OXIDATION OF TOLUENE BY AIR IN THE PRESENCE OF OXYGEN COMPOUNDS ON VANADIUM CATALYSTS*

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Addition of 10 – 30 vol.% of C_1 – C_4 alcohols, acetone, acetic acid or acetic anhydride to toluene increases several times the yield of benzaldehyde. The effect of these compounds over V_2O_5–K_2SO_4 catalysts supported on SiO_2 is positive at molar ratio $K_2SO_4 : V_2O_5 < 0.5$. At the ratio $K_2SO_4 : V_2O_5 \geq 0.5$ the effect is more complex and depends on the conditions used. In the case of V : Ag : K catalyst with the molar ratio 1 : 0.3 : 0.3, added compounds increase the yield of benzaldehyde, except 2-propanol. No effect of these additives was observed over $H_9PV_6Mo_6O_{40}$ catalyst supported on SiO_2.

The vapor phase oxidation of toluene by air has been studied by many researchers[1–3] with the aim to find conditions and catalyst for the selective oxidation to benzaldehyde or benzoic acid. The high oxidation performance of V_2O_5 is exploited in many catalysts, mainly in combination with potassium sulfate[4,5], silver oxide[3,6], molybdenum trioxide[7,8], bismuth trioxide[9], etc. The most active and selective catalyst for benzaldehyde production was reported by Gunduz and Akpolat[2]. Over the V_2O_5 catalyst supported on K_2SO_4–SiO_2 they obtained a 65% yield of benzaldehyde at 95% conversion of toluene.

Vanadium based catalysts contain two types of active centers[10]. It is supposed, that the active site with a V=O bond is responsible for the selective side chain oxidation of alkylaromatics, and the centre with a V–OH bond is responsible mainly for the oxidation of aromatic nucleus and total oxidation of toluene. Vanadium active sites have oxidation state V^{5+} or V^{4+}. Andrejkov et al.[11] reported, that active sites with reduced vanadium are more active and selective then oxidized ones.

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In our work we tried to increase the selectivity of toluene oxidation by changing the concentration and the ratio of these active sites. Easily oxidable organic compounds were added, which can reduce vanadium (e.g. short chain alcohols) or can react with OH groups (e.g. acetic anhydride).

EXPERIMENTAL

Materials

SiO_2 was in the form of a 30% water solution (silica sol). K_2SO_4, NH_4VO_3, $AgNO_3$, NaH_2PO_4, MoO_3, KOH, as well as toluene and other organic compounds were analytical grade.

Catalyst Preparation

Preparation of support. An appropriate amount of KOH was added to the aqueous solution of SiO_2. The solution of potassium silicate formed was adjusted to a pH of 5.5 – 6.0 by the addition of 10% H_2SO_4. The precipitated gel was dried at 110 °C for 24 h and used as a support (specific surface area 175 m^2/g).

Catalyst I *(V_2O_5–K_2SO_4–SiO_2)*. A total of 1.35 g of NH_4VO_3 and appropriate amount of K_2SO_4 were added portionwise to a warm solution of 2.2 g of oxalic acid in 15 cm^3 of water. An amount of 6 g of dry support (particle size 0.3 – 1.0 mm) was added under mixing. After evaporation of water the catalyst was dried at 110 °C and activated at 450 °C in the air flow for 4 h.

Catalysts II *(V_2O_5–Li_2SO_4–SiO_2)* and III *(V_2O_5–Tl_2SO_4–SiO_2)*. Equivalent amount of Li_2SO_4 or Tl_2SO_4, respectively, were used instead of potassium sulfate.

Catalyst IV *(V_2O_5–Ag–K_2SO_4–SiO_2)*. A total of 0.29 g of K_2SO_4 and 0.57 g of $AgNO_3$ were used. The amount of other chemicals and the procedure of preparation were the same.

Catalyst V *($H_9PV_6Mo_6O_{40}$ supported on SiO_2)*. The heteropolyacid (HPA) $H_9PV_6Mo_6O_{40}$ was prepared from 0.202 g of NaH_2PO_4, 1.0 g of V_2O_5 and 1.264 g of MoO_3 by the method described by Polotebnova et al.[12]. An amount of 6 g of dry support (particle size 0.3 – 1.0 mm) was added to the concentrated solution of HPA under mixing. After evaporation of water the catalyst was dried and calcinated as described above.

Oxidation of Toluene

A tubular stainless steel microreactor with i.d. 12 mm (OL 115/10, FOK GYEM, Hungary) was used. Toluene was pumped to the upper part of the reactor (flow rate 3 – 9 cm^3/h), where it was evaporated in an air stream (flow rate 60 – 180 dm^3/h). The outlet gases were cooled in two consecutive coolers, kept at –20 °C and –70 °C, respectively. The catalyst (5 g, particle size 0.3 – 1 mm) was diluted with the pure support (1 : 1) to avoid adverse thermal effects. No reaction of toluene was observed on the pure support at reaction conditions. Axial temperature profiles of the catalyst bed were measured. The difference between the lowest and the highest temperatures in the catalyst bed did not exceed 20 °C. In the Tables average temperatures of the catalyst bed are given.

The amount of toluene and benzaldehyde condensed in the cooler and cold trap was checked by the Quadrex 200 mass spectrometer. About 95% of benzaldehyde and 3 – 25% of toluene condense in a cooler kept at –20 °C at the molar ratio O_2 : toluene = 25 – 50 in the feed. In the consecutive cold trap, kept at –70 °C, condense practically all benzaldehyde and about 98% of toluene.

The liquid products were joined, weighed and then analyzed by gas chromatography using a column packed with 10% of APIEZON L + 1% of H_3PO_4 on CHROMOSORB W 0.125 – 0.16 mm.

For calculation of toluene conversion (X_T) only toluene found in liquid products was taken into account as unconverted one. Selectivity of reaction to benzaldehyde (S_{BzH}) was calculated from its condensed amount and from the converted toluene. Yield of benzaldehyde (Y_{BzH}) was calculated as a product of X_T and S_{BzH}. From the amount of benzaldehyde, produced during given experiment, an average rate of benzaldehyde production (r_{BzH}) was computed as moles of benzaldehyde per mole of V_2O_5 and hour. The values of X_T, S_{BzH}, Y_{BzH} and r_{BzH} determined as mentioned above are given in Tables I – V.

Surface areas of the catalysts were measured by the Pulse Chemisorb 2700 apparatus (Micromeritics).

Determination of the Oxidation State of Vanadium

Both the total concentration and the average oxidation number of vanadium were determined after dissolution of a catalyst sample in the mixture of 25 cm^3 of 4 M H_2SO_4 and 25 cm^3 of 4 M HF by the method described by Niwa and Murakami[13]. The solution was diluted to 100 cm^3 and titrated by 0.02 M $KMnO_4$, and 0.1 M iron(II) ammonium sulfate solution.

TABLE I
Oxidation of toluene to benzaldehyde over V_2O_5–K_2SO_4–SiO_2 catalyst with different molar ratio of potassium to vanadium (K/V) in the surface phase. Toluene feed 10.9 mol/mol h, molar ratio O_2 : toluene = 30 : 1

K/V Molar ratio	Temperature °C	X_T %	S_{BzH} %	Y_{BzH} %	r_{BzH}[a]
0	427	50.9	1.9	1.0	0.125
0[b]	418	60.8	2.3	1.4	0.156
0.228	403	40.0	2.5	1.0	0.091
0.228	413	52.0	2.5	1.3	0.119
0.496	403	37.4	5.6	2.1	0.256
0.496	408	25.9	9.7	2.5	0.304
0.496	410	22.8	12.0	2.7	0.334
0.496	432	40.0	17.3	6.9	0.804
0.672	390	30.3	2.6	0.8	0.103
0.672	400	37.3	2.3	0.8	0.116
0.672	415	38.2	7.1	2.7	0.248
0.672[b]	432	39.9	26.1	10.4	1.024
0.672[b]	438	45.1	20.6	9.3	0.916
1.0	404	30.5	8.3	2.5	0.322
1.0	413	36.3	6.5	2.3	0.282
1.0	423	52.4	3.0	1.6	0.228
1.0	432	50.3	1.9	1.0	0.126
1.0	450	49.3	3.5	1.7	0.139

[a] In $mol_{BzH}/mol_{V_2O_5}$ h; [b] toluene feed 9.1 mol/mol h, molar ratio O_2 : toluene = 50 : 1.

RESULTS AND DISCUSSION

For preliminary experiments the V_2O_5–K_2SO_4–SiO_2 catalyst was used. The catalyst composition and reaction conditions of oxidation were the same as described Gündüz and Akpolat[2], but the yield of benzaldehyde (Y_{BzH}) did not exceed 10%. The catalyst prepared by the method of Gündüz and Akpolat[2] is composed of 10.4% V_2O_5, 34.6% K_2SO_4 and 55.0% SiO_2. However, these are the average values and the real concentration of K_2SO_4 in the active surface phase of the catalyst can be much lower. In order to increase the concentration of K_2SO_4 directly in the surface phase of our catalyst, K_2SO_4 was added not only to the support, but also to the solution of NH_4VO_3, used for the impregnation of the support.

From Table I it follows, that the addition of K_2SO_4 to the surface phase of the catalyst increases the average rate of benzaldehyde production (r_{BzH}) mainly by increasing the selectivity of benzaldehyde formation (S_{BzH}) and not by increasing the conversion of toluene (X_T). At molar ratio of O_2 : toluene = 30 : 1 the highest Y_{BzH} as well as the maximum of S_{BzH} and r_{BzH} were observed at K : V ≈ 0.5 – 0.7 : 1. At higher K/V in the surface phase the selectivity of benzaldehyde formation decreases. This is probably a result of benzaldehyde overoxidation, because at $K/V \geq 1$ increased formation of maleic anhydride and benzoic acid was observed.

In agreement with results of Gündüz and Akpolat[2] Y_{BzH} and S_{BzH} increases with decreasing feed of toluene and increasing molar ratio of O_2 : toluene (Table I).

The X_T value increases with temperature on all the catalysts. However, the produced amount of benzaldehyde has a maximum in the temperature interval 400 – 440 °C, depending on the K/V ratio. Above this maximum an increased formation of benzaldehyde overoxidation products was observed. The temperature of maximal r_{BzH} slightly decreases with the increasing concentration of K_2SO_4 in the surface phase of the catalyst.

An addition of cooxidant e.g. acetone, acetic acid, acetic anhydride, methanol and ethanol mostly decreases X_T and increases S_{BzH} (Tables I – V). To know, whether the influence of cooxidant on production of benzaldehyde is positive or negative, average rates of benzaldehyde production were calculated. The influence of cooxidant on r_{BzH} depends on the composition of the catalyst and reaction conditions. From Tables I and II it follows, that at the ratio of K/V = 0.228 all tested compounds increase several times r_{BzH} and Y_{BzH}. At higher ratio of K/V the increase of r_{BzH} was observed only in the presence of ethanol and acetone. Other alcohols have no effect and acetic acid and acetic anhydride decrease the r_{BzH}. Table II also reveals, that an increase of V_2O_5 in the catalyst decreases r_{BzH} and suppressed the influence of ethanol and acetone mainly at the ratio of K/V > 0.6. The decrease of r_{BzH} confirms, that oxidation of toluene proceeds mainly on the surface of catalyst.

TABLE II
The effect of cooxidant (20 vol.%) on the toluene oxidation over V_2O_5–K_2SO_4–SiO_2 catalyst (10% V_2O_5)

Cooxidant	K/V molar ratio	Temperature °C	F_T[a]	O_2/toluene	X_T %	S_{BzH} %	r_{BzH}[b]
None	0.228	420	9.1	37.5	51.9	2.5	0.119
Acetic acid	0.228	420	14.2	24.0	13.0	63.1	1.160
Acetic anhydride	0.228	420	10.9	31.4	17.0	40.0	0.478
Ethanol	0.228	420	9.1	37.6	37.1	18.0	0.601
	0.228	420	7.6	44.7	36.1	21.5	0.590
Methanol	0.228	410	10.9	31.2	50.3	7.1	0.390
	0.228	420	19.6	17.3	51.1	6.3	0.635
None	0.496	415	20.4	16.7	53.7	3.8	0.417
None	0.496	430	9.1	36.9	37.1	13.6	0.476
Acetic acid	0.496	420	10.9	31.2	35.7	9.1	0.355
Acetic anhydride	0.496	420	18.2	19.0	22.5	6.5	0.265
Ethanol	0.496	420	21.8	16.5	37.8	10.1	0.750
Ethanol[c]	0.496	430	9.1	37.5	22.7	45.1	0.933
Methanol	0.496	420	19.4	17.4	16.3	14.6	0.476
None	0.672	420	11.3	30.1	61.2	4.6	0.319
None	0.672	430	9.8	51.7	45.1	20.6	0.915
Acetone	0.672	420	11.1	46.5	53.1	12.8	0.749
	0.672	425	9.1	56.0	49.2	15.0	0.682
Ethanol	0.672	420	9.6	52.9	23.1	67.6	1.505
1-Propanol	0.672	420	9.4	54.3	45.1	18.3	0.779
	0.672	440	9.6	53.1	61.0	12.5	0.739
2-Propanol	0.672	420	10.2	49.9	32.0	27.4	0.896
	0.672	430	10.2	49.8	36.0	20.1	0.743
1-Butanol	0.672	430	11.1	45.6	56.0	14.6	0.895
None	1.0	420	11.8	28.6	36.3	6.5	0.282
None	1.0	430	13.3	25.7	50.3	1.9	0.127
Ethanol	1.0	420	10.7	48.0	31.0	18.5	0.611
	1.0	430	10.9	31.5	37.1	12.5	0.628
None	0.530[d]	430	8.5	23.7	39.0	5.7	0.125
Acetone	0.530[d]	430	8.0	23.0	10.5	60.4	0.253
None	0.762[d]	430	8.2	25.0	29.7	10.3	0.161
Ethanol	0.762[d]	430	8.2	25.0	13.5	27.4	0.155
None	0.512[e]	430	8.5	24.0	16.2		

The influence of ethanol on toluene oxidation over the catalyst *II* (Li/V = 0.584) and catalyst *III* (Tl/V = 0.584) is similar as mentioned for the catalyst *I* (Table III). An addition of ethanol increases the r_{BzH} over both catalysts.

At temperatures below 400 °C the highest catalytic activity and S_{BzH} were observed over catalyst *III*. Over this catalyst slight production of benzaldehyde starts at 320 °C. The observed Y_{BzH} was 0.5%. The same Y_{BzH} on other catalysts was observed only at temperatures around 390 °C. However, above 400 °C catalyst *III* quickly deactivates. Deactivation is probably caused by the formation of $Tl_3V_5O_{14}$ compound in the surface phase of the catalyst[14] with the melting point of 400 °C. Melting of the surface compounds decreases the specific surface of the catalyst, what leads to the decrease of the r_{BzH}.

Over the catalyst *III*, ethanol not only increases the r_{BzH}, but also decreases the rate of catalyst deactivation. Therefore at temperatures above 400 °C the differences between r_{BzH} in the presence and absence of ethanol are very high. It should be mentioned, that the rates observed in the presence of ethanol do not exceed rates, observed over the other catalysts under comparable conditions.

Over the catalyst *IV* (Ag : K : V = 0.3 : 0.3 : 1) every cooxidant, except 2-propanol, increases r_{BzH} (Table IV). The highest rates were observed in the presence of acetic acid and methanol. At temperatures up to 440 °C the catalyst *IV* does not deactivate, but over 430 °C the r_{BzH} decreases as a result of its overoxidation.

TABLE III
The effect of cooxidant (20 vol.%) on the toluene oxidation over catalysts: V_2O_5–Me_2SO_4–SiO_2, metal/V = 0.584, where metal is Li or Tl

Cooxidant	Metal	Temperature °C	$F_T{}^a$	O_2/toluene	X_T %	S_{BzH} %	$r_{BzH}{}^a$
None	Li	420	13.8	24.7	46.1	2.1	0.135
		440	13.6	24.8	52.8	1.8	0.353
Ethanol	Li	420	10.9	31.2	26.9	15.0	0.440
		440	9.8	34.7	31.2	21.0	0.643
None	Tl	370	26.0	19.7	30.1	10.1	0.078
		390	12.5	27.2	50.3	2.8	0.175
		410	12.2	27.7	52.4	0.8	0.048
		420	12.7	40.3	66.0	0.1	0.010
Ethanol	Tl	370	25.8	19.8	14.2	13.3	0.490
		390	12.3	27.8	19.0	20.0	0.470
		410	12.2	27.7	26.9	15.6	0.511

Over the catalyst *V* the rate of toluene oxidation is comparable to the rates over other catalysts and the presence of ethanol does not increase significantly the r_{BzH} (Table V).

Under reaction conditions all additives are oxidized to carbon oxides and water over the catalysts tested. The presence of additives can change the average oxidation number of vanadium at the catalyst surface, i.e. it can increase the concentration of reduced active sites of the catalyst[11]. The determination of the oxidation number of vanadium at reaction conditions is difficult. When a catalyst is cooled down in the presence of an inert gas, vanadium is reduced by adsorbed compounds. Nobbenhuis et al.[15] suggest the catalyst cooling down in the flow of the reaction mixture. The rates of reduction and

TABLE IV
The effect of cooxidants (20 vol.%) on the toluene oxidation over catalyst V_2O_5–Ag–K_2SO_4–SiO_2, Ag : K : V = 0.3 : 0.3 : 1

Cooxidant	Temperature °C	F_T [a]	O_2/toluene	X_T %	S_{BzH} %	r_{BzH} [a]
None	420	9.4	30.5	37.4	5.9	0.209
	430	9.6	29.6	43.0	9.5	0.395
	440	9.4	30.7	48.6	6.6	0.303
Acetic acid	415	11.4	29.6	13.5	56.0	0.870
	420	9.8	34.2	27.4	39.0	1.089
	430	11.4	29.6	15.3	62.3	1.097
Methanol	420	9.3	37.0	9.8	76.2	0.688
	430	9.1	37.6	13.3	93.3	1.120
Ethanol	420	11.3	30.0	25.5	20.6	0.595
	430	9.4	35.9	37.1	24.5	0.863
	440	8.5	40.0	36.1	23.3	0.713
1-Propanol	415	8.5	40.1	31.8	13.1	0.353
	420	9.6	35.3	32.5	16.5	0.517
	440	10.2	33.7	45.5	17.5	0.809
2-Propanol	420	9.1	37.6	26.3	14.1	0.334
	430	9.6	35.5	21.3	16.3	0.334
1-Butanol	420	10.4	33.1	33.2	21.4	0.732
	430	10.2	33.1	43.9	21.4	0.967
	440	8.9	38.2	33.0	21.1	0.622
	430	9.4	35.5	30.1	23.7	0.683

[a] See Table II (footnotes [a] and [b]).

oxidation of vanadium change with decreasing temperature in different way. In air it is oxidized and in the presence of a reaction mixture the oxidation number depends on the reduction properties of organic compounds used.

In our experiments the catalyst was cooled down in air and in the flow of the reaction mixture. The average oxidation number of vanadium was in the range of 4.6 – 4.9. For example the catalyst V_2O_5–K_2SO_4–SiO_2 with K/V = 0.496, after 8 h oxidation of toluene in the presence of ethanol, was cooled down in the flow of the reaction mixture. The average oxidation number of the cooled catalyst was 4.66. When the same catalyst was after 8 h oxidation of pure toluene cooled down in the flow of the reaction mixture, the average oxidation number of the catalyst was 4.80. It should be mentioned, that a significant reduction of vanadium by toluene begins around 400 °C and by ethanol below[16] 300 °C. Therefore it is questionable whether the value of the vanadium oxidation number under real oxidation conditions is the same as determined after catalyst cooling down. From the measured data it was impossible to find out dependence between the oxidation number of vanadium, amount of the reduced active sites of the catalyst and the type of the cooxidant used.

The tested catalysts were examined by temperature programmed reduction (TPR) in the flow of hydrogen in temperature range of 20 – 610 °C. A good agreement was found between the temperature determining the start of the catalyst reduction by hydrogen and the lowest temperature of the catalyst at which the oxidation of toluene proceeds. The temperature of the both processes is around 400 °C. However, it was not possible to find out a correlation between the shape of the TPR curve of the tested catalyst and the properties of oxidized organic compound.

TABLE V
The effect of cooxidant (20 vol.%) on the toluene oxidation over catalyst $H_9PV_6Mo_6O_{40}$ supported on SiO_2

Cooxidant	Temperature °C	F_T[a]	O_2/toluene	X_T %	S_{BzH} %	r_{BzH}[a]
None	420	12.7	26.8	46.9	4.7	0.279
	430	18.7	18.1	36.9	13.5	0.945
	430	23.6	14.9	37.2	6.1	0.540
	440	13.8	24.5	60.6	3.1	0.260
Ethanol	420	10.5	32.5	13.2	27.1	0.334
	430	22.7	15.2	30.8	8.1	0.554
	440	10.2	33.3	16.6	18.0	0.305

[a] See Table II (footnotes [a] and [b]).

The used cooxidants can be adsorbed on the surface of catalyst and form surface compounds[17] as V–O–R or V–O–CO–R. The formation of these compounds is an intermediate step in the oxidation of alcohols and other compounds with alkyl chains. Toluene is adsorbed during its oxidation via CH_3 group only on one active site[18]. For the oxidation of the aromatic ring, molecule of toluene needs adsorption on several active sites in close neighborhood. During oxidation of cooxidants, a part of active sites is occupied by them or by mentioned surface compounds. Occupation of active sites is confirmed by decreased rate of toluene oxidation. Therefore, cooxidant can decrease the concentration of free groups of active sites, which can adsorb toluene via aromatic ring and increase selectivity of the toluene oxidation via CH_3 group.

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