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"Dehydrogenation" Mechanism for Ammoxidation of Alkylaromatic Hydrocarbons

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Ammoxidation of toluene and other alkylaromatics over supported V–Sb–Bi oxide catalysts is studied by means of pulse, flow, temperature-programmed reactions, and IR spectroscopy. It has been found that reaction occurs by alternate reduction and oxidation of the catalyst surface. Aromatic nitrile is formed at the reduction stage via amine- and imine-like intermediates. Ammonia exhibits an activation effect on the overall hydrocarbon conversion. According to this study and data on the reactivity of different substituted toluenes and on the activity of alkali-doped catalysts, the hydrocarbon activation is assumed to take place by the attack of a basic site of the catalyst via heterolytic dissociation of a C–H bond in a benzylic position. On the basis of these results a "dehydrogenation" mechanism for ammoxidation of alkylaromatics is proposed and used for the analysis of reaction kinetics.

INTRODUCTION

Many oxide catalysts, such as V_2O_5, V–Mo, V–Sn, V–Ti, and others, are active in both the ammoxidation and the partial oxidation of alkylaromatic hydrocarbons. The same catalysts also demonstrate high activity and selectivity in ammoxidation of aromatic aldehydes to the corresponding nitriles. These facts are consistent with the so-called "oxidation" mechanism according to which nitrile is produced via an aldehyde or an acid as the intermediate compound. Murakami and co-workers (*1*) have proposed that the reaction mechanism of toluene ammoxidation on V_2O_5 consists of three steps: (i) oxidative adsorption of toluene, accompanied by abstraction of hydrogens in the side chain; (ii) reaction of the adsorbed species with ammonia; and (iii) reoxidation of the catalyst by oxygen. Using infrared spectroscopy, they showed that the oxidative adsorption of toluene results in the formation of a surface benzoate ion, $C_6H_5COO^-$, which gives benzonitrile by reaction with ammonium ion (*2*). The same mechanism was accepted later for ammoxidation of xylenes over supported vanadium pentoxide (*3*).

On the other hand, there is a group of catalysts that are very effective in ammoxidation but are not active in partial oxidation of alkylaromatic compounds. For instance, the supported V–Sb–Bi oxide system developed by us (*4*) catalyzes with high activity and selectivity (95–98%) the processes of ammoxidation of toluene and xylenes. In the absence of ammonia, the oxidation of hydrocarbons over this catalyst yields mainly benzene, CO_2, and water; the selectivity to aromatic aldehydes and acids does not exceed 10%, yet it is effective in the oxidative dehydrogenation of hydrocarbons (*5*). Such behavior of the catalyst cannot be explained by the "oxidation" mechanism proposed by Murakami *et al.* (*1–3*).

The purpose of this paper is to clarify the reaction mechanism of ammoxidation of alkylaromatic hydrocarbons over V–Sb–Bi oxide catalysts. Kinetic, pulse, adsorp-

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tion–desorption, IR spectroscopy, and temperature-programmed reaction data are also summarized.

EXPERIMENTAL

Supported V–Sb–Bi oxide catalysts are prepared by impregnation of γ-Al_2O_3 with solutions of ammonium metavanadate, antimony chloride, and bismuth nitrate followed by calcination in an air stream at 450°C. The preparation procedure is described in Ref. (*4*). Alkali and alkaline earth elements were added to the catalyst as hydroxides during the impregnation stage. Surface areas measured by thermal desorption of argon were 75–85 m^2/g.

The acidity of the catalyst was characterized by the amount of *n*-butylamine adsorbed on the surface from solution (water-free benzene). The quantity of *n*-butylamine that remained in solution after adsorption was determined by titration with hydrochloric acid. The basicity of the samples was measured in a similar manner by adsorption of benzoic acid, the excess of which was titrated with the potassium hydroxide solution.

Heat of adsorption of oxygen which was used as a measure for the energy of oxygen bond with the catalyst surface was estimated by means of high-temperature microcalorimetry of the heat of reaction of CO doses with the surface heated at 400°C under vacuum and then in oxygen. In these experiments, the extent of catalyst reduction did not exceed a monolayer, and the amount of CO_2 produced always corresponded to the dose of CO. Two types of experiments were carried out. In the course of catalyst reduction, small doses of oxygen were periodically added to the sample between the CO additions, and the heat of oxygen sorption was recorded. Values of the oxygen bond energy obtained by all these methods coincided for the samples studied. In calculations of the extent of surface reduction the area occupied by the surface oxygen ion was assumed to be equal to 7.84 Å^2.

Ammoxidation of toluene, ethylbenzene, isopropylbenzene, and xylenes was carried out in a flow apparatus equipped with a gradientless reactor with a vibro-fluidized bed of catalyst. The rates of product formation, determined after the catalyst activity stationary state had been reached, were compared for similar conversions (10–15%). The ammoxidation of toluene was also studied by a pulse method. In these experiments, pulses of toluene (R), ammonia (N), oxygen (O), and various mixtures of them (RN,RO,ON,RON) in helium were injected into the reactor. Analysis of the reaction mixture was carried out on a chromatograph connected to the reactor through a six-way valve, which served as a dosing system. Hydrocarbons, nitriles, ammonia, and CO_2 were analyzed in a Porapak-P column at temperatures rising linearly from 40 to 120°C. Oxygen and carbon monoxide were separated in a molecular sieve column at a room temperature.

Temperature-programmed reactions (TPR) of toluene and ammonia on the catalyst surface were studied on a specially constructed apparatus that could operate in the flow and the pulse regimes. After adsorption of the dosants at specified temperatures, the catalyst was cooled to room temperature and then was heated linearly to 400°C at a rate of 10°C/min. The flow rate of helium was 90 ml/min. Thermal desorption spectra were recorded simultaneously by thermal conductivity and flame-ionization detectors. Trapped liquid products and gaseous components of individual peaks were analyzed by gas chromatography.

IR spectra were recorded at room temperature on a UR-20 spectrometer in the region 4000–1000 cm^{-1}. The spectral splitwidth was 8 cm^{-1} at 1000 cm^{-1}. The IR cell was made of quartz and constructed to permit heating of the sample to 500°C. The catalyst was used in the form of a rectangular wafer with dimensions 30 × 8 mm. Toluene and ammonia were purified by repeated freezing under vacuum.

TABLE 1

Rates of Alkylaromatic Ammoxidation at 360°C in Comparison with Relative Rates of Isotopic Exchange of α-Hydrogen Atoms

Reactant	Ammoxidation rate (μ mol/m^2 · h)	Rate of α-hydrogen exchange[a]
Toluene	37.0	1.0
Ethylbenzene	38.1	0.12
i-Propylbenzene	9.4	0.08
p-Xylene	29.8	0.31
o-Xylene	19.0	0.60
m-Xylene	16.9	0.60

[a] Ref. (*17*).

RESULTS

Ammoxidation of Alkylaromatic Hydrocarbons by Flow Reaction

Under the same conditions, the ammoxidation reaction over the V–Sb–Bi oxide catalysts converts toluene, ethylbenzene, and isopropylbenzene to benzonitrile with a selectivity of 94–97%. The rate of benzonitrile formation (Table 1) increases in the sequence.

$$C_6H_5CH_3 \simeq C_6H_5CH_2CH_3 > C_6H_5CH(CH_3)_2.$$

This implies that the substitution of hydrogen atoms for methyl groups in the α-position of the benzene ring decreases the rate of mild oxidation of the alkyl C–H bond. The same effect is observed when a second methyl group is attached to the ring; xylenes undergo ammoxidation 1.5–2.0 times more slowly than toluene.

Pulse Toluene Ammoxidation

The pulse technique was used to study the approach to a steady state of the catalyst and its interactions with various mixtures of toluene, ammonia, and oxygen. After the sample was heated at 500°C in an oxygen flow for 1 h and then in helium flow for 1 h, pulses of toluene, oxygen, and ammonia mixture (RON) were successively injected onto the sample at 320°C. Figure 1 shows that initial pulses interact with the oxidized surface of the sample, yielding primarily carbon dioxide. Selectivity with respect to benzonitrile is poor. In subsequent pulses, the rate of ammoxidation increases while the rate of deep oxidation decreases. Simultaneously, the reduction of the catalyst surface and the amount of adsorbed hydrocarbon and ammonia increase. After 5–10 pulses are applied to the sample, the rates of all these processes become constant. At this steady state, the catalyst demonstrates high selectivity to benzonitrile (95–97% under the conditions studied). The extent of reduction is equal to 3.0–4.5% of a monolayer and several times more ammonia than toluene is adsorbed.

The results of interactions of various mixtures with a steady-state catalyst are presented in Fig. 2. Benzonitrile is formed from all pulses containing toluene (RN,R,RO) and does not form when pulses of oxygen and ammonia (O,ON,N) are injected onto the catalyst. Apparently, the hydrocarbon does not form strongly adsorbed structures that are able to transform into nitrile by reaction with molecular oxygen or ammonia. Most of the benzonitrile forms from interaction of the toluene and ammonia mixture (RN) with oxygen on the

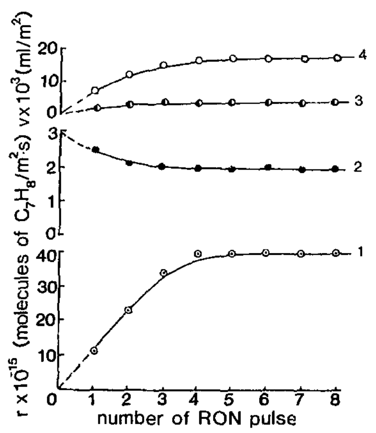


FIG. 1. Rates of toluene ammoxidation (1) and deep oxidation (2) and amounts of adsorbed toluene (3) and ammonia (4) as functions of the number of catalytic mixture RON pulses given on the catalyst at 320°C.

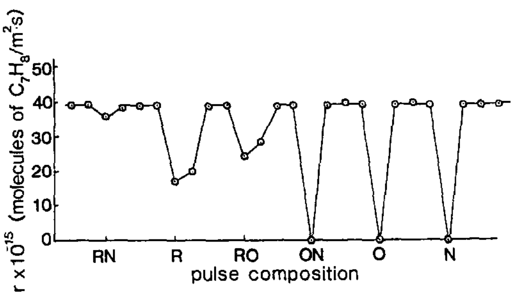


FIG. 2. Rates of benzonitrile formation under the interactions of reactants with a steady-state catalyst at 320°C (unplotted pulses correspond to catalytic mixture RON).

catalyst surface. The rate of this process coincides with the rate of the catalytic reaction (pulse RON). It seems that ammonia reacts from the adsorbed state because benzonitrile is also formed in R and RO pulses. However, in these cases, the steady state of the catalyst is being disturbed. As one can see, after admission of R and RO pulses, the rate of benzonitrile formation in the following pulse, RON, is essentially lower than that at steady state. This decrease is not observed when the pulses containing ammonia (RN,ON,N) are admitted to the steady-state catalyst. Thus, the stationary state of the V–Sb–Bi oxide catalyst can be retained if ammonia is present in the reaction mixture.

Effect of Ammonia on Catalyst Properties

As was mentioned above, introduction of ammonia into the toluene–oxygen mixture sharply decreases the rate of complete oxidation and causes the appearance of nitrile among the reaction products. With increasing ammonia concentration, not only the selectivity of nitrile formation but also the overall rate of hydrocarbon conversion rises (Table 2). We suppose that this activation effect of ammonia is caused by its adsorption: when adsorbed on the catalyst surface, ammonia forms new sites active for a mild oxidation of toluene. Data from the pulse measurements confirm this. It has been noted above that the adsorption of ammonia takes place during the approach to steady state. Moreover, initially adsorbed ammonia enhances the conversion of toluene-oxygen mixture. From 1 to 6 pulses of ammonia were admitted to the steady-state catalyst in the toluene–oxygen mixture, and then toluene–oxygen pulses were admitted again and changes in the conversion rate were measured. Results of these experiments (Table 3) indicate that the conversion rate of toluene significantly increases with the quantity of the preliminary adsorbed ammonia. With the consumption of adsorbed ammonia, the conversion rate decreases to 12.8 × 10^{15} molecules $C_7H_8/m^2 \cdot s$, which corresponds to the rate of steady-state oxidation of toluene in the absence of ammonia.

During the reaction, ammonia is adsorbed on the acid sites of the catalyst surface. This conclusion is based on the following data. After the catalyst is treated with the reaction mixture a considerable fraction of the acid sites is bound and the number of bound sites increases with increasing ammonia concentration in the reaction mixture (Table 2). Infrared spectra of adsorbed pyridine indicate that this treatment of the catalysts decreases predominantly the Lewis acidity. At the same time, the concentration of basic sites is enhanced (Table 2). Apparently, this increase in basicity is due to blocking of the Lewis acid sites (metal cations) by ammonia and the formation of partially dehydrogenated species that have electron-donating properties, such as NH_2, NH, and HNO. The presence of such adsorbed species of ammonia on the V–Sb–Bi catalyst is confirmed indirectly by thermal desorption data. With increasing temperature, samples treated in the reaction mixture at 400–500°C release the products of ammonia oxidation (N_2, N_2O). The latter are not observed under steady-state conditions. Apparently, these products are formed upon decomposition of the ammonia species on the catalyst surface. It should be noted that the amount of N_2O and N_2 in the thermal desorption products also increases with increasing ammonia con-

TABLE 2

Effect of Ammonia Concentration in the Reaction Mixture on Catalytic and Acid–Base Properties of V–Sb–Bi Catalyst

C_{NH_3} (%)	$r \times 10^{-15}$ (molec.C_7H_8/m^2 · s)	S (%)	Acidity (μeqv.$C_4H_9NH_2$/m^2)	Basicity (μeqv.C_6H_5COOH/m^2)	Amount of desorbed N_2O and N_2 ($\times 10^{-3}$ cm^3/m^2)
—	15.7	—	2.20	1.89	—
2.0	19.0	39.5	2.01	2.21	1.60
5.7	21.7	90.8	1.65	2.74	2.40
10.0	23.1	93.5	1.46	3.26	3.19
15.0	23.6	95.0	1.19	3.89	3.29

centration, in linear proportion to the rate of toluene ammoxidation (Table 2).

Temperature-Programmed Reactions of Toluene and Ammonia

Temperature-programmed desorption of toluene from an oxidized surface of the catalyst leads to the appearance of two maxima in the spectrum: one at low temperature (~225°C) and one at high temperature (~410°C) (Fig. 3a). Chromatographic analysis of the desorption products showed that the high-temperature peak corresponds to the products of complete oxidation (CO_2, H_2O) and demethylation (C_6H_6) of toluene. The low-temperature peak consists of carbon dioxide, water, benzaldehyde, and reversibly chemisorbed toluene. However, the total content of two latter compounds does not exceed 15–20%.

The same two-peak spectrum is observed for the temperature-programmed reaction of toluene to ammonia initially adsorbed on the oxidized catalyst at 400°C (Fig. 3b). Here also the high-temperature peak represents mainly CO_2, water, and benzene. Essential changes are established for the composition of low-temperature desorption products. With increasing quantities of preadsorbed ammonia, the content of benzonitrile increases to 85% versus 14% for benzaldehyde in experiments performed without initial adsorption of ammonia. The proportion of the low-temperature peak in the whole amount of desorbed substances also increases from 1.2 to 26.7%.

In the third series of experiments, ammonia was adsorbed on the catalyst containing adsorbed toluene and the temperature-programmed reaction was carried out. In this case, the general structure of the TPR spectra remained the same. The composition of

TABLE 3

Effect of Initial Ammonia Adsorption on Toluene Oxidation at 400°C

Pulses	Adsorbed 0.013 ml NH_3/m^2 rx10^{-15} (molec.C_7H_8/m^2 · s)		Adsorbed 0.058 ml NH_3/m^2 rx10^{-15} (molec.C_7H_8/m^2 · s)	
	Total	Benzonitrile	Total	Benzonitrile
1	14.7	6.14	18.0	7.42
2	13.4	1.28	14.1	2.75
3	12.8	—	13.1	0.32
4	12.8	—	12.8	—

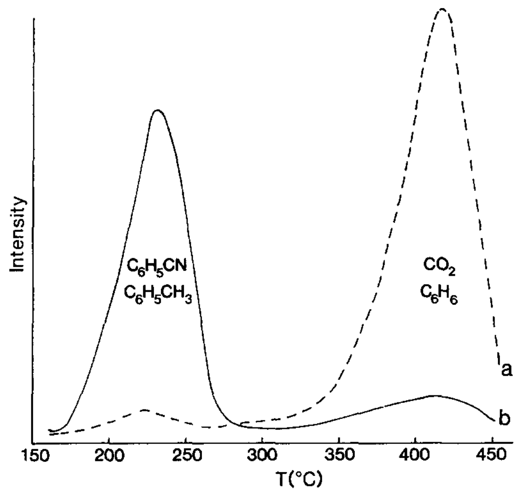


FIG. 3. Temperature-programmed reactions of toluene on (a) oxidized and (b) ammonia-covered catalyst surfaces.

desorbed products depends significantly on the temperature of the preliminary adsorption of toluene. The low-temperature reaction of ammonia to toluene adsorbed at 175°C leads mainly to production of benzonitrile, the concentration of which amounts to 90% of the desorption products. If toluene is adsorbed on the oxidized catalyst at a temperature that is higher (400°C) than that sufficient for the formation of its deeply oxidized surface structures, the interaction between adsorbed toluene and ammonia does not proceed selectively with respect to benzonitrile even in the low-temperature region; about 75% of the products desorbed at 175–290°C represent carbon dioxide.

Similar experiments carried out with benzonitrile showed that the preliminary adsorbed ammonia also decreases the overoxidation of benzonitrile.

Infrared Spectra of Adsorbed Toluene and Ammonia

Infrared spectra of ammonia adsorbed on an oxidized surface of the catalyst at room temperature reveal two forms with absorption bands at 1235, 1615, and 1445 cm^{-1}, respectively. The first corresponds to a Lewis acid site, and the second is an ammonium ion arising from the interaction of ammonia with protons delocalized from Brønsted acid sites. Because they are sufficiently thermostable, these species are removed upon heating under vacuum at temperatures above 300°C. Calcination of the catalyst under ammonia at 200–300°C followed by evacuation at the same temperature leads to the appearance of several absorption bands in the region 1510–1590 cm^{-1} that can be assigned to the dehydrogenated ammonia species $(NH_{3-n})^{-n}$ (*6, 7*). The intensity of these bands decreases when hydrogen is introduced into the cell. Simultaneously, the absorption bands of ammonium cations and coordinated ammonia appear in the spectrum.

Room temperature adsorption of toluene on an oxidized catalyst surface (heated under oxygen at 500°C) produces adsorbed species whose spectrum is presented in Fig. 4b. Evacuation at 20°C causes the desorp-

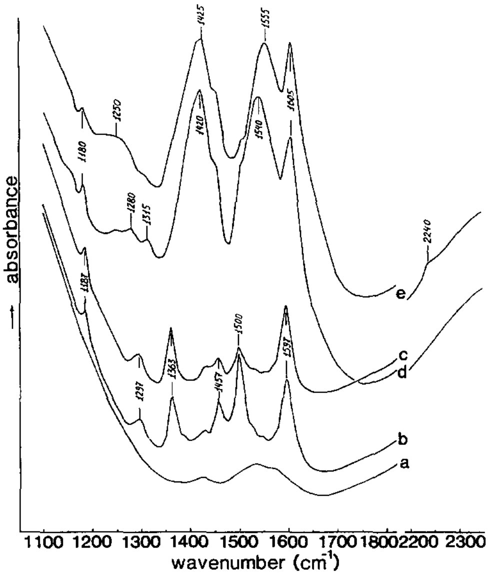


FIG. 4. Infrared spectra of (a) oxidized catalyst and of toluene (b) adsorbed at 20°C, (c) after evacuation at 20°C, (d) after heating under toluene at 350°C, and (e) after evacuation at 200°C, followed by contact with ammonia at 200°C.

tion of weakly bound toluene accompanied by decreases in the ring vibrations at 1457, 1500, and 1603 cm^{-1} and in the δCH_3 vibrations at 1380 cm^{-1}, but leaves on the surface the strongly adsorbed toluene responsible for bands at 1187, 1297, 1363, 1457, 1500, and 1597 cm^{-1} (Fig. 4c). This species is identified as a carbonium ion, $C_7H_9^+$, which has been observed earlier on supported MoO_3(8) and V_2O_5 (*9*). Detailed analysis of data reported elsewhere (*10*) shows that it probably also exists on the surface of the V–Ti oxide catalyst. At room temperature, the carbonium ion is substituted for the ammonium ion when gaseous ammonia introduced into the cell contacts strongly adsorbed toluene. This fact is evidence that the latter is being formed with the participation of Brønsted acid sites.

The $C_7H_9^+$ species is demolished by a brief heating at 100°C. Further heat treatment at 200°C leads to the appearance of two strong absorption bands at 1420 and 1540 cm^{-1}, which are ascribed to the symmetric and asymmetric stretching vibrations of the carboxylate group (*11*). Absorptions of vibrations in the benzene ring are also observed (Fig. 4d). This spectrum is therefore identified as an adsorbed benzoate ion, $C_6H_5COO^-$. The formation of the same structure on the surface of some oxide catalysts has been previously reported (*2, 9, 10*). The intensity of its bands increases when the temperature is raised to 400°C. The benzoate structures arising upon calcination of the catalyst under toluene at 350°C are able to react with gaseous ammonia, producing benzonitrile at temperatures as low as 200°C. As Fig. 4e shows, the spectrum obtained after the reaction with ammonia contains an absorption band at 2240 cm^{-1} which is due to a cyano group attached to alkylbenzenes (*12*). The intensity of this band increases with increasing interaction temperature, becoming maximum at 400°C.

The essentially different behavior of adsorbed toluene is observed on the catalyst surface treated initially with a mixture of ammonia and oxygen at 400°C. Room temperature adsorption of toluene on such a surface (Fig. 5b) leads also to the formation of carbonium ions, $C_7H_9^+$, but their concentration is considerably lower than that on the oxidized surface of the catalyst (Fig. 4b). Heating at 100°C (Fig. 5c) removes the characteristic absorption bands at 1187, 1297, and 1363 cm^{-1} and leaves the bands caused by vibrations of methyl groups (1390 cm^{-1}) and aromatic rings (1457, 1502, 1605 cm^{-1}). The band at 1430 cm^{-1}, whose intensity increases as the temperature and the time of toluene contact with the catalyst increase, is assigned to the symmetric valent vibrations of the CH_2 group in the adsorbed benzyl fragment. The same band has been observed in the spectrum of benzyl species adsorbed on ZnO (*13*). The spectrum of toluene adsorbed at 150°C (Fig. 5d) shows bands at 2280 and 1660 cm^{-1}, which are characteristic of the valent vibrations of C≡N and C=N bonds, respectively (*14*). When the temperature is raised, the intensity of these bands is enhanced, reaching a maximum at 250°C. At higher temperatures, the intensity decreases and is accompanied by an increase in the intensity of benzoate ion vibrations with frequencies at 1420 and 1540 cm^{-1}

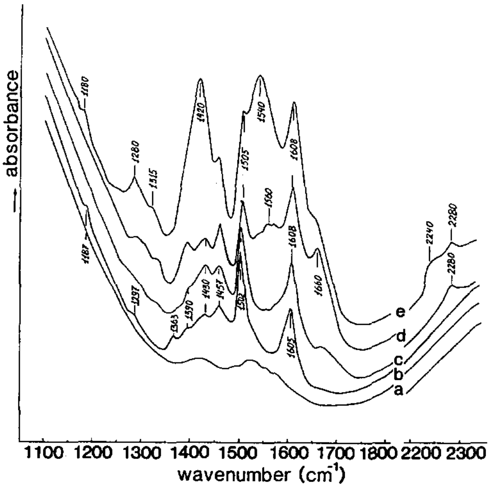


FIG. 5. Infrared spectra of (a) a catalyst treated with the ammonia–oxygen mixture at 400°C and of toluene adsorbed at (b) 20, (c) 100, (d) 150, and (e) 300°C.

(Fig. 5e) that can be attributed to the gradual consumption of nitrogen-containing species on the catalyst surface.

On the catalyst surface treated with pure ammonia at 400°C, toluene is adsorbed at room temperature in the form of a weakly bound complex. The interaction of toluene with such a catalyst at temperatures of 150°C and higher leads to the formation of many of the above-mentioned surface species, but the intensities of their absorption bands in the spectra are extremely low. The admission of a toluene and oxygen mixture at 300°C produces benzoate structures whose reactivity with respect to ammonia is high in comparison with that of structures formed on the oxidized catalyst surface. When a mixture of toluene, oxygen, and ammonia is admitted to the catalyst, benzoate ions are not observed in the spectrum and a band with a maximum at 2240 cm^{-1}, which is characteristic of weakly bound benzonitrile (not corresponding to a Lewis acid site), appears.

DISCUSSION

Pulse measurements carried out for toluene ammoxidation have revealed that intensive formation of benzonitrile takes place when toluene is admitted to adsorbed ammonia, but not the reverse. The presence of ammonia species on the catalyst surface accelerates the overall toluene conversion by creating new sites that participate in the mild activation of hydrocarbon. During steady state, the ammoxidation rate coincides with the rate of benzonitrile production during the interaction of the toluene and ammonia mixture with the oxygen on the catalyst surface. This is clearly demonstrated by the pulse data listed in Table 4. This observation is evidence of the redox mechanism for toluene ammoxidation over the catalyst studied. Investigation of temperature-programmed reactions of toluene and ammonia has established that the ammoxidation reaction occurs selectively on an ammonia-covered catalyst surface, whereas on an oxidized surface the deep oxidation of toluene predominates. On the basis of these findings, the reaction mechanism can be written as

$$(1)\ Z + O_2 \xrightarrow{k_1} ZO_2 \qquad 3/2$$

$$(1')\ ZO_2 + Z \xrightarrow{\text{fast}} 2\,ZO \qquad 3/2$$

$$(2)\ ZO + NH_3 \xrightarrow{k_2} ZNH + H_2O \qquad 1$$

$$(3)\ ZNH + C_6H_5CH_3 \xrightarrow{k_3} ZC_6H_5CH_2NH_2 \qquad 1$$

$$(3')\ ZC_6H_5CH_2NH_2 + 2\,ZO \xrightarrow{\text{fast}} C_6H_5CN + 2\,H_2O + 3\,Z \qquad 1$$

$$C_6H_5CH_3 + NH_3 + 3/2\,O_2 = C_6H_5CN + 3\,H_2O,$$

where ZO and Z denote the oxidized and reduced active sites. Steps 1 and 1′ constitute the stage of catalyst reoxidation. It is thought that oxygen is adsorbed in a molecular form, followed by rapid dissociation to an appropriate form available for the reaction. A reduction in catalyst surface takes place after steps 2, 3, and 3′. At this stage, the surface intermediates of imide (ZNH) and benzylamine ($ZC_6H_5CH_2NH_2$) types are being formed. The latter undergoes further oxidative dehydrogenation to benzonitrile via benzylimine as an intermediate compound. Under similar conditions, the rate of this process is 10 times higher than the rate of toluene ammoxidation, and therefore step 3′ is accepted as being the fastest.

The above mechanism corresponds to the kinetic equation

$$r = \frac{2\,k_1k_2k_3P_{NH_3}P_{O_2}}{2\,k_1k_3P_{C_7H_8}P_{O_2} + 2\,k_1k_2P_{NH_3}P_{O_2} + 3\,k_2k_3P_{C_7H_8}P_{NH_3}}$$

which fairly well describes the data obtained. The extent of agreement between experimental and calculated rates is illustrated in Fig. 6. The average difference between the experimental and the calculation

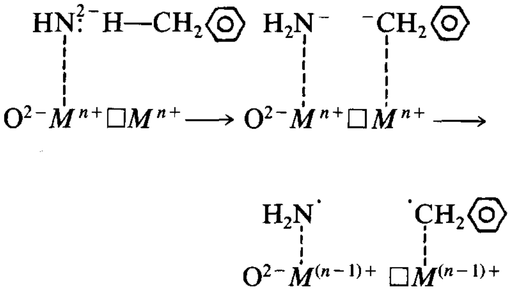
TABLE 4

Rates and Selectivities of Benzonitrile Formation in Catalytic Reaction (RON) and Reduction (RN) of a Steady-State Catalyst

T (°C)	Pulse composition	Toluene conversion (%)	$r \times 10^{-15}$ (molecules $C_7H_8/m^2 \cdot s$)	S (%)
272	RON	78.0	20.8	98.6
	RN	53.4	14.4	99.2
	RON	78.0	20.9	99.1
320	RON	77.0	39.4	95.3
	RN	67.5	35.8	96.8
	RON	75.8	38.6	95.7
400	RON	81.0	190.2	92.7
	RN	71.8	180.0	94.4
	RON	79.7	188.9	93.4

rate is equal to 11.3%. The maximum divergence in single experiments does not exceed 35%.

The mechanism under consideration is also applicable to ammoxidation reactions of more complex alkylaromatic compounds. With xylenes, for instance, the steps for ammoxidation of the second methyl group must complete the mechanism. These steps can be realized by a consecutive as well as by a parallel process. Correspondingly, there will be variations of this mechanism, which can be conditionally named the dehydrogenation mechanism in contrast to the oxidation mechanism according to whether the ammoxidation reaction proceeds via aromatic aldehyde or acid. A similar dehydrogenation mechanism has been proposed recently (*15*), but with one essential difference. Otamiri and Andersson (*15*) assume that the hydrogen abstracted from the methyl group is bound to the surface oxygen or hydroxyl. In our study, the cleavage of methyl C–H bonds occurs through the participation of ammonia-adsorbed species such as NH^{2-}. With its unshared pair of electrons, the nitrogen atom is able to promote a heterolytic dissociation of the chain C–H bond polarized by superconjugation with the aromatic ring. From this point of view, the kinetic scheme of the reaction mechanism given above should be modified to reflect the interaction between toluene and adsorbed ammonia. The corresponding step 2 may be detailed as



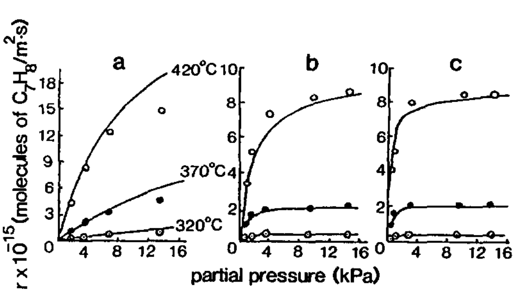


FIG. 6. Rate of benzonitrile production as functions of (a) toluene, (b) ammonia, and (c) oxygen partial pressure at various temperatures (lines, calculation; points, experiment).

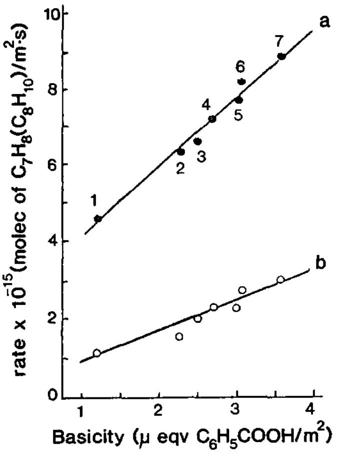


FIG. 7. Rates of (a) toluene and (b) *m*-xylene ammoxidation at 360°C as functions of basicity of V–Sb–Bi catalysts (1) without additive and containing (2) Li_2O, (3) Na_2O, (4) K_2O, (5) MgO, (6) CaO, and (7) BaO.

Here M^{n+}, O^{2-}, and □ are the surface metal cation, oxygen anion, and oxygen vacancy, respectively. The presence of the latter on a steady-state surface is revealed by pulse experiment data.

Thus it is thought that the hydrogen abstracted in a protonic form associates with the surface NH^{2-} group, whereas the carbanion is stabilized near the metal cation. Such a mechanism of mild toluene activation assumes that the hydrocarbon acts as a CH acid and that the catalyst plays the part of the solid base. The rate of this interaction should increase when the hydrocarbon acidity, as well as the catalyst basicity, is enhanced. Both these models have been tested.

The data on alkylaromatic reactivity presented in Table 1 indicate that the substitution of hydrogen atoms in the α-position on the benzene ring for methyl groups leads to a decrease in the rate of hydrocarbon mild oxidation along the chain C–H bond. The same effect is observed when the methyl group substitutes the hydrogen atom in the ring. It is evident that toluenes substituted for electron-donating substituents are less reactive than unsubstituted toluene. According to Ref. (16), such a result is evidence in favor of an ionic mechanism of hydrocarbon activation proceeding via a carbanion-like intermediate. This idea is also supported by a comparison of the ammoxidation rate to the kinetic acidity of alkylaromatic compounds characterized by the relative rate of base-catalyzed isotopic exchange of α-hydrogen atoms (*17*). As Table 1 shows, the reactivity in ammoxidation of the hydrocarbons under study is in a conformity with their CH acidity.

Validation of the second model can be shown by modifying the V–Sb–Bi oxide system with small amounts of alkali and alkaline earth metal oxides. Addition of 0.2 wt% of these compounds to the catalyst enhances by two to three times its activity for toluene and *m*-xylene ammoxidation (Fig. 7). Such a promoting effect cannot be ascribed to an increase in the mobility of catalyst oxygen because there is no notable difference in the energies of the surface oxygen bond for the unmodified and modified samples (Fig. 8). At the same time, the addition of alkali and alkaline earth elements to the catalyst decreases its acidity and enhances its basicity. Moreover, a linear correlation between the rate of ammoxidation and the concentration of basic sites on the catalyst surface is observed (Fig. 7). These results allow us to interpret the promoting effect under consideration as an increase in the amount of surface basic sites that participate in catalysis. The functions of basic sites can

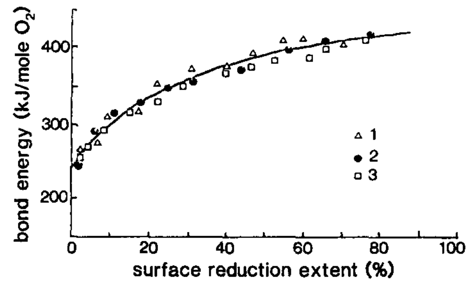


FIG. 8. Energies of oxygen bond for V–Sb–Bi catalysts (1) unmodified and modified with (2) K_2O and (3) BaO vs the extent of catalyst surface reduction.

be performed by the surface oxygen ions, adsorbed ammonia, and other nucleophilic species possessing an affinity for protons.

Thus, our data suggest that the first step in the interaction of alkylaromatic hydrocarbon with a steady-state V–Sb–Bi catalyst is the heterolytic abstraction of α-hydrogen to produce negatively charged benzyl species. Then, by means of one electron transfer to the catalyst, this species is transformed to the corresponding radical capable of recombining with the NH_2 radical to form aromatic amine, which is further rapidly dehydrogenated to nitrile via imine intermediate. Many of these compounds, as discussed under Results, have been detected spectroscopically on the catalyst surface by studying the adsorption of toluene and ammonia. Judging from the intensities of the absorption bands, their relative contents strongly depend on the state of the catalyst surface. Dehydrogenated ammonia species like NH_2 and NH are formed in measurable quantities on the reduced and deprotonated surface obtained by successive high-temperature treatments of catalysts in ammonia and under vacuum. Benzyl structures are observed on surfaces treated at 400°C with a mixture of oxygen and ammonia and are not detected on oxidized surfaces or those treated with pure ammonia. Apparently, optimal surface reduction is necessary for the effective generation of benzyl species. Chemical reactions of this species on ammonia-covered surfaces at higher temperatures lead to the appearance of imine- and nitrile-like surface structures that are formed successively according to changes in the intensities of the characteristic absorption bands. This observation supports the idea that the ammoxidation reaction proceeds over the catalyst studied via amine and imine intermediates, even though the benzylamine structure has not been detected because of its very fast conversion. When the adsorbed ammonia becomes exhausted, the benzyl species undergoes oxidation to benzoate ion, which is able to react with ammonia, giving benzonitrile.

On a clean oxidized catalyst surface containing a considerable number of Brønsted acid sites, toluene is adsorbed mainly at room temperature in the protonated form, $C_7H_9^+$. Upon heating under toluene, $C_7H_9^+$ is oxidized by the catalyst oxygen to a strongly bound benzoate structure that can be removed from the surface by means of overoxidation at 400–500°C or by reaction with ammonia at lower temperatures. Adsorption of toluene on the oxidized surface at temperatures similar to those of catalytic reaction (300–400°C) results in the formation of deeply oxidized surface structures that are desorbed, according to the TPR data, as CO_2 and water. Their reaction with ammonia occurs nonselectively with respect to benzonitrile. These results indicate that the initially adsorbed ammonia not only accelerates the mild hydrocarbon activation but also prevents its deep oxidation when adsorbed at high temperatures.

In conclusion, it should be noted that the proposed mechanism is expected to occur on ammoxidation catalysts that are active in oxidative dehydrogenation and not selective in partial oxidation of hydrocarbons. Over these catalysts, ammoxidation reactions occur selectively at ammonia concentrations much higher than that of the stoichiometric requirement. By this means, the activating effect of ammonia with respect to hydrocarbon oxidation takes place. The absence of these external features may point to the existence of another mechanism. For instance, according to Refs. (*10, 18, 19*), the vanadium–titanium oxide catalyst is somewhat effective in toluene oxidation to benzaldehyde as well as in its ammoxidation. Benzonitrile productivity shows a maximum at an ammonia concentration that is close to stoichiometric. Ammonia has an inhibiting effect on toluene conversion. Doping of the catalyst with an alkali element (cesium) decreases its activity. And finally, the substituted toluenes, with both electron-donating and electron-withdrawing substituents, demonstrate a reactivity higher than that of unsubstituted toluene. In our opinion, such behavior of the V–Ti catalyst confirms the oxidation mechanism according to which nitrile is produced via the benzaldehyde intermediate. As for toluene activation, it may proceed in two ways: (i) by homolytic cleavage of the methyl C–H bond with formation of a benzyl radical, or (ii) by heterolytic dissociation of the same bond with formation of a cation-like benzyl species. The first variant of this oxidation mechanism together with the benzylamine route is accepted by Busca *et al.* (*10*).

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