OXIDATION OF ALKYLAROMATIC HYDROCARBONS OVER V_2O_5–Sb_2O_3/TiO_2 CATALYST

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Monoalkylbenzenes, polymethylbenzenes, *para*-substituted toluenes and monomethylnaphthalenes were oxidized in the vapor phase by oxygen-containing gas in the presence of water over a Sb_2O_3-promoted V_2O_5/TiO_2 catalyst. This type of catalyst yields carboxylic acids with high selectivity. In the oxidation of substituted alkylbenzenes only alkyl groups were oxidized. No products of oxidative dimerization were detected. Only in the oxidation of methylnaphthalenes, also products of aromatic ring oxidation are formed. A correlation between experimental data and results of quantum-chemical calculations of bond dissociation energies is discussed.

Key words: Oxidation; Alkylaromatics; Carboxylic acids; V_2O_5.

The oxidation ability of vanadium oxide catalysts has been widely exploited in a number of oxidation reactions, including oxidation of alkylaromatics[1]. For the vapor phase oxidation, the use of vanadium catalysts supported on low-temperature modified TiO_2 – anatase is well known and this system is generally accepted as the most active and selective[1–10]. The reason for the superior high activity and selectivity of the system was attributed to crystallographic fit between V_2O_5 and TiO_2 (anatase) planes[11], to formation of a highly dispersed amorphous vanadia layer and its stability on the surface of anatase[1,5,6], acidity of catalyst[7] or reducibility of vanadium oxide overlayer[8]. On the other hand, some authors concluded[12] that the specific titania phase is not a critical parameter for physical and chemical nature of the surface vanadium oxide phase. The reason for the superior high activity and selectivity of anatase-supported vanadia in side-chain oxidation of methylbenzenes has not been fully understood. The main factor that determines the structure and composition of supported vanadium is the nature of the support surface (the concentration and the type of surface OH groups)[13]. This can be influenced by a low amount of impurities present in TiO_2 or by addition of promoters[7]. Modification of the catalytic activity by promoters is a commonly used method for increasing the selectivity to desired products. Sb_2O_3 was shown[10,14] to be the most effective promoter of vanadium catalysts for the benzoic acid production from toluene. Such catalysts show a very high selectivity in producing benzoic acid at high conversion of toluene. Enhancement of the selectivity in producing partial oxidation products and detailed study of the influence of reaction conditions on the toluene oxidation over promoted V_2O_5/TiO_2 catalysts were reported[10,15].

Czerwenka *et al.*[3] have reported the reactivity of *para*-substituted toluenes over V_2O_5/TiO_2, which is in the order: methoxy > *tert*-butyl > H. Quantum-chemical calculations of charge density and bond lengths using the MINDO/2 method have shown that substituents in the *para*-position have practically no effect on either the charge or the C–H bond length in the CH_3 group of toluene. According to these authors, the reactivity of substituted toluenes is only affected by the electron density in the aromatic ring and by the values of ionization energy of the molecules. Ueshima and Saito[16] mentioned that reactivities of *para*-substituted toluenes are related to their ionization potentials. They reported that conversion of *para*-substituted toluenes in the vapor phase oxidation over V_2O_5-Tl_2O catalyst decreases with increasing values of ionization potentials. A following order of the reactivity of *para*-substituted toluenes was observed: OCH_3 > isopropyl ≈ *tert*-butyl > CH_3 > H.

EXPERIMENTAL

Catalyst Preparation and Characterization

For catalyst preparation, an impregnation method was used. A detailed description of this procedure is reported in our previous paper[14]. The catalyst prepared from NH_4VO_3, Sb_2O_3 and anatase, after calcination, has the composition 4 wt.% Sb_2O_3 and 5 wt.% V_2O_5/TiO_2 (molar ratio Sb : V = 1 : 2). The catalyst was dried for 15 h at 120 °C and then calcined in air for 4 h at 450 °C with a heating rate of 5 °C min^{-1} in order to prevent the formation of a solid solution of V^{4+} in TiO_2 (ref.[7]) and the transformation of anatase to rutile[17]. The specific surface area of freshly prepared and used catalysts was 7.2 and 7.4 m^2 g^{-1}, respectively.

Temperature-programmed reduction (TPR) profiles of catalysts were reported in our previous papers[14,15].

Oxidation Procedure and Analytical Methods

Catalytic tests and analyses of the reaction mixtures of monoalkylbenzenes were the same as published earlier for toluene oxidation[14]. Acids formed in the oxidation of polymethylbenzenes, *para*-substituted toluenes and monomethylnaphthalenes were converted to methyl esters and analyzed by gas chromatography (Chrompack Packard 9000 with FID), using a 1.8-m packed column (i.d. 0.3 cm) with 10% silicone UCW 982 on Chromatone NAW DMCS.

Identification of products by the GC/MS method was performed on a Varian 3400 gas chromatograph equipped with an MS detector ITD 800 (Finnigan). A 30-m capilllary column (fused silica, DB-5, i.d. 0.2 mm, film thickness 0.25 μm) was used. Mass spectra (EI) were measured at electron energy 70 eV using a rate of 1 s/scan at 220 °C.

Conversion of monoalkylbenzenes and polymethylbenzenes, X_i, was calculated from the difference of substrate peak in the product mixture and in the nitrogen inlet stream. Both conversion of *para*-substituted toluenes and monomethylnaphthalenes and the selectivity of oxidation of all alkylaromatic hydrocarbons were calculated on the basis of analysis of condensed products. 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 yield of products was calculated from the conversion and selectivity.

RESULTS AND DISCUSSION

Oxidation of Alkylaromatic Hydrocarbons

On the basis of the results obtained in the toluene oxidation over catalysts with different vanadium and promoter loadings[14,15], the 4 wt.% Sb_2O_3–5 wt.% V_2O_5/TiO_2 catalyst was chosen for the oxidation of various substrates. Reaction conditions were the same as in our previous experiments.

Oxidation of monoalkylbenzenes. Toluene oxidation was described in our previous paper[15]. The products formed confirm that only the oxidation of methyl group takes place in the reaction[18]. Products of aromatic ring oxidation or oxidative dimerization

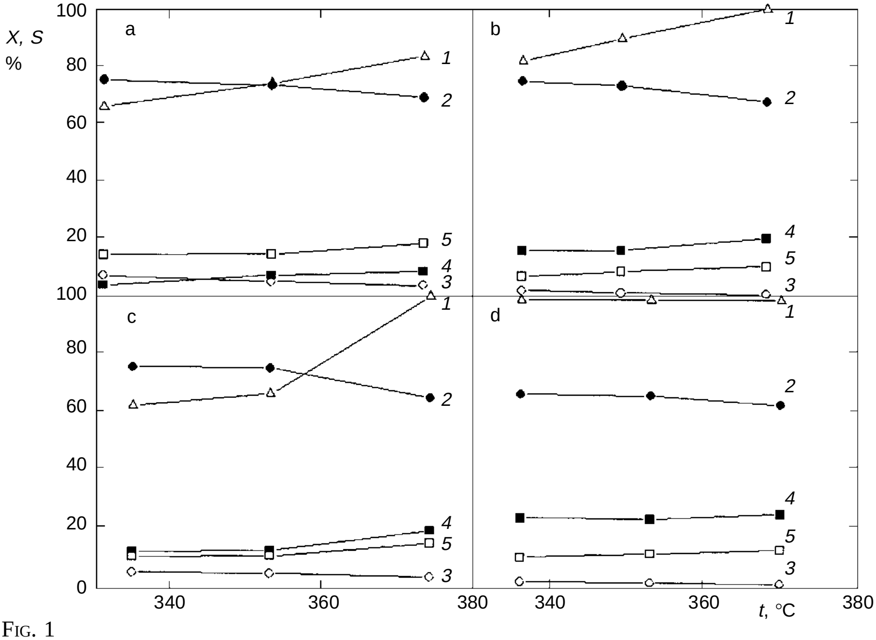


FIG. 1
Oxidation of monoalkylbenzenes over 4 wt.% Sb_2O_3–5 wt.% V_2O_5/TiO_2 catalyst. Reaction conditions: 0.1 MPa, molar ratio substrate : O_2 : water = 1 : 8 : 50, space velocity 10 000 h^{-1}. Conversion X_i (*1*) and selectivity S to benzoic acid (*2*), benzaldehyde (*3*), CO (*4*) and CO_2 (*5*). a Toluene, b ethylbenzene, c propylbenzene, d cumene

were not detected in the reaction mixture. In Fig. 1a are presented the results of toluene oxidation. An increase in reaction temperature from 331 to 373 °C increases the conversion from 65.7 to 83.3% and decreases S_{BzOH} from 75.1 to 69.1%. In addition, a slight decrease in S_{BzH} and an increase in CO_x production were observed. Oxidations of ethylbenzene (Fig. 1b), propylbenzene (Fig. 1c) and cumene (Fig. 1d) yield exclusively benzoic acid and benzaldehyde. An increase in reaction temperature from 335 to 374 °C increases the conversion of ethyl- and propylbenzene up to 100%. The decrease in both S_{BzOH} (≈75 to ≈65%) and S_{BzH} was for ethyl- and propylbenzene almost the same as for toluene. The situation with CO_x production was practically the same. In the case of cumene, a complet conversion was observed over the whole temperature range tested. Selectivities in producing oxidation products were lower in comparison with other monoalkylbenzenes and almost independent of the reaction temperature (≈65% to benzoic acid and ≈1% to benzaldehyde).

Oxidation of polymethylbenzenes. The increase in reaction temperature from 340 to 380 °C increases the conversion of both *o*- and *p*-xylene up to 100%. The oxidation of *o*-xylene (Fig. 2a) yields almost exclusively phthalic acid and its anhydride (80% selectivity), but also ≈8% of benzoic acid is formed. In *p*-xylene oxidation, the situation is rather different (Fig. 2b). Only poor selectivity to partial oxidation products was observed. In the reaction mixture, benzoic acid, 4-methylbenzoic acid, 4-formylbenzoic acid and terephthalic acid were detected. The selectivity in producing partial oxidation products decreases with increasing reaction temperature. The oxidation of pseudocumene gives a mixture of partial oxidation products. By GC/MS, products of methyl groups oxidation were detected, but no aldehydic groups. The reaction mixture contains 2,4-dimethylbenzoic acid, phthalic acid, isophthalic acid, terephthalic acid, 4-methylphthalic acid, 4-methylisophthalic acid and trimellitic acid.

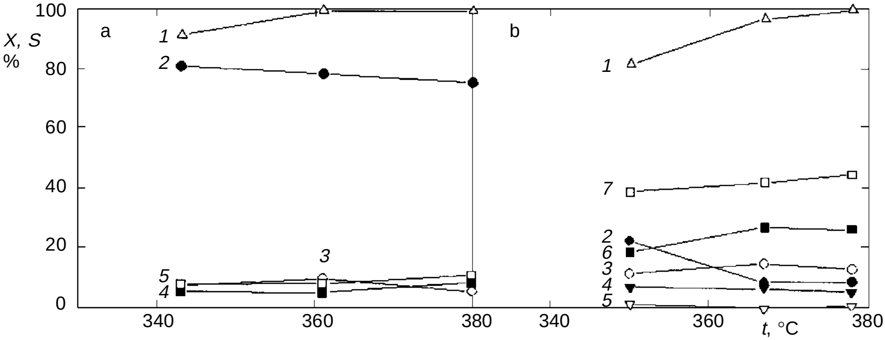


FIG. 2

Oxidation of xylenes over 4 wt.% Sb_2O_3–5 wt.% V_2O_5/TiO_2 catalyst. Reaction conditions see Fig. 1. a Conversion of *o*-xylene (*1*) and selectivity *S* to phthalic acid (*2*), benzoic acid (*3*), CO (*4*) and CO_2 (*5*); b conversion of *p*-xylene (*1*) and selectivity *S* to 4-methylbenzoic acid (*2*), benzoic acid (*3*), terephthalic acid (*4*), 4-formylbenzoic acid (*5*), CO (*6*) and CO_2 (*7*)

Oxidation of para-substituted toluenes. The influence of substituents on substrate reactivity and product selectivity for both electron-donating (CH_3, NH_2, OH) and electron-withdrawing (Cl and NO_2) groups was tested. As mentioned above, the oxidation of *p*-xylene produces a mixture of acids, and a high amount of CO and CO_2. *p*-Toluidine was used as a saturated solution in benzene. The reaction in the temperature range tested (330–360 °C) leads to the formation of tars. No products of oxidation of *p*-toluidine were found by GC/MS. *p*-Cresol was oxidized as an 82% solution in benzene. Conversion in the temperature range of 310–360 °C increased from 58 to 94% (Fig. 3a). A low selectivity of partial oxidation at 335 °C (14% for 4-hydroxybenzoic acid and ≈5% for 4-hydroxybenzaldehyde) was observed. In comparison with toluene, 4-chlorotoluene is more reactive in the vapor phase oxidation. Selectivity of the 4-chlorobenzoic acid formation is comparable to S_{BzOH} in the toluene oxidation. The presence of the chlorine substituent decreases the selectivity to aldehyde and increases S_{CO_x}. The results of 4-chlorotoluene oxidation are presented in Fig. 3b. 4-Nitrotoluene was oxidized as a 30% solution in benzene. The conversion was comparable to other *para*-substituted toluenes, but the selectivity in producing 4-nitrobenzoic acid was lower than 12%. On the other hand, a very high production of CO_2 was observed (near 60 mole %).

Oxidation of monomethylnaphthalenes. The results of both 1-methylnaphthalene and 2-methylnaphthalene oxidation are presented in Fig. 4. In the product mixture of 1-methylnaphthalene oxidation, 1-naphthaldehyde, 1-naphthoic acid, phthalic acid and benzoic acid were identified. In the temperature range 330–420 °C, conversion of 1-methylnaphthalene increases from 46 to almost 100%. In the same range, the initial high selectivity in producing 1-naphthoic acid decreases from 65.5 to 3% and in the case of 1-naphthaldehyde from 14.7 to 6.6%. The decrease in selectivity of the methyl

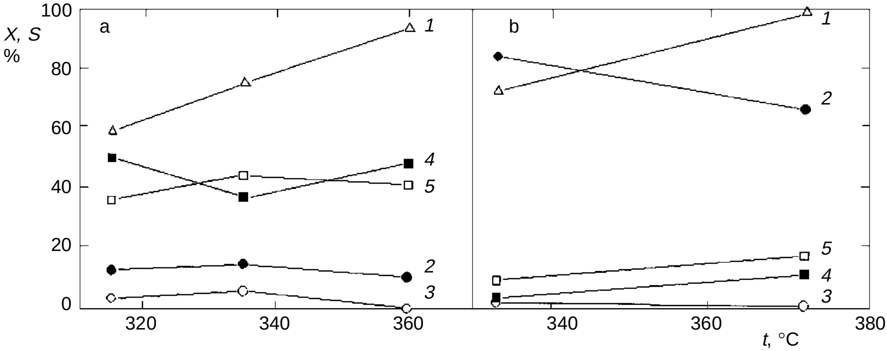


FIG. 3

Oxidation of *para*-substituted toluenes over 4 wt.% Sb_2O_3–5 wt.% V_2O_5/TiO_2 catalyst. Reaction conditions see Fig. 1. a Conversion of *p*-cresol (*1*) and selectivity *S* to 4-hydroxybenzoic acid (*2*), 4-hydroxybenzaldehyde (*3*), CO (*4*) and CO_2 (*5*); b conversion of 4-chlorotoluene (*1*) and selectivity *S* to 4-chlorobenzoic acid (*2*), 4-chlorobenzaldehyde (*3*), CO (*4*) and CO_2 (*5*) group oxidation is caused by an increased selectivity in yielding products of aromatic ring oxidation, as evident from the formation of phthalic and benzoic acids. A maximum formation of phthalic acid was observed at 386 °C, whereas the benzoic acid production increases in the whole temperature range tested. The CO_x formation, as a result of nonselective oxidation, has a maximum at 360 °C. In the oxidation of 2-methylnaphthalene, in addition to 2-naphthaldehyde, 2-naphthoic acid, phthalic acid and benzoic acid, also trimellitic acid (1,2,4-benzenetricarboxylic acid) and traces of 4-methylphthalic acid were identified.

Quantum-Chemical Calculations

Quantum-chemical calculations were performed for the estimation of charge density (CD) and bond dissociation energies (BDE). The semiempirical AM1 method[19] was utilized, as implemented in the MOPAC integrated software package[20]. All calculations were derived from a single-determinant wavefunction (RHF) with no configuration interaction, based on the DFP optimization algorithm[21]. Equilibrium geometries were tested with respect to the position only for positive eigenvalues in the Hessian matrix of the energy. The results of charge density on alkyl-group carbons and of BDE calculations are summarized in Table I.

According to Fox and Kollman[22], benzylic C–H BDE are hardly affected, in contrast to ionization potentials, which are sensitive to ring substituents. By the density functional method BLYP/6-31*, performed for a series of *para*-substituted toluenes, Wu *et al.*[23] have shown in their study of the effect of substituent on the benzylic carbon–hydrogen BDE that both the electron-donating and electron-withdrawing *para*-substituents reduce

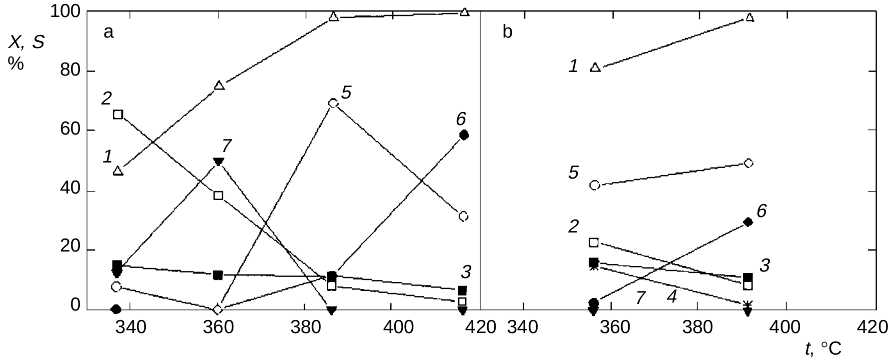


FIG. 4
Oxidation of methylnaphthalenes over 4 wt.% Sb_2O_3–5 wt.% V_2O_5/TiO_2 catalyst. Reaction conditions see Fig. 1. Conversion X_i (*1*) and selectivity *S* to naphthoic acid (*2*), naphthaldehyde (*3*), trimellitic acid (*4*), phthalic acid (*5*), benzoic acid (*6*) and CO_x (*7*). a 1-Methylnaphthalene, b 2-methylnaphthalene

benzylic C–H BDE. As can be seen from Table I, this effect was observed also in our results (toluene exhibits the highest benzylic C–H BDE out of *para*-substituted toluenes), except for *p*-cresol. In comparison with other C–H BDEs of *para*-substituted toluenes, C–H BDE of *p*-cresol was strongly overestimated; therefore it was excluded from graphic presentation.

The reaction centre of a monoalkylaromatic hydrocarbon is located on the carbon with the highest charge density. The presence of aromatic ring weakens the C–C bond between α- and β-carbons of the alkyl group. This bond exhibits the lowest BDE and in the vapor phase oxidation it is broken and products oxygenated on the α-carbon are formed. An increase in benzylic C–H BDE causes a decrease in hydrocarbon conversion (Fig. 5). CO and CO_2 produced by alkyl-group oxidation were excluded for the calculation of selectivity. From Fig. 6 it is evident that the selectivity in producing benzoic acid, benzaldehyde and CO_2 increases whereas the production of CO decreases with C–H BDE increase.

TABLE I

Calculated bond dissociation energies (BDE) and charge densities on α-carbons (CD) of alkyl groups of hydrocarbons

Hydrocarbon		BDE, kJ mol^{-1}				CD on C_α
		C_α–H	C_α–C_r	C_α–C_β	C_r–X_p	
Toluene		312.63	355.56	–	–	–0.1791
Ethylbenzene		279.20	314.97	219.87	–	–0.1239
Propylbenzene		282.09	309.74	214.10	–	–0.1237
Cumene		268.24	288.36	224.01	–	–0.0707
Pseudocumene	1-Me	308.95	345.43	–	–	–0.1790
	2-Me	307.57	343.46	–	–	–0.1800
	3-Me	314.09	357.10	–	–	–0.1720
o-Xylene		306.73	337.86	–	–	–0.1735
p-Xylene		311.29	358.28	–	–	–0.1779
p-Toluidine		306.39	351.37	–	379.78	–0.1787
4-Nitrotoluene		307.65	350.12	–	154.43	–0.1916
p-Cresol		323.09	357.94	–	430.58	–0.1743
4-Chlorotoluene		307.27	357.65	–	346.64	–0.1806
1-Methylnaphthalene		306.27	326.94	–	–	–0.1740
2-Methylnaphthalene		315.47	327.31	–	–	–0.1730

Similarly to monoalkylbenzenes, polymethylbenzenes and *para*-substituted toluenes show a decrease in conversion in the order of increasing C–H BDEs (see lines *2* and *3* in Fig. 5). Owing to the complexity of the product mixture composition for different hydrocarbons, it was not possible to find a dependence of the selectivity on BDE, as it was done in the case of monoalkylbenzenes.

Mechanism of Oxidation

On the basis of mechanisms of methyl group oxidation described by Andersson for toluene[18] and by Bond for *o*-xylene[24], and on the basis of products detected in the reaction mixture, the following reaction mechanism is proposed for alkyl-group oxidation of alkylbenzenes in the vapor phase (Scheme 1). The key species, which can produce both aldehydic or carboxylic groups is the surface carbonyl species **5**.

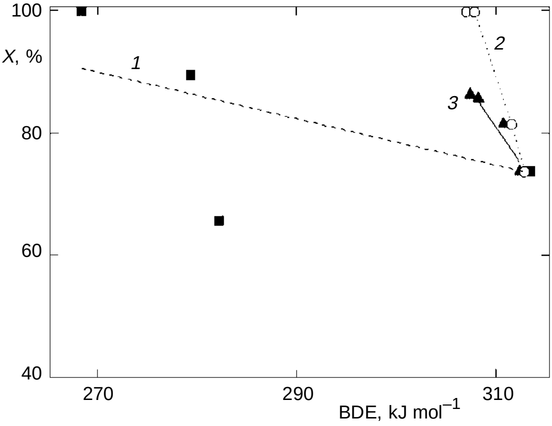


FIG. 5
Influence of benzylic C–H BDE on conversion of aromatic hydrocarbons in oxidation over 4 wt.% Sb_2O_3–5 wt.% V_2O_5/TiO_2 catalyst. Monoalkylbenzenes (*1*), polymethylbenzenes (*2*) and *para*-substituted toluenes (*3*). Reaction conditions: 0.1 MPa, 353 °C, molar ratio substrate : O_2 : water = 1 : 8 : 50, space velocity 10 000 h^{-1}

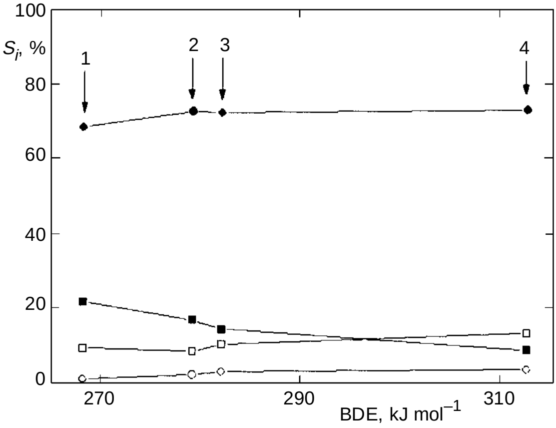
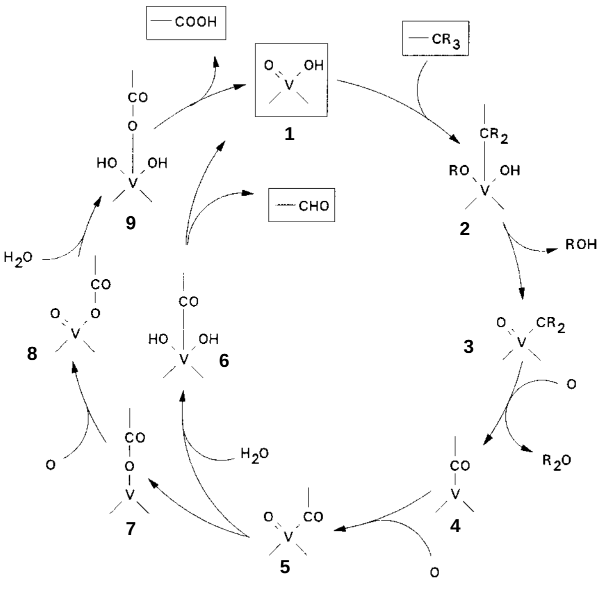


FIG. 6
Influence of benzylic C–H BDE of monoalkylbenzenes on selectivity in oxidation over 4 wt.% Sb_2O_3–5 wt.% V_2O_5/TiO_2 catalyst (for symbols, see Fig. 1). Reaction conditions see Fig. 5. 1 Cumene, 2 ethylbenzene, 3 propylbenzene, 4 toluene



(R = H, methyl or ethyl group, respectively)

SCHEME 1

Conclusions

1) Oxidation of alkylbenzenes over Sb_2O_3-promoted V_2O_5/TiO_2 catalyst yields only products of alkyl-group oxidation, giving acids and aldehydes with high and low selectivity, respectively.

2) The oxidation of alkylnaphthalenes produces both alkyl-group and aromatic-ring oxidation products.

3) A correlation exists between benzylic C–H bond dissociation energy of alkylbenzenes and their reactivity in the oxidation.

4) The proposed mechanism of alkyl-group oxidation involves surface carbonyl species.

REFERENCES

1. Bond G. C., Tahir S. F.: Appl. Catal. *71*, 1 (1991).
2. Haber J., Kozlowska A., Kozlowski R.: J. Catal. *102*, 52 (1986).
3. Czerwenka M., Grzybowska B., Gasior M.: Bull. Pol. Acad. Sci., Chem. *35*, 353 (1987).
4. Jonson B., Rebenstorf B., Larsson R., Andersson S. L. T.: J. Chem. Soc., Faraday Trans. 1 *84*, 3547 (1988).
5. Centi G., Pinelli D., Trifiro F.: J. Mol. Catal. *59*, 221 (1990).
6. Huuhtanen J., Sanati M., Andersson A., Andersson S. L. T.: Appl. Catal., A *97*, 197 (1993).
7. Nobbenhuis M. G., Hug P., Mallat T., Baiker A.: Appl. Catal., A *108*, 241 (1994).
8. Deo G., Wachs I. E.: J. Catal. *146*, 323 (1994).

9. Matralis H. K., Papadopoulou C., Kordulis C., Aguilar Elguezabal A., Cortes Corberan V.: Appl. Catal., A *126*, 365 (1995).
10. Miki J., Osada Y., Konoshi T., Tachibana Y., Shikada T.: Appl. Catal., A *137*, 93 (1996).
11. Vejux A., Courtine P. J.: J. Solid State Chem. *23*, 93 (1978).
12. Deo G., Turek A. M., Wachs I. E., Machej T., Haber J., Das N., Eckert H., Hirt A. M.: Appl. Catal., A *91*, 27 (1992).
13. Pinaeva L. G., Lapina O. B., Mastikhin V. M., Nosov A. V., Balzhinimaev B. S.: J. Mol. Catal. *88*, 311 (1994).
14. Antol M., Prandova K., Hronec M.: Collect. Czech. Chem. Commun. *61*, 1665 (1996).
15. Antol M., Kaszonyi A., Hronec M.: Collect. Czech. Chem. Commun. *61*, 1675 (1996).
16. Ueshima M., Saito N.: Chem. Lett. *7*, 1341 (1992).
17. Depero L. E., Bonzi P., Zocchi M., Casale C., De Michele G.: J. Mater. Res. *8*, 2709 (1993).
18. Andersson S. L. T.: J. Catal. *98*, 138 (1986).
19. Dewar M. J. S., Zoebisch E. G., Healy E. F., Stewart J. J. P.: J. Am. Chem. Soc. *107*, 3902 (1985).
20. Stewart J. J. P.: QCPE Bull. *3*, 101 (1983).
21. Fletcher R., Powell M. J. D.: Comput. J. *6*, 163 (1963); Davidov W. C.: Comput. J. *11*, 406 (1968).
22. Fox T., Kollman P. A.: J. Phys. Chem. *100*, 2950 (1996).
23. Wu Y.-D., Wong Ch.-L., Chan K. W. K., Ji G.-Z., Jiang X.-K.: J. Org. Chem. *61*, 746 (1996).
24. Bond G. C.: J. Catal. *116*, 531 (1989).