OXIDATION OF TOLUENE OVER V_2O_5–Sb_2O_3/TiO_2 CATALYSTS. ENHANCEMENT OF SELECTIVITY TOWARDS BENZOIC ACID

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The effect of reaction parameters, additives and cooxidants on the selectivity of toluene oxidation to benzoic acid in the vapor phase has been studied. The presence of ethanol as cooxidant in the reaction stream does not improve the selectivity of toluene oxidation towards partial oxidation products via methyl group oxidation. However, the presence of carbon dioxide has a positive effect on the selectivity to benzoic acid formation. The catalysts were characterized by temperature programmed reduction.

Key words: Oxidation; Toluene; Benzoic acid; V_2O_5; CO_2.

Vanadium oxide catalysts have been widely exploited in a number of oxidation reactions, including also oxidation of alkyl aromatics[1]. For the vapor phase oxidation the use of vanadium-based catalysts supported on low-temperature modified TiO_2 – anatase is well known. This system is the most active and selective for side-chain oxidation of methyl benzenes[2,3]. Jonson et al.[4] have described the oxidation of toluene over unpromoted V_2O_5/TiO_2 catalysts. Modification of catalytic activity by promoters is a commonly used method for increasing the selectivity to desired products. As it was shown in previous papers[5–9], Sb_2O_3 is the most effective promoter of vanadium catalysts for the benzoic acid production. Such catalysts ensure very high selectivity towards benzoic acid at high conversion of toluene. In the most recent paper of Japanese authors[9], a detailed study of the influence of reaction conditions over promoted V_2O_5/TiO_2 catalyst was reported.

EXPERIMENTAL

Catalyst Preparation and Characterization

For the catalyst preparation an impregnation method was used. A detailed description of this procedure is reported in our previous paper[5]. All catalysts were dried at 120 °C for 15 h and then calcinated at 450 °C for 4 h with heating rate 5 °C min^{-1} in the air, to prevent both the formation of a solid solution of V^{4+} in the TiO_2 (ref.[10]) and the transformation of anatase to rutile[11]. The composition and the specific surface area of catalysts are summarized in Table I. Temperature programmed

reduction (TPR) experiments and measurements of the specific surface area of catalysts were performed as reported earlier[5].

Oxidation of Toluene

Catalytic tests and analytical procedure were the same as described earlier[5]. Toluene conversion X_T was calculated from the difference between toluene signal in the product mixture and in nitrogen stream. The selectivities of reaction to benzoic acid S_{BzOH} and to benzaldehyde S_{BzH} were calculated on the basis of analysis of condensed products, and selectivities to carbon oxides S_{CO} and S_{CO_2} were obtained from the amount of CO and CO_2 present in the off-gas. The yields of products were calculated from X_T and the selectivity.

RESULTS AND DISCUSSION

Effect of Reaction Temperature

Over all tested vanadium catalysts, the conversion of toluene increases with the reaction temperature in the range 330–380 °C. The rate of benzoic acid production r_{BzOH} increases with the temperature. Over some catalysts this rate reaches a minimum located in the interval 340–360 °C. The rate of benzaldehyde production r_{BzH} decreases with the temperature. The decrease of the selectivity to partial oxidation products via methyl group oxidation at higher temperatures is caused mainly by increased production of carbon oxides, as a result a non selective overoxidation of toluene.

Effect of Water

This effect was measured over 4 wt.% Sb_2O_3–5 wt.% V_2O_5/TiO_2 catalyst at a molar ratio PhMe : O_2 : H_2O = 1 : 8 : 0–102. The results obtained are summarized in Table II.

TABLE I
Composition and surface area of catalysts

Sb : V molar ratio	wt.%			Area, m² g⁻¹	
	V_2O_5	Sb_2O_3	TiO_2	fresh	spent
0	5.0	0	95	6.3	6.3
0.05	5.0	0.4	94.6	7.1	6.0
0.2	5.0	1.6	93.4	7.4	7.8
0.5	5.0	4.0	91	7.2	7.4
0.75	5.0	6.0	89	7.4	8.1

From available literature it is known that the presence of water should decrease the formation of carbon oxides and as a consequence, the selectivity to methyl group oxidation products is increased[9,12]. Table II reveals that the presence of water increases S_{BzOH} up to molar ratio H_2O : PhMe = 40. At higher values, however, no further improvement of S_{BzOH} and S_{BzH} was observed. Miki et al.[9] reported also an enhancement of the selectivity of toluene oxidation to benzoic acid up to molar ratio H_2O : PhMe = 10. The activity of tested catalyst has a maximum in the range of molar ratio water : toluene = 50–80.

Effect of Sb₂O₃ Promoter

From our preliminary experiments[5] it is evident that Sb_2O_3 is a very effective promoter of vanadium catalysts for the benzoic acid production. Such catalysts obey very high

TABLE II

The effect of water on toluene oxidation over 4 wt.% Sb_2O_3–5 wt.% V_2O_5/TiO_2 catalyst. Reaction conditions: 350 °C, 0.1 MPa, molar ratio PhMe : O_2 = 1 : 8, space velocity 10 000 h^{-1}

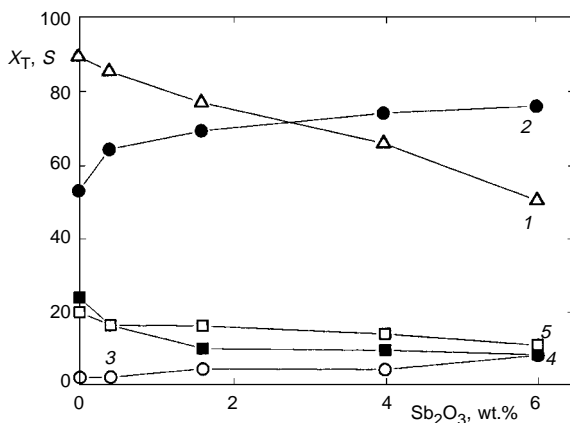| H_2O : PhMe molar ratio	X_T, %	Selectivity, %			
		BzOH	BzH	CO	CO_2
0	63.1	52.6	11.7	12.7	22.9
41	71.4	78.2	5.3	5.5	11
50	73.9	73.3	4.9	7.2	14.5
73	75	75.3	10.6	6.3	7.8
83	70.6	78.3	5.7	5.4	10.7
102	58.2	75.6	12	5.3	7.1

FIG. 1

Influence of Sb_2O_3 promoter on catalytic activity and product selectivity of 5 wt.% V_2O_5/TiO_2 catalysts. Reaction conditions: 373 °C, 0.1 MPa, molar ratio PhMe : O_2 : water = 1 : 4 : 25, space velocity 10 000 h^{-1}. Conversion X_T (1) and selectivity S to benzoic acid (2), benzaldehyde (3), CO (4), and CO_2 (5)

S_{BzOH} at high conversion of toluene. Results obtained over catalysts containing 0.4, 1.6, 4, and 6 wt.% Sb_2O_3 in 5 wt.% V_2O_5/TiO_2 (Fig. 1) demonstrate that the selectivity to benzoic acid increases and X_T decreases with increasing Sb_2O_3 content. However, the benzoic acid production decreases as a result of decrease of catalyst activity.

Temperature programmed reduction experiments were done for the sake of the catalyst characterization. Figure 2 illustrates the effect of Sb_2O_3 loading on TPR profiles of 5 wt.% V_2O_5/TiO_2 catalysts. With increasing amount of Sb_2O_3 the catalyst reducibility decreases, what is in a good correlation with the observed decrease of activity of toluene oxidation[5]. The phenomenon of pronounced decrease of vanadium reduction rate after reaching a maximum was observed for catalysts with the molar ratio Sb : V = 0.5 and 0.75. As it was clarified by additional experiments, this phenomenon is not linked with the melting of catalyst surface phase resulting in a decrease of the specific surface area of catalyst.

Oxidation of Toluene in the Presence of Ethanol

Ethanol as a cooxidant was tested over 4 wt.% Sb_2O_3–5 wt.% V_2O_5/TiO_2 catalyst. As we have reported earlier[13], the addition of cooxidant can increase the selectivity of toluene oxidation over SiO_2 supported vanadia catalysts. It follows from Table III, that the toluene conversion and also rates of benzoic acid, benzaldehyde and CO_2 production are almost the same in the presence and absence of ethanol. Formation of higher amount of carbon monoxide during the oxidation indicates that CO is produced from oxidation of ethanol and not toluene. It means that, in contrast to oxidation of toluene over V_2O_5/SiO_2-type catalysts[13], no improvement of selectivity of formation of side-chain oxidation products over Sb_2O_3–V_2O_5/TiO_2 catalyst in the presence of water was observed by the simultaneous oxidation of ethanol and toluene.
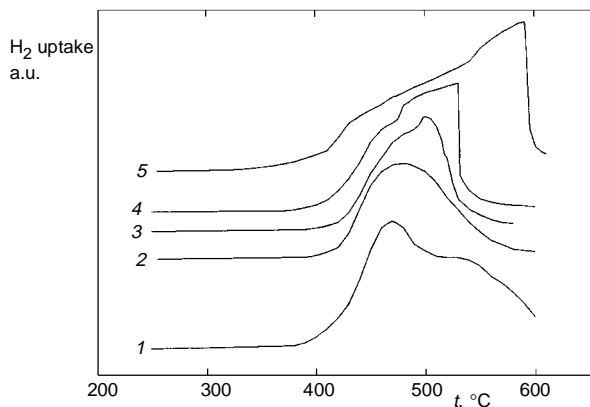

Fig. 2

Influence of Sb_2O_3 promoter on TPR profiles of 5 wt.% V_2O_5/TiO_2 catalysts at Sb : V molar ratios: *1* 0, *2* 0.05, *3* 0.2, *4* 0.5, and *5* 0.75

Influence of CO₂

The promoting effect of CO_2 on the liquid phase oxidation of tetrahydrofuran and styrene is known[14]. An analogy for the vapor phase oxidation of styrene over V_2O_5/TiO_2 catalyst was found[15], i.e. an improvement of benzoic acid production was observed. In the vapor phase oxidation of *o*-xylene, *p*-xylene and *p*-ethyltoluene over Fe/Mo/borosilicate molecular sieve[16] an improvement in the substrate conversion, suppressing of burning and altered product distribution in the presence of CO_2 were observed. In our experiments over 4 wt.% Sb_2O_3–5 wt.% V_2O_5/TiO_2 catalyst (Fig. 3), no

TABLE III
Influence of ethanol addition on toluene oxidation over 4 wt.% Sb_2O_3–5 wt.% V_2O_5/TiO_2 catalyst. Reaction conditions: 0.1 MPa, space velocity 10 000 h^{-1}

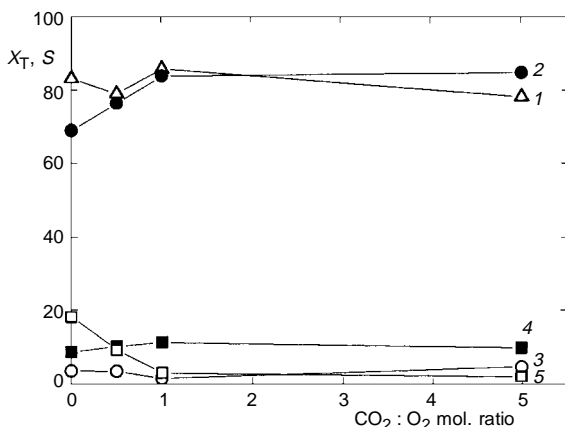| Temperature °C	PhMe : O₂ : water : ethanol molar ratio	X_T %	Rate of production, mol $mol_{V_2O_5}^{-1}$ h^{-1}			
			BzOH	BzH	CO	CO₂
333	1 : 8 : 50 : 0	65.7	1.17	0.11	0.39	1.56
	1 : 8 : 56 : 0.5	54.7	1.06	0.10	2.21	1.30
353	1 : 8 : 50 : 0	73.9	1.51	0.10	1.04	2.08
	1 : 8 : 56 : 0.5	75.5	1.44	0.10	2.60	1.82
373	1 : 8 : 50 : 0	83.3	1.61	0.09	1.43	2.99
	1 : 8 : 56 : 0.5	87.8	1.62	0.09	3.90	2.60
374	1 : 4 : 24 : 0	65.3	3.01	0.16	2.60	3.90
	1 : 4 : 26 : 0.25	59.4	2.74	0.17	4.94	3.51

FIG. 3
Oxidation of toluene over 4 wt.% Sb_2O_3–5 wt.% V_2O_5/TiO_2 catalyst in the presence of CO_2. Reaction conditions: 371 °C, 0.1 MPa, molar ratio PhMe : O₂ : water = 1 : 8 : 50, space velocity 10 000 h^{-1}. Conversion X_T (*1*) and selectivity *S* to benzoid acid (*2*), benzaldehyde (*3*), CO (*4*), and CO₂ (*5*)

improvement of catalyst activity was observed (X_T changes from 77.8 to 85.8%). However, similarly to observations of Yoo et al.[16], also in the oxidation of toluene, CO_2 suppresses the burning (decrease of S_{CO_2} from 18.3 to 1.7%) and increases the S_{BzOH} from 69.1 to 84.4%. On the other hand, both S_{BzH} and S_{CO} remain unchanged.

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