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Kinetics and Mechanisms in the Ammoxidation of Toluene over a TiO₂(B)-Supported Vanadium Oxide Monolayer Catalyst. 2. Combustion Reactions

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To obtain knowledge about combustion mechanisms operating in the ammoxidation of toluene, the formation of carbon oxides was studied over a TiO₂(B)-supported vanadium oxide catalyst with monolayer loading. The partial pressures of reactants were varied and kinetic rate expressions, completely describing experimental data, were derived. A comparison of the expressions obtained with those for the formation of nitrile and aldehyde shows that carbon oxides are formed at sites that are not involved in the mechanism of partial oxidation. Furthermore, CO₂ and CO are formed in routes having a common type of active ensemble. All of the adsorption steps are fast and in equilibrium. For the formation of CO₂ and CO, the rate-limiting step in both cases comprises a chemical transformation of which the details are unknown. The introduction of ammonia leads to a strong decrease of the rates for formation of carbon oxides.

For selective oxidation and ammoxidation of alkylaromatic compounds, the preferred catalysts consist of vanadium oxide supported on TiO₂ (Sanati and Andersson, 1990a). Several studies have been devoted to their characterization in order to determine the structure of the catalytically active and selective surface phase (Wachs et al., 1985; Kozlowski et al., 1983; Bond et al., 1986; Busca et al., 1986; Cavani et al., 1987; Haber et al., 1986; Bond and Flamerz, 1989). However, in this context, not much information has been obtained specifically on the source of formation of carbon oxides. In a study of the oxidation of *o*-xylene, Wachs et al. (1985) concluded that exposed titania sites lead to combustion of partial oxidation products. Later, they reported that carbon oxides can also be directly formed from *o*-xylene at vanadium oxide monolayer species (Saleh and Wachs, 1987). Mechanistic studies of oxidation and ammoxidation of toluene on V-Ti-O catalysts using infrared spectroscopy (van Hengstum et al., 1986; Busca et al., 1987; Miyata et al., 1988) have been concerned mainly with the routes for formation of aldehyde and nitrile, respectively. Recently, a dynamic approach to selectivity in heterogeneous partial oxidation was published (Cavani et al., 1988). According to this approach, which is a further development of the concept of site isolation (Callahan and Grasselli, 1963), the selectivity for the useful product is at maximum at a well-defined degree of surface oxidation.

For the formations of nitrile and CO₂, the existence of a common adsorbed precursor or intermediate has been concluded in some kinetic studies of the ammoxidation of alkylaromatics over catalysts containing vanadium (Prasad and Kar, 1976; Das and Kar, 1979; Cavalli et al., 1987b). In a comprehensive kinetic study of the ammoxidation of toluene over V₂O₅, however, it was concluded that there is no common intermediate for the nitrile and combustion routes (Otamiri and Andersson, 1988). Also, in a temperature programmed reaction study of 3-picoline amm-

oxidation over reduced vanadium oxides, the stability against degradation of both nitrile and its preceding intermediate complex was demonstrated (Andersson et al., 1984).

Knowledge about combustion mechanisms is of vital importance in deciding possible actions for improvement of catalyst performance (Otamiri and Andersson, 1988). In this article we present a detailed kinetic investigation of the formation of carbon oxides in the ammoxidation of toluene over a TiO₂(B)-supported vanadium oxide monolayer catalyst. The kinetics and mechanisms for selective reactions are described in the preceding article (Sanati and Andersson, 1990a).

Experimental Section

Experimental details, which are completely described elsewhere (Sanati and Andersson, 1990a), are summarized here. The support, obtained by acidic hydrolysis of K₂-Ti₄O₉ (Sanati and Andersson, 1990b), was impregnated with a toluene solution of VOCl₃ and was further calcined in air at 500 °C. According to atomic absorption analysis, the vanadium content was 11.6 μmol of V/m² of support.

Kinetic experiments were carried out at atmospheric pressure using a differential plug flow reactor. Measurements were made at three temperatures, namely, 340, 370, and 400 °C. The reactant pressures were varied in the ranges as follows: oxygen (*P*_O), 2.85-28.5 kPa; toluene (*P*_T), 0.38-1.28 kPa; and ammonia (*P*_A), 0-5.71 kPa. It was verified that the rate measurements were not controlled by mass- and heat-transfer gradients.

Results

Influence of Partial Pressure of Oxygen. The variation of the rate for formation of CO₂ (*r*_{CO₂}) with the partial pressure of oxygen at a high and at a low partial pressure of ammonia is given in Figures 1 and 2, respectively. The corresponding rate dependence for the for-

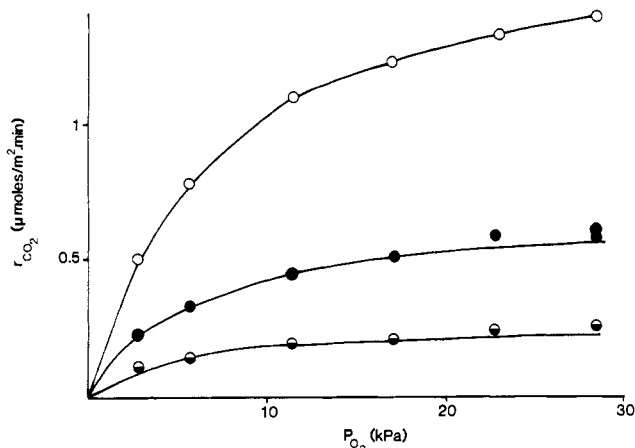


Figure 1. Rate for formation of CO_2 as a function of partial pressure of oxygen at (◐) 340, (●) 370, and (○) 400 °C. $P_A = 2.85$ kPa and $P_T = 0.77$ kPa.

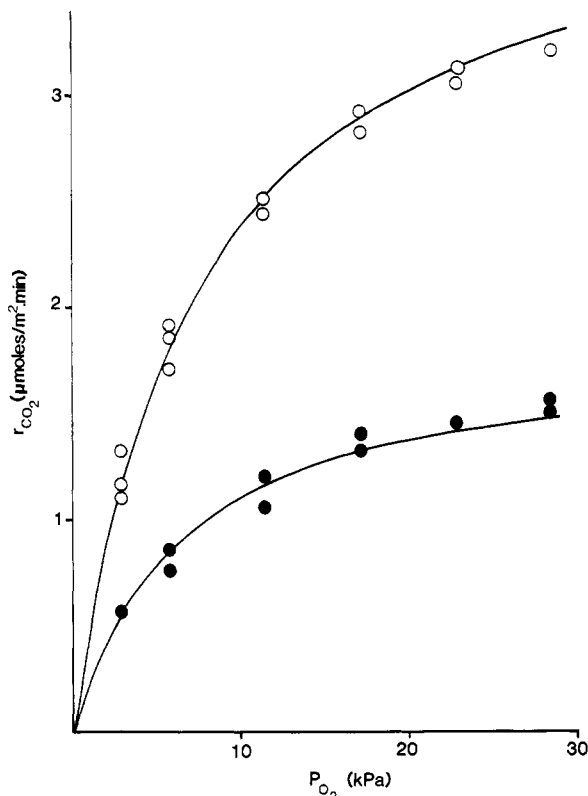


Figure 2. Rate for formation of CO_2 as a function of partial pressure of oxygen at (●) 370 and (○) 400 °C. $P_A = 0.14$ kPa and $P_T = 0.77$ kPa.

mation of CO (r_{CO}) is given in Figures 3 and 4. A comparison shows that the rate of formation of CO_2 , at all pressures, is higher than that for the formation of CO. For both products, plots of $1/r$ versus $1/P_O$ show that the rate dependence is of the general form

$$r = a_1 P_O / (1 + a_2 P_O) \quad (1)$$

where a_1 depends on the partial pressure of ammonia. Both a_1 and a_2 might also depend on the partial pressure of toluene.

Influence of Partial Pressure of Ammonia. Figures 5 and 6 show the influence of the partial pressure of ammonia on the rate for formation of CO_2 and CO, respectively. In both cases it is observed that, with a small increase in the partial pressure of ammonia, the rate rapidly decreases to less than half of the value obtained in the absence of ammonia. At a high partial pressure of am-

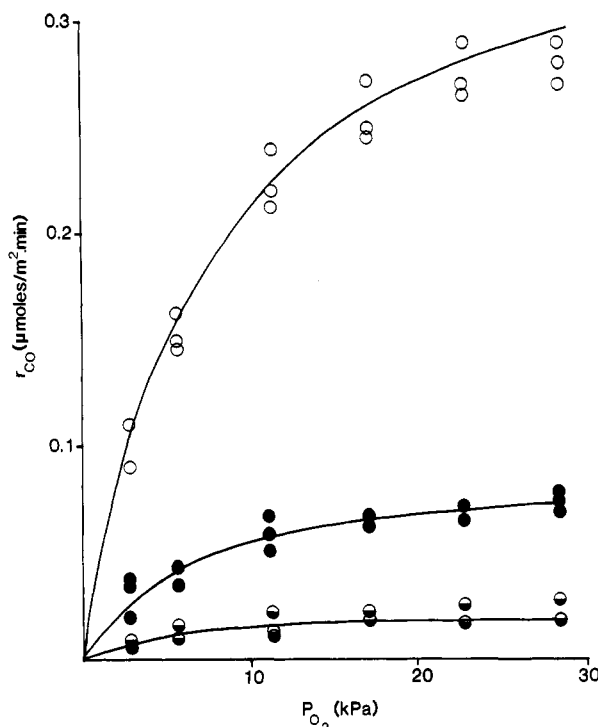


Figure 3. Rate for formation of CO as a function of partial pressure of oxygen at (◐) 340, (●) 370, and (○) 400 °C. $P_A = 2.85$ kPa and $P_T = 0.77$ kPa.

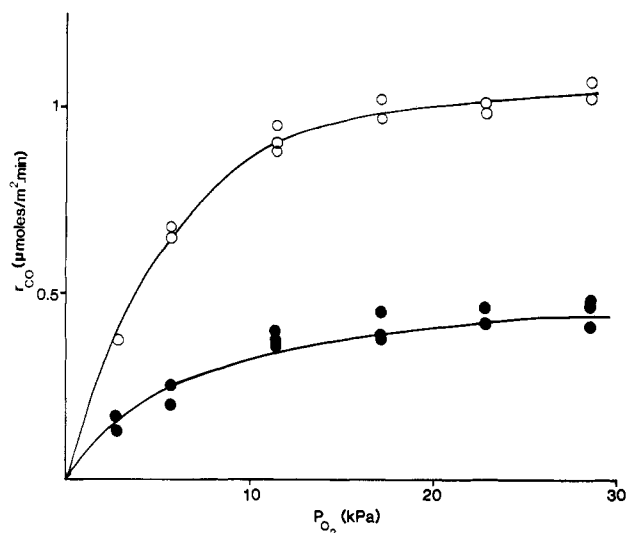


Figure 4. Rate for formation of CO as a function of partial pressure of oxygen at (●) 370 and (○) 400 °C. $P_A = 0.14$ kPa and $P_T = 0.77$ kPa.

monia, the rates tend to a constant value. It is also apparent that ammonia influences the formation of CO more than that of CO_2 .

From analysis of experimental data by plotting inverse rate versus partial pressure of ammonia, and the corresponding linearized form, it can be concluded that the dependencies observed for the formations of carbon oxides are of the form

$$r = (a_3 + a_4 P_A) / (1 + a_5 P_A) \quad (2)$$

From the fact that the rates exhibit invariance with respect to partial pressure of oxygen at low and high pressures of ammonia, Figures 1–4, it follows that combination of (1) and (2) gives

$$r = (a_6 P_O + a_7 P_O P_A) / (1 + a_8 P_O + a_9 P_A + a_{10} P_O P_A) \quad (3)$$

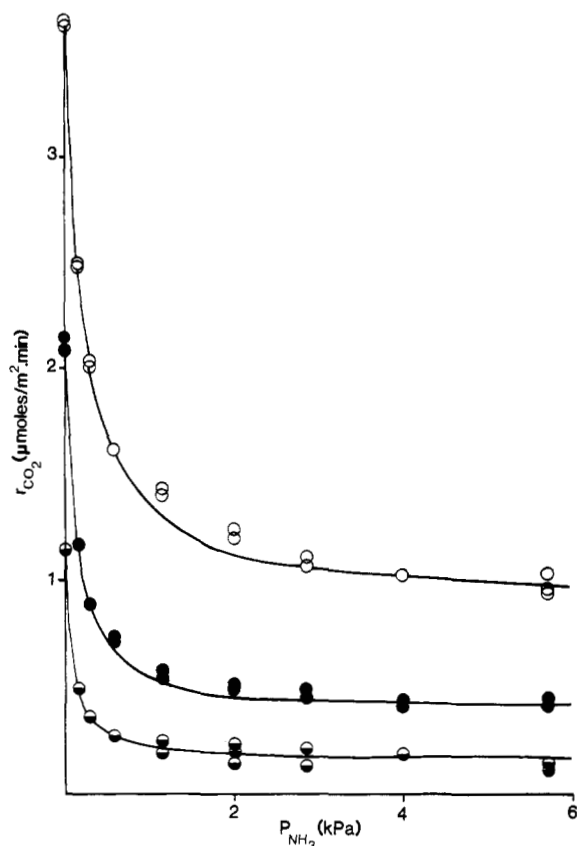


Figure 5. Effect of partial pressure of ammonia on rate for formation of CO_2 at (○) 340, (●) 370, and (○) 400 °C. $P_O = 11.4$ kPa and $P_T = 0.77$ kPa.

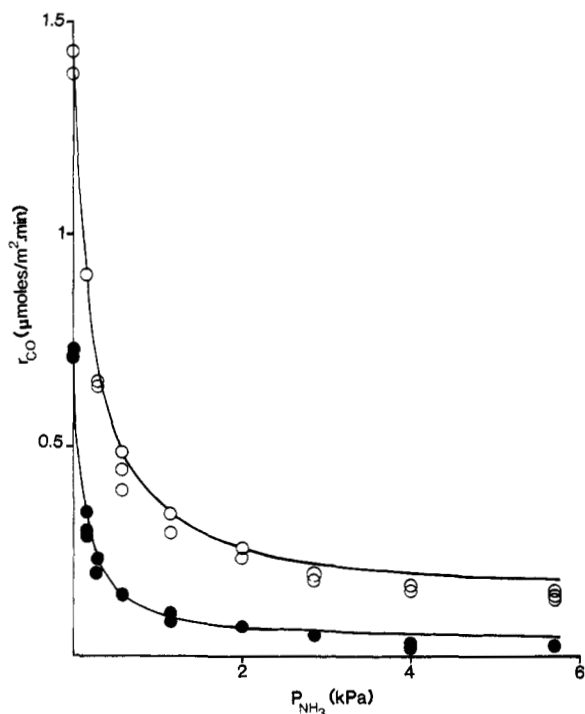


Figure 6. Effect of partial pressure of ammonia on rate for formation of CO at (●) 370 and (○) 400 °C. $P_O = 11.4$ kPa and $P_T = 0.77$ kPa.

where a_i , $i = 6, \dots, 10$, are possibly functions of the partial pressure of toluene.

Influence of Partial Pressure of Toluene. Series of experiments were run varying the partial pressure of toluene at various constant pressures of oxygen and ammonia. The rates measured for the formation of carbon oxides are

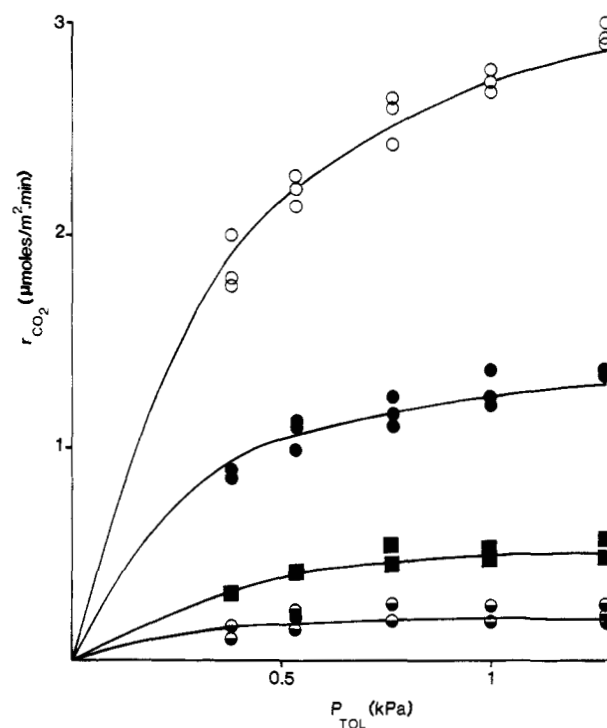


Figure 7. Variation of rate for formation of CO_2 with partial pressure of toluene at $P_O = 11.4$ kPa. (○) 340 °C, $P_A = 2.85$ kPa; (■) 370 °C, $P_A = 2.85$ kPa; (●) 370 °C, $P_A = 0.14$ kPa; and (○) 400 °C, $P_A = 0.14$ kPa.

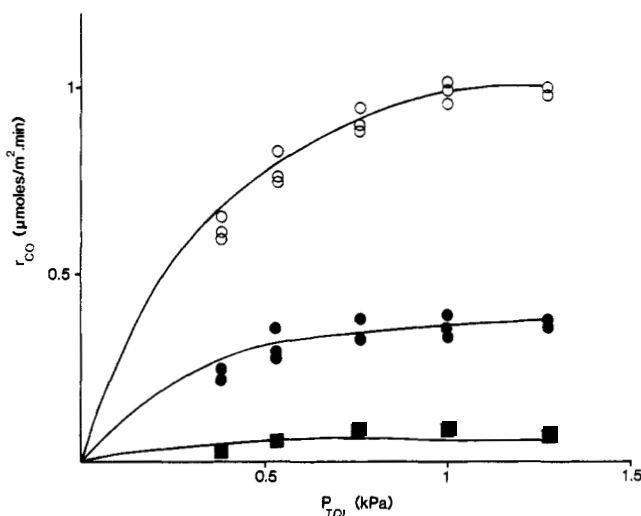


Figure 8. Variation of rate for formation of CO with partial pressure of toluene at $P_O = 11.4$ kPa. (■) 370 °C, $P_A = 2.85$ kPa; (●) 370 °C, $P_A = 0.14$ kPa; and (○) 400 °C, $P_A = 0.14$ kPa.

presented in Figures 7–9. In each series the data could be fitted to a straight line when $1/r$ versus $1/P_T$ was plotted, which shows that the dependencies for carbon oxides can be expressed as

$$r = a_{11}P_T/(1 + a_{12}P_T) \quad (4)$$

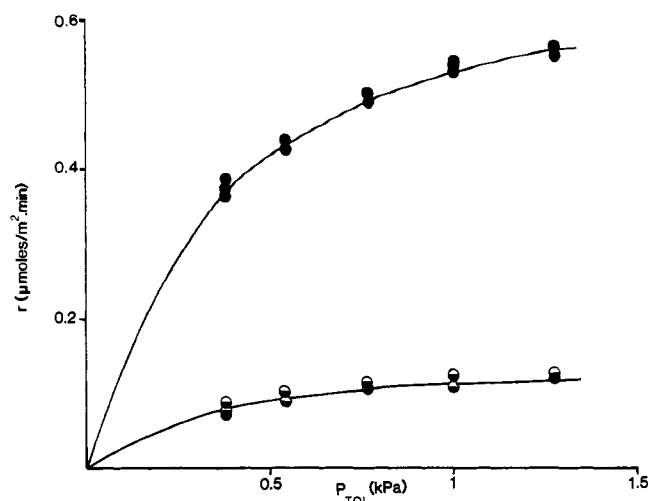
It was found that a_{11} is a function of the partial pressures of oxygen and ammonia, while a_{12} is a real constant. Final rate expressions that fit to all the data were obtained by combining equations of the general forms expressed by (3) and (4). This gave the equations below:

$$r_{\text{CO}_2} = (n_1P_OP_T + n_2P_OP_AP_T)/(1 + n_3P_O + n_4P_A + n_5P_T + n_6P_OP_A + n_7P_OP_T + n_8P_AP_T + n_9P_OP_AP_T) \quad (5)$$

$$r_{\text{CO}} = (n_{10}P_OP_T + n_{11}P_OP_AP_T)/(1 + n_3P_O + n_4P_A + n_5P_T + n_6P_OP_A + n_7P_OP_T + n_8P_AP_T + n_9P_OP_AP_T) \quad (6)$$

Table I. Effective Constants and Apparent Activation Energies

	units	temperature, °C			E_{app} , kcal/mol
		340	370	400	
$n_1 = k_1 K_O K_T S_T$	$\text{mol}/(\text{m}^2 \cdot \text{min} \cdot \text{kPa}^2) \times 10^6$	2.47	2.91	3.42	4.9
$n_2 = k_2 K_O K_A K_T S_T$	$\text{mol}/(\text{m}^2 \cdot \text{min} \cdot \text{kPa}^3) \times 10^6$	4.75	4.35	3.97	-2.6
$n_3 = K_O$	kPa^{-1}	0.188	0.160	0.136	-4.5
$n_4 = K_A$	kPa^{-1}	13.8	8.16	4.81	-14.4
$n_5 = K_T$	kPa^{-1}	6.52	4.35	2.90	-11.0
$n_6 = K_O K_A$	kPa^{-2}	2.59	1.31	0.650	-18.9
$n_7 = K_O K_T$	kPa^{-2}	1.23	0.696	0.394	-15.5
$n_8 = K_A K_T$	kPa^{-2}	90.0	35.5	13.9	-25.4
$n_9 = K_O K_A K_T$	kPa^{-3}	16.8	5.68	1.90	-29.9
$n_{10} = k_1 K_O K_T S_T$	$\text{mol}/(\text{m}^2 \cdot \text{min} \cdot \text{kPa}^2) \times 10^7$	7.52	9.94	13.4	7.9
$n_{11} = k_2 K_O K_A K_T S_T$	$\text{mol}/(\text{m}^2 \cdot \text{min} \cdot \text{kPa}^3) \times 10^7$	1.86	3.37	6.27	16.7

Figure 9. Variation of rate for formation of CO_2 (●) and CO (○) with partial pressure of toluene. $P_O = 2.85 \text{ kPa}$ and $P_A = 2.85 \text{ kPa}$.

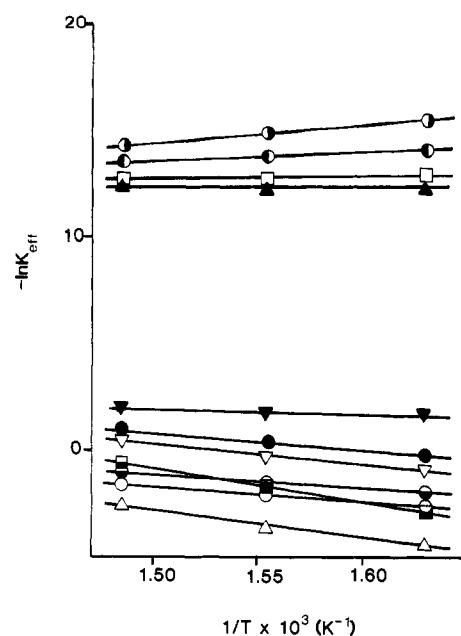
Calculation of Effective Constants. Values of the effective constants n_i , $i = 1, \dots, 11$, of (5) and (6) were calculated following the principles briefly outlined above. Obtained values are given in Table I together with the apparent activation energy values that were calculated from the Arrhenius plots shown in Figure 10. Calculated constants were used to draw the curves in Figures 1–9. It is seen that (5) and (6) perfectly describe the observed data.

Mechanism of Total Oxidation of Toluene. A reaction scheme that is in agreement with the final rate expressions for the formation of carbon oxides (see Appendix) is given in Figure 11. The relationships between the constants of each mechanistic step and those of (5) and (6) are included in Table I.

With reference to Figure 11, the active site, S, is considered to consist of a certain geometric configuration exposing vanadium ions, which serve as adsorption sites for the reactants. After adsorption of both toluene and oxygen, a surface reaction step is rate limiting. Subsequent steps, comprising further reaction with oxygen and formation of carbon oxides, are fast and equilibrated. A similar mechanism operates also when ammonia, in addition to oxygen and toluene, is adsorbed at the active ensemble.

Discussion

In studies of the ammoxidation of alkylaromatic compounds, it has frequently been concluded that there is a common intermediate for selective and nonselective reaction pathways (Prasad and Kar, 1976; Das and Kar, 1979; Cavalli et al., 1987b). Over a silver–cerium vanadate catalyst used in the ammoxidation of toluene (van den

Figure 10. Arrhenius plots of effective constants: (□) n_1 ; (▲) n_2 ; (▼) n_3 ; (○) n_4 ; (●) n_5 ; (▼) n_6 ; (●) n_7 ; (Δ) n_8 ; (□) n_9 ; (●) n_{10} ; (○) n_{11} .

Berg et al., 1984), the initial selectivity to nitrile was almost 100%, indicating that the carbon oxides obtained at high conversions are consecutively formed from nitrile. Figures 5 and 6 show that the rates for formation of carbon oxides steeply decrease with increase in partial pressure of ammonia. A similar behavior has also been observed by others in studies of the ammoxidation of toluene over anatase-supported vanadium oxide catalysts (Cavalli et al., 1987a,b). The decrease in rate was claimed to be due to the fact that ammonia stabilizes the initial intermediate of toluene activation and, thus, prevents it from being burnt off. In the case of the $\text{TiO}_2(\text{B})$ -supported monolayer catalyst used in the present investigation, a comparison of the rate dependence for formation of benzaldehyde on partial pressure of toluene obtained at a low pressure of ammonia (Sanati and Andersson, 1990a) with those for carbon oxides measured under identical conditions, Figures 7 and 8, clearly shows that carbon oxides are not formed from aldehyde. Concerning aromatic nitriles, they have been found stable against degradation (Prasad and Kar, 1976; Das and Kar, 1979; Andersson et al., 1984). Also, from a comparison of (5) and (6) with the rate equations for formation of nitrile and aldehyde (Sanati and Andersson, 1990a) it becomes obvious that carbon oxides are initial products formed in a separate route parallel to the route for formation of selective products. The observed decrease in rate for combustion with increase in partial pressure of ammonia, according to the mechanism in Figure 11, is mainly due to the introduction of a new re-

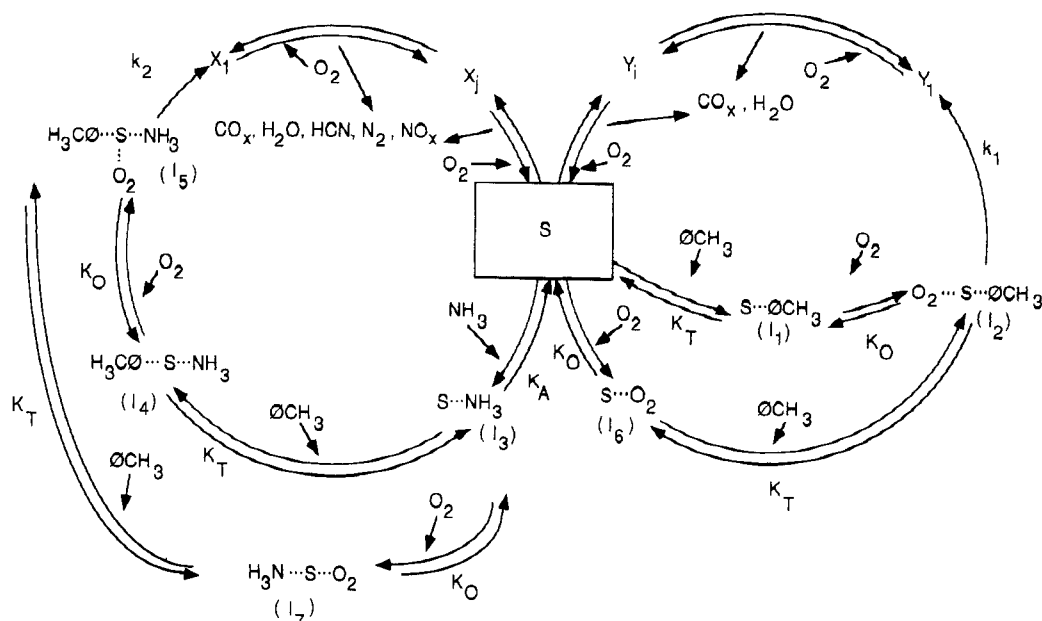


Figure 11. Reaction mechanism for combustion of toluene.

action pathway through new intermediates. Measurements of conversions to CO_2 and CO as a function of residence time showed that consecutive formation of CO_2 from CO was negligible under the differential conditions used in the present investigation. Comparison with thermodynamic data (Stull et al., 1969), also involving the water gas shift reaction, showed that the CO_2/CO ratios measured did not correspond to equilibrium values.

In a kinetic investigation of the ammoxidation of toluene over crystalline V_2O_5 (Otamiri and Andersson, 1988), it was observed that carbon oxides and the products of partial oxidation are formed at different types of sites. Studies of the oxidation of *o*-xylene (Gasior and Machej, 1983) and the ammoxidation of 3-picoline (Andersson et al., 1986) over V_2O_5 have shown that phthalic anhydride and nicotinonitrile, respectively, are formed at (010) planes. Combustion was in both cases correlated to the presence of (100) and (001) planes. A characteristic of the latter two types of faces is that they have projecting, structurally undercoordinated oxygen species, which are electrophilic reagents, while the (010) plane exposes double bonded oxygen species (Andersson et al., 1986). Over MoO_3 , it was observed that both benzonitrile and carbon oxides are formed from toluene, principally at the terminations in the [001] direction (Andersson and Hansen, 1988). In addition to cations, these terminations were demonstrated to expose both double bonded and undercoordinated oxygen species. A general conclusion was drawn considering the results just mentioned together with those reported on the oxidation of propylene and isobutene over MoO_3 (Volta and Tati-bouet, 1985; Volta et al., 1984). Namely, the presence of both oxygen vacancies and double bonded oxygen species at the surface is a prerequisite for selective reaction to occur, and electrophilic, strongly undercoordinated, oxygen species are the source for formation of carbon oxides. Additional evidence for this conclusion exists in the literature (Haber, 1985; Gasymov et al., 1982). Consequently, the site active for carbon oxide formation, denoted as S in Figure 11, possibly consists of an ensemble of cations at which the reactants can adsorb. Dioxygen is probably adsorbed in the form of O_2^- species, which can dissociate, giving O^- species. Both types of species have electrophilic character. Also, considering the site isolation theory (Callahan and Grasselli, 1963; Cavani et al., 1988), it cannot be excluded that carbon oxides are formed either at a

surface ensemble having an overabundance of active oxygen species in the nearest proximity of the adsorption site or because of too strong chemisorption of the hydrocarbon. In a previous report (Sanati and Andersson, 1990b), it was concluded that the monolayer on $\text{TiO}_2(\text{B})$ consists of interconnected tetrahedrally coordinated V^{4+} species having one vanadyl oxygen bond. These species were thought to be responsible for nitrile and aldehyde formations. However, it is not unlikely that another type of vanadium species, being involved in the degradation process, can be present at less frequent faces of $\text{TiO}_2(\text{B})$.

Considering the values of the kinetic constants in Table I, it can be concluded that the heats of adsorption for oxygen, toluene, and ammonia are -4.5 , -11.0 , and -14.4 kcal/mol, respectively. The values obtained for toluene and ammonia are close to those reported in a kinetic investigation using a coprecipitated vanadium-anatase catalyst (Cavalli et al., 1987b). The relatively low value obtained for oxygen indicates adsorption in diatomic form (Bielanski and Haber, 1979). According to the derived mechanism, the rate-limiting step is a surface reaction with one or several of the adsorbed reactants involved. Unfortunately, not much information is available either on this step or on the nature of the series of intermediates indicated X_j and Y_i in the combustion route. Haber (1984) is of the opinion that electrophilic O_2^- and O^- species attack the organic molecule in the region of its highest electron density; i.e., in the case of toluene, the aromatic ring is attacked. As a result, intermediate complexes are formed that undergo rapid total oxidation. According to Suvorov (1968), alkylphenols and alkylquinones are intermediates in the degradation process of alkylbenzenes. On further oxidation, carbon oxides are ultimately produced. Concerning combustion of toluene in the presence of ammonia, Simon and Germain (1975, 1980) have suggested that, after an initial dealkylation, adsorbed benzene species can react with adsorbed ammonia to produce a quinone diimine intermediate, which then degrades to form carbon oxides. In Figure 11, the final products from ammonia have been given as HCN , N_2 , and nitrogen oxides, which are known to be formed in ammoxidation and in the oxidation of ammonia (Cavalli et al., 1987b; Andersson, 1981; Il'chenko and Golodets, 1975; Kosaki et al., 1979). Only the fate of activated ammonia involved in toluene combustion routes is considered in the figure. Additional oxidation of am-

Table II. Rate Constants and Activation Energies

		temperature, °C			E_a , kcal/mol
		340	370	400	
CO ₂	$k_1 S_T$, mol/(m ² ·min) × 10 ⁶	2.01	4.18	8.67	20.4
	$k_2 S_T$, mol/(m ² ·min) × 10 ⁶	0.281	0.766	2.09	27.3
CO	$k_1 S_T$, mol/(m ² ·min) × 10 ⁷	6.13	14.3	34.0	23.4
	$k_2 S_T$, mol/(m ² ·min) × 10 ⁷	0.110	0.593	3.30	46.6

monia can occur at sites not involved in toluene conversion. This oxidation is not treated in the present work; for that purpose studies without toluene coadsorption are more suited. However, it was verified that the total conversion of ammonia was low and did not influence the kinetic treatment of toluene (amm)oxidation.

From derived rate expressions it follows that the mechanisms for formations of CO₂ and CO are of a similar type. Since the denominators of (5) and (6) are equal, it can be concluded that both products are formed in routes comprising identical active ensembles. Rate constants and activation energies for the rate limiting steps are given in Table II. If the activation energies of k_1 for the formations of CO₂ and CO are compared, it is seen that the values are almost the same. This indicates that both products are possibly formed from a common intermediate when ammonia is not coadsorbed at the active ensemble. The product distribution, then, must be controlled by the mechanistic details of the degradation process of the common intermediate. A comparison of the activation energy values of k_2 , for the formation of CO₂ and CO, shows that the values clearly differ. The implication is that when ammonia is coadsorbed, CO₂ and CO are formed in parallel routes from different intermediates that, however, are adsorbed at a common type of active ensemble. Comparing the ratio k_2/k_1 for the formation of CO₂ and CO, respectively, it is seen that this ratio is much less for CO than for CO₂. Consequently, ammonia influences the formation of CO more than that of CO₂, which is also seen from a comparison of Figures 5 and 6. This may imply that O₂⁻ species participate in the formation of CO₂, while O⁻ species are possibly involved in the combustion to CO, since dissociation of adsorbed dioxygen species is made more difficult as a result of the adsorption of ammonia at some of the cations of the active ensemble. Another consequence of ammonia adsorption decreasing the rates for combustion is the introduction of new reaction pathways through new intermediates. The possibility that O₂⁻ and O⁻ species are involved in the formation of CO₂ and CO, respectively, has also been considered in a study of the ammoxidation of toluene over crystalline V₂O₅ (Otamiri and Andersson, 1988). In that case, however, the two products were found to be formed at different types of active site, with one of the steps in the reoxidation process being rate limiting. Over the TiO₂(B)-supported vanadium oxide catalyst, all reoxidation steps are fast.

Acknowledgment

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Appendix

Using expressions for equilibrium constants, the concentrations of the intermediates shown in Figure 11 can be expressed in terms of partial pressures of reactants and concentration of the active site S as follows:

$$[I_1] = K_T P_T [S]$$

$$[I_2] = K_O K_T P_O P_T [S]$$

$$[I_3] = K_A P_A [S]$$

$$[I_4] = K_A K_T P_A P_T [S]$$

$$[I_5] = K_O K_A K_T P_O P_A P_T [S]$$

$$[I_6] = K_O P_O [S]$$

$$[I_7] = K_O K_A P_O P_A [S]$$

The concentrations of intermediates X₁, X_j, Y₁, and Y_j are negligible due to the measurements being made at low conversions.

The rate of formation of carbon oxide can be expressed in terms of rate-limiting steps. Thus

$$r = k_1 K_O K_T P_O P_T [S] + k_2 K_O K_A K_T P_O P_A P_T [S]$$

After insertion of the relationship between the concentration of S and that of the total number of active sites, denoted S_T, a general form for the rate expression is obtained, which agrees with (5) and (6). The relations between the effective constants of these equations and the constants used in Figure 11 are given in Table I.

Registry No. V₂O₅, 1314-62-1; CO, 630-08-0; CO₂, 124-38-9; toluene, 108-88-3.

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Selective Deactivation of a Bifunctional Reforming Catalyst

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The deactivation of a commercial reforming catalyst having Pt/Re supported on γ -alumina was studied in a microtubular reactor and in a piston-recycling reactor during the reforming of naphtha fractions. The coke formation and the changes of the reaction rates were determined. The results of this work establish the selective deactivation by coke depositions. The deactivation effects significantly influenced the formation of aromatics. A model of coke formation and the relationship between coke and the activity of individual reaction rates is developed, explaining the data quantitatively and agreeing with the reaction mechanism in important aspects.

Introduction

Catalyst deactivation is a common problem in the petrochemical industry. This phenomenon has negative consequences on the activity and selectivity of the catalyst. Deactivation in the reforming process is caused by coke formation and deposition. As a rule, the main deactivation effects can be directly attributed to coke formation. The coke is derived from the degradation of reactants or reactants or products subject to successive condensations with elimination of hydrogen.

The problem of experimental study and mathematical modeling of catalyst deactivation in the reforming process is characterized by the coupling of reaction kinetics and the deactivation of the catalyst. From this point of view,

extensive investigations have been concerned with special experimental methods and the evolution of deactivation models for several hydrocarbons. A thorough review of catalytic reforming was presented by Sterba and Haensel (1976). Apart from mechanism, kinetics, and technical aspects, they express the effect of sulfur on the rate constants. The results show that there is a changed hydrogen-dehydrogen relation in the range of higher sulfur amounts (>50 ppm). Malet et al. (1989) examined the effect of chlorine and the thermal pretreatment of bimetallic catalysts. Parera et al. (1986) dealt with the role of sulfur in the reforming catalyst. They observed an increased C₁ formation for presulfurized catalyst. The influence of sulfur on formation of coke was studied by