-(4-Methoxyphenyl)propan-1-one, $C_{10}H_{12}O_2$.

During thermocatalytic oxidation, non-selective conversion of trans-anethole occurs mainly into products of isomerization (cis-anethole with a yield of 28% at 408 K), oxidation to ketone (1-(4-methoxyphenyl)propan-2-one with a yield of 21% at 408 K); and very small amount of 1-(4-methoxyphenyl)propan-1-one; 4-methoxybenzaldehyde and two unidentified compounds Table 1, Fig. 2.

According to the GC/MS chromatogram, peaks 5 and 6 correspond to $C_{12}H_{16}O$, 2,3,4,5,6-pentamethylbenzaldehyde, Fig. 2; however, the corresponding mass spectra match the NIST 2014 library data with only 47.4% probability. The difference is detected at the following m/z values: (105), (119), (133), (175).

Table 1. Oxidation of trans-anethole with air over V-SiBEA zeolites. Temperatures 353-408 K, mass of catalysts – 0.12 g, trans-anethole – 0.0134 mole, molar ratio trans-anethole/air–1/10, run time – 2 h

Entry	Composition of reaction products	Catalysts		
		V-SiBEA(I) (0.9 %V)	V-SiBEA (II) (2.2%V)	V-SiBEA (II) (2.2%V)
		Reaction temperatures, K		
		353	353	408
		Conversion of trans-anethole, %		
		37.7	55.0	73.8
		Yield of products, % /Selectivity, %		
1	1-Methoxy-4-propylbenzene, C ₁₀ H ₁₄ O	1.0/2.6	1.1/1.9	1.2/1.6
2	1-Methoxy-4-[(Z)-prop-1-enyl]benzene, C ₁₀ H ₁₂ O ₂ , (cis-anethole)	15.7/41.6	21.8/39.0	28.1/38.1
3	4-Methoxybenzaldehyde, C ₈ H ₈ O ₂ , (p-anisaldehyde)	1.5/3.9	2.5/4.5	3/4.0
4	1-Methoxy-4-[(E)-prop-1-enyl]benzene, C ₁₀ H ₁₂ O ₂ , (trans-Anethole)	–	–	–
5	Unidentified	1.9/5.0	3.2/5.8	5.1/6.9
6	Benzene, 1-methoxy-4-(1-methylpropyl)-, C ₁₁ H ₁₆ O	0.7/1.8	2.1/3.8	1.1/1.4
7	1-(4-Methoxyphenyl)propan-2-one, C ₁₀ H ₁₂ O ₂ , (4-Methoxyphenylacetone)	13.0/34.5	18.2/33.1	21.4/29.0
8	Unidentified	3.2/8.5	4.3/7.8	7.6/10.3
9	1-(4-Methoxyphenyl)propan-1-one, C ₁₀ H ₁₂ O ₂	0.7/1.8	1.8/3.2	2.1/2.8

By increasing the vanadium content in the catalyst from 0.9 to 2.2%, the conversion of trans-anethole increases both during the thermocatalytic reaction and when exposed to ultrasound, Table 1 and Table 2, Fig. 2 and Fig. 3. However, the thermocatalytic conversion of trans-anethole is not selective, but mainly proceeds in the direction of isomerization and oxidation reactions with the predominant formation of cis-anethole and 4-methoxyphenylacetone, Table 1; wherein the yields of 4-methoxybenzaldehyde are low – 1.5-3%. In the presence of ultrasound, the yield of the desired 4-methoxybenzaldehyde increases significantly from 27.2 to 63.4% with increasing vanadium content and temperature, Table 2; at the same time, there are rather high values of selectivity to 4-methoxybenzaldehyde – 91.8-80.0%, respectively.

Table 2. Ultrasound-assisted (200 W, 25 kHz) oxidation of trans-anethole over V-SiBEA zeolites. Temperatures – 353 and 408 K, mass of catalysts – 0.12 g, trans-anethole – 0.0134 mole, molar ratio trans-anethole/air–1/10, run time–1.5 h

Entry	Composition of reaction products	Catalysts		
		V-SiBEA(I) (0.9 %V)	V-SiBEA (II) (2.2%V)	V-SiBEA (II) (2,2%V)
		Reaction temperatures, K		
		353	353	408
		Conversion of trans-anethole, %		
		29.6	48.8	79.2
		Yield of products, % /Selectivity, %		
1	1-Methoxy-4-[(Z)-prop-1-enyl]benzene, C ₁₀ H ₁₂ O ₂ , (cis-anethole)	2.0/6.7	3.4/6.9	5.1/6.4
2	4-Methoxybenzaldehyde, C ₈ H ₈ O ₂ , (p-anisaldehyde)	27.2/91.8	43.3 /88.7	63.4/80.0
3	1-Methoxy-4-[(E)-prop-1-enyl]benzene, C ₁₀ H ₁₂ O ₂ , (trans-Anethole)	–	–	–
4	1-(4-Methoxyphenyl)propan-2-one, C ₁₀ H ₁₂ O ₂ . (4-Methoxyphenylacetone)	0.1/0.3	0.9/1.8	4.9/6.1
5	1-(4-Methoxyphenyl)propane-1,2-dione, C ₁₀ H ₁₀ O ₃	0.3/1.0	0.8/1.6	5.8/7.3

Conclusion

The oxidation of trans-anethole with air to 4-methoxybenzaldehyde was studied in the liquid phase over the V-containing (0.9 and 2.2%) deeply dealuminated zeolite catalysts V-SiBEA at 353–408 K. It was shown that the conversion of trans-anethole to the target 4-methoxybenzaldehyde correlates with the content of vanadium redox sites in the catalyst. The highest conversion (79%) and selectivity for 4-methoxybenzaldehyde (80%) were obtained over V-SiBEA (2.2% V) only in the presence of ultrasound (200 W, 25 kHz) at 408 K. Apparently, the ultrasound-assisted oxidation of trans-anethole proceeds by a different mechanism than its thermocatalytic conversion.

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ფიზიკური ქიმია

ტრანსანეთოლის ჰაერით ჟანგვის რეაქციაზე V-BEA ცეოლითური კატალიზატორის და ულტრაბგერის გავლენა

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გამოკვლეული იყო 353–408 K ტემპერატურებზე ტრანსანეთოლის (1-მეთოქსი-4-[(E)-პროპ-1-ენილ]ბენზოლის კატალიზური ჟანგვა ჰაერით 0.9 და 2.2% V-ის შემცველ ღრმად დეალუმინირებული V-SiBEA ცეოლითების ($v_{Si}/v_{Al}=1480$) თანდასწრებით და აგრეთვე ულტრაბგერის (100–300 W, 25 კჰც) დასხივებისას. თერმოკატალიზური ჟანგვის დროს ხდება ტრანსანეთოლის არაშერჩევითი გარდაქმნა, ძირითადად, იზომერიზაციის და ჟანგვის პროდუქტებად – მიიღება ცის-ანეთოლი და 1-(4-მეთოქსიფენილ)პროპან-2-ონი, წარმოიქმნება აგრეთვე ძალიან მცირე რაოდენობით 1-მეთოქსი-4-პროპილბენზოლი, 4-მეთოქსიბრნზალდეჰიდი, 1-(4-მეთოქსიფენილ)პროპან-1-ონი და ორი დაუდგენელი სტრუქტურის ნაერთი. ტრანსანეთოლის ჰაერით კატალიზური ჟანგვისას V-SiBEA ცეოლითებზე ულტრაბგერის თანაობისას ტრანსანეთოლი ძირითადად იჟანგება სამიზნე 4-მეთოქსიბენზალდეჰიდამდე; ამ

დროს მისი შერჩევითობაა 80% 408 K-ზე და ანეთოლის გარდაქმნის ხარისხია 79.2%, მხოლოდ მცირე რაოდენობით (6%-მდე) მიიღება ცის-ანეთოლი და კეტონები: $C_{10}H_{12}O_2$, 1-(4-მეთოქსიფენილ)პროპან-2-ონი და $C_{10}H_{10}O_3$, 1-(4-მეთოქსიფენილ)პროპან-1,2-დიონი. რეაქციის პროდუქტების ანალიზი ჩატარდა GC/MS მეთოდით.

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