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Oxidation of toluene to benzaldehyde over $VSb_{0.8}Ti_{0.2}O_4$ Effect of the operating conditions

Susana Larrondo, Andrés Barbaro, Beatriz Irigoyen, Norma Amadeo*

Laboratorio de Procesos Catalíticos, Depto. Ing. Química, Facultad de Ingeniería, UBA,
Pabellón de Industrias. Ciudad Universitaria, 1428 Buenos Aires, Argentina

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Abstract

In the present work, the kinetic toluene oxidation on $VSb_{0.8}Ti_{0.2}O_4$ based catalyst was studied. A reaction network, which involves three steps: the partial oxidation of toluene to benzaldehyde, a consecutive oxidation of benzaldehyde to carbon oxides and a parallel oxidation of toluene to carbon oxides, was proposed. The kinetic parameters were estimated assuming the redox mechanism proposed by Mars and van Krevelen. The products distribution was strongly affected by the reaction temperature. The adjustment of activation energies for total and partial oxidation of toluene led to the same values. The activation energy for the benzaldehyde oxidation was lower than the one for its formation. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Toluene oxidation; Vanadium antimonate; Kinetic parameters

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1. Introduction

The processes of catalytic partial oxidation of aromatic hydrocarbons in vapor phase are of great importance in chemical technology [1–3]. These reactions involve complex processes showing a variety of products under different conditions [4]. However, thorough discussions of complete reaction schemes seldom appear in the literature [5]. Precise rate expressions are difficult to obtain because of the existence of reaction networks. Kinetic expressions are usually of the power-rate law type and are applicable within limited experimental ranges. Mars–van Krevelen redox mechanism is very often used for selective and total oxidation reaction. Gunduz and Akpolat [6] have investigated the vapor-phase oxidation of toluene to benzaldehyde over V_2O_5 catalyst. The kinetic studies showed that the reaction was second order with respect to the hydrocarbon and zero order with respect to oxygen. The Mars–van Krevelen mechanism fitted the experimental data, but the authors did not take into account the existence of secondary reactions.

Trimm and Irshad [7] have carried out kinetic studies of the oxidation of unsubstituted and substituted toluene over molybdenum trioxide. They have found that the reaction was controlled by the rate of reduction of the catalyst and the initial rate was first order in toluene partial pressure and independent of the partial pressure of oxygen. The results were interpreted in terms of a kinetic expression of the power-rate law type.

Andersson [8] has postulated a reaction network for catalytic oxidation of toluene over a variety of metal oxide catalysts. He has suggested that the initial hydrocarbon-activating step would be rate determining.

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* Corresponding author.
E-mail address: norma@indust.di.fcen.uba.ar (N. Amadeo).

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Nomenclature

BA	benzaldehyde
CO_x	carbon oxides
E_a	activation energy
F_{v0}	volumetric feed rate
k_i	specific rate constant
k_i^0	Arrhenius law preexponential factor
$Ø_{ox}$	oxidized catalyst sites
$Ø_r$	reduced catalyst sites
P_i	partial pressure of component i
r_i	reaction rate of step i
T	temperature
Tol	toluene
y_i	molar fraction of component i

Greek symbol

θ	surface degree of coverage by oxygen

Van der Wiele and Van den Berg [9] have studied the oxidation of toluene by air over pure bismuth molybdate catalyst. The kinetic results, considering a complex reaction system, indicated that a Mars–van Krevelen mechanism fitted the experimental data. The reaction was found to be first order in the hydrocarbon partial pressure and first order in oxygen partial pressure.

Bulushev et al. [10] have proposed a parallel–consecutive reaction scheme for partial toluene oxidation over vanadia/titania catalyst from the results of steady-state and transient kinetics studies.

In a previous work, it was found that the vanadium antimonate doped with titanium with nominal composition $VSb_{0.8}Ti_{0.2}O_4$ [11] presents good catalytic performance in the toluene oxidation reaction. The products obtained with this catalytic system were benzaldehyde and carbon oxides.

In the present work, a kinetic study of vapor-phase oxidation of toluene by air using a $VSb_{0.8}Ti_{0.2}O_4$ catalyst is reported. The aim is to propose a kinetic scheme suitable to identify the main reaction steps, to determine a kinetic expression based on a redox mechanism and to analyze the influence of the operating variables, such as temperature, toluene/oxygen feed ratio and space–time on the toluene conversion, benzaldehyde selectivity and carbon oxides selectivity.

2. Experimental

2.1. Catalyst preparation and characterization

The catalysts were prepared according to the method published by Berry et al. [12], by mechanical mixing of pure vanadium(V) oxide, antimony(III) oxide and titanium(IV) oxide (Mallinckrodt reagent grade). The amounts of each oxide in the sample corresponded to that necessary to obtain a stoichiometric solid of composition $VSb_{0.8}Ti_{0.2}O_4$. The reactant powders (2 g) were gently grinded, in order to have good mixing, were put into quartz crucibles and were heated in air in a conventional furnace according to the following schedule: heating from 25 to 600°C over 10 h, temperature kept at 600°C during 12 h, heating from 600 to 750°C over 6 h, temperature kept at 750°C during 9 h, furnace cooling down. The catalysts were characterized by X-ray diffraction using Cu Kα radiation.

2.2. Catalytic tests

Toluene oxidation was carried out in a conventional fixed-bed flow reactor, operated isothermally at atmospheric pressure. The reactor was made with a Pyrex glass tube of 13 mm inner diameter. Toluene was fed by means of a carrier air stream flowing through a saturator. The feed toluene/air molar ratio was controlled by adjusting both the saturator temperature and the input air flow rate. The reaction temperature was measured with a sliding thermocouple placed inside the bed. Since the oxidation reactions are highly exothermal, the catalyst bed was diluted (1:10) with glass particles, of the same diameter range, in order to avoid adverse thermal effects.

The composition of the input and output streams were analyzed by on-line gas chromatography. An HP 6890, equipped with an FID detector and HP INNOWAX 30 m/320 μm/0.25 μm polyethyleneglycol column, was used to analyze the concentrations of toluene in the feed and the output streams, and the concentration of partial oxidation products in the output. The composition of the total oxidation products was determined with a Shimadzu GC 8A chromatograph equipped with a TCD detector and Porapak Q 2 m/molecular sieve 5A columns.

The reactor was operated in integral conditions. A complete kinetic study involving different temperatures, contact times, organic reactant concentration and oxygen concentration was done. The catalytic tests were performed under the following conditions: catalyst mass = 100–400 mg, temperature = 673–713 K, total feed rate = 200–600 ml/min, toluene molar fraction = 0.001–0.01, oxygen molar fraction = 0.04–0.2 (nitrogen balance), particle diameter $< 120\,\mu$m. The experiments were carried out at 15 space–times, five temperatures, 10 toluene partial pressures and six oxygen partial pressures.

3. Results and discussion

3.1. Catalyst characterization

The X-ray diffraction patterns confirmed the presence of only one phase with rutile structure, similar to that previously reported as $VSb_{0.8}Ti_{0.2}O_4$ [12].

3.2. Catalytic measurements

In order to ensure that the kinetic experiments provided meaningful results, preliminary catalytic tests were carried out at different space–times, particle diameters and total gas flows. Some of them were performed without catalyst in order to study the contribution of the thermal oxidation. These tests showed a negligible contribution of homogeneous oxidation. The absence of internal and external diffusion limitations for particle diameters below 120 μm and total gas flow equal to or greater than 100 ml/min was confirmed.

The catalyst showed activity without the necessity of pretreating and the activity was stable during a typical run period of 12 h. Benzaldehyde and carbon oxides were the main oxidation products. Satisfactory carbon balance between reactor inlet and outlet was observed.

Selectivity to oxidation products was calculated as

$$\frac{\text{mole of products} \times \text{No. of C atoms in the product}}{\text{mole of toluene converted} \times 7} \times 100$$

Products yields were calculated as

$$\frac{\text{mole of products} \times \text{No. of C atoms in the product}}{\text{mole of toluene in the feed} \times 7} \times 100$$

3.3. Analysis of the reaction network

In Fig. 1, selectivities are plotted as a function of toluene conversion at 673 and 713 K. These experi-

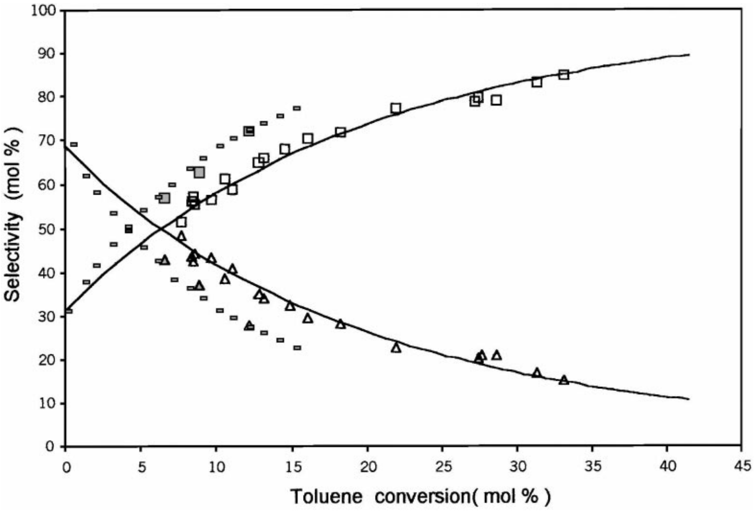
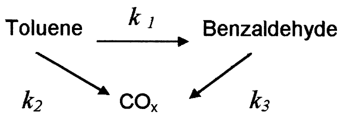


Fig. 1. Selectivity vs. toluene conversion: $Y^0_{\mathrm{Tol}} = 0.55$ mol%; $Y^0_{\mathrm{O_2}} = 19.9$ mol%; nitrogen balance. (▲) Benzaldehyde selectivity at 673 K; (■) CO_x selectivity at 673 K; (△) benzaldehyde selectivity at 713 K; (□) CO_x selectivity at 713 K.

ments were carried out in an integral reactor, varying the space–time and keeping constant the feed composition and the temperature. The shape of the curve representing the selectivity to benzaldehyde shows that the benzaldehyde is an intermediate in the consecutive transformation to carbon oxides and the rate of benzaldehyde oxidation is greater than the rate of formation. The extrapolation of both curves to zero conversion of toluene leads us to the conclusion that nearly 30% of toluene would be oxidized by parallel reaction to carbon oxides. Therefore, the reaction kinetic scheme proposed is the following:



3.4. Estimation of the kinetic parameters

The classical redox mechanism proposed by Mars and Van Krevelen [13] was adopted in this work. The basic concepts of this mechanism may be interpreted by assuming two successive steps:

1. Hydrocarbon + oxidized catalyst $\xrightarrow{k_1, k_2 \text{ or } k_3}$ oxidized products + reduced catalyst
2. Reduced catalyst + $O_2(g) \xrightarrow{k_4}$ oxidized catalyst

Table 1
Rate expressions for each step of the kinetic mechanism proposed

Reaction step	Rate expression
$\mathrm{Tol} + \O_{\mathrm{ox}} \rightarrow \mathrm{BA} + \mathrm{H_2O} + \O_{\mathrm{r}}$	$r_1 = k_1 P_{\mathrm{Tol}}^{m} \theta$
$\mathrm{Tol} + \O_{\mathrm{ox}} \rightarrow 7\mathrm{CO}_x + 4\mathrm{H_2O} + \O_{\mathrm{r}}$	$r_2 = k_2 P_{\mathrm{Tol}}^{m} \theta$
$\mathrm{BA} + \O_{\mathrm{ox}} \rightarrow 7\mathrm{CO}_x + 3\mathrm{H_2O} + \O_{\mathrm{r}}$	$r_3 = k_3 P_{\mathrm{BA}}^{m} \theta$
$\O_{\mathrm{r}} + \mathrm{O_2} \rightarrow \O_{\mathrm{ox}}$	$r_4 = k_4 P_{\mathrm{O_2}}^{n} (1 - \theta)$

Table 2
Model kinetic parameters

Parameter	Optimal value
k_1^0 (mol/min atm g_{cat})	7.00×10^6
k_2^0 (mol/min atm g_{cat})	3.21×10^6
k_3^0 (mol/min atm g_{cat})	2.09×10^7
k_4^0 (mol/min atm g_{cat})	1.87×10^6
$E_{a_1} = E_{a_2}$ (cal/mol)	2.78×10^4
E_{a_3} (cal/mol)	1.58×10^4
E_{a_4} (cal/mol)	2.75×10^4

The rate expressions derived from this mechanism are presented in Table 1. Order "*m*" in hydrocarbon and order "*n*" in oxygen partial pressures were assumed.

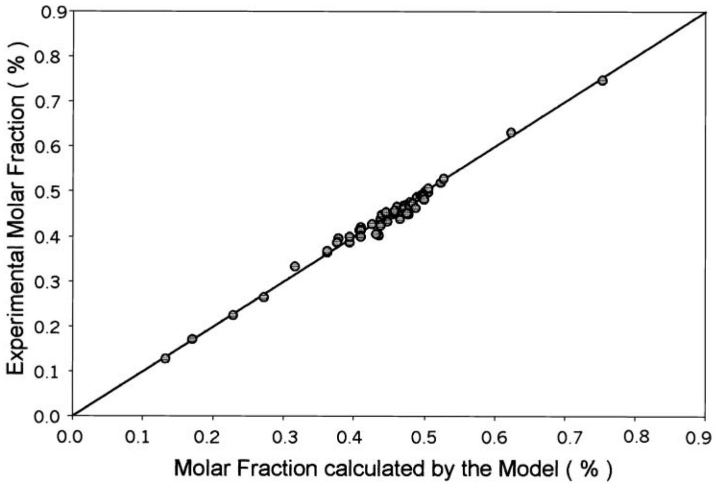


Fig. 2. Experimental values of toluene molar fraction versus calculated values from the kinetic model.

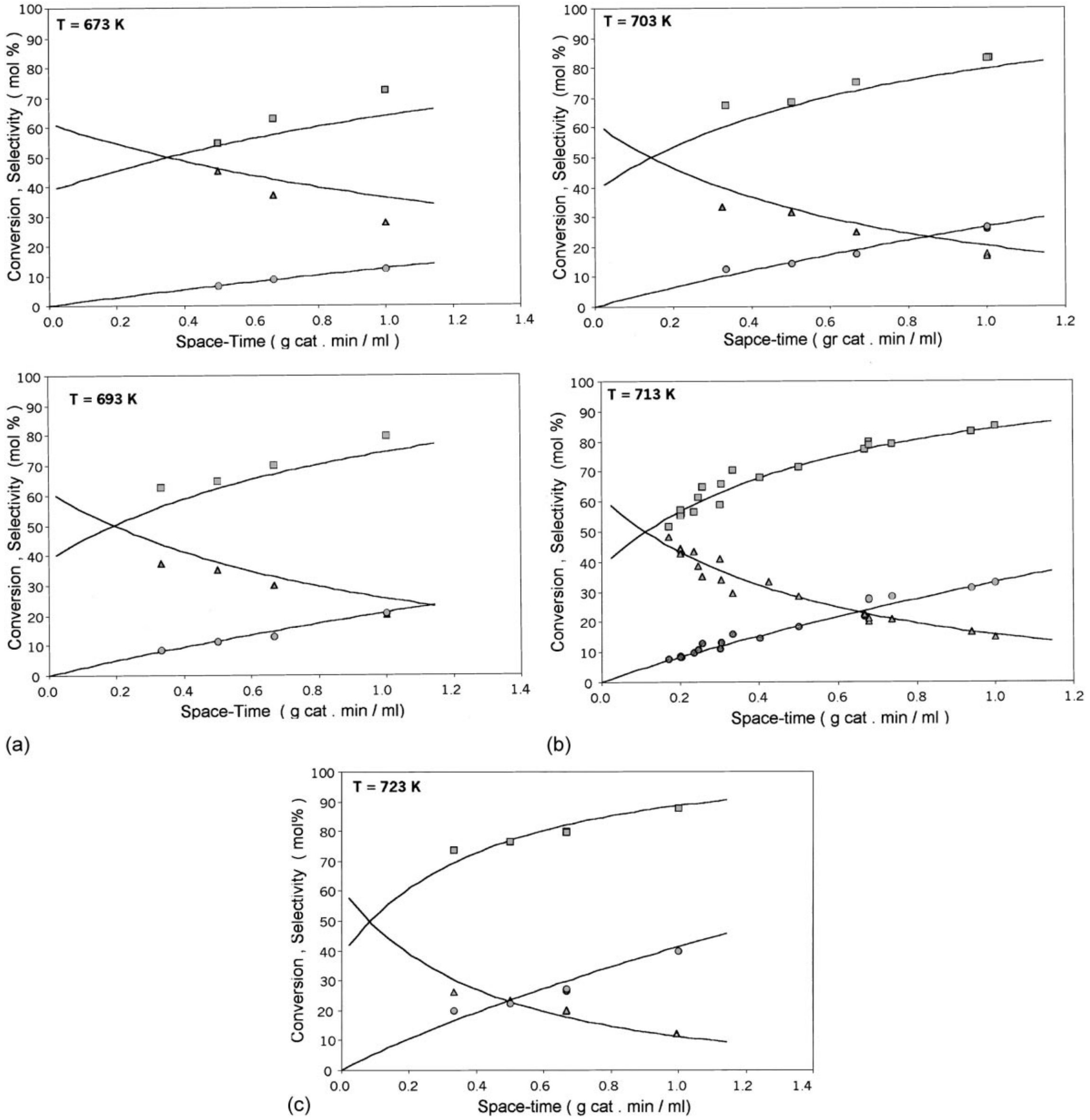


Fig. 3. Toluene conversion and product selectivity vs. space–time for different temperatures: $Y^0_{\mathrm{Tol}} = 0.54$ mol%; $Y^0_{\mathrm{O_2}} = 19.9$ mol%; nitrogen balance. (●) Toluene conversion; (▲) benzaldehyde selectivity; (■) CO_x selectivity.

Under steady-state conditions, the rate of catalyst reduction equals the rate of catalyst reoxidation ($r_4 = r_1 + \beta r_2 + \lambda r_3$). Then, the surface degree of coverage by oxygen θ is

$$\theta = \frac{k_4 P^n_{\mathrm{O_2}}}{k_4 P^n_{\mathrm{O_2}} + (k_1 + \beta k_2)\, P^m_{\mathrm{Tol}} + \lambda k_3 P^m_{\mathrm{BA}}} \qquad (1)$$

where β and λ represent the number of moles of oxygen consumed by total oxidation of 1 mol of toluene and 1 mol of benzaldehyde, respectively. The values of these constants, obtained from the experimental measurements, are $\beta = 8.11$ and $\lambda = 7.11$. When the surface is completely oxidized ($\theta = 1$), carbon oxides are mainly formed. The progressive reduction of

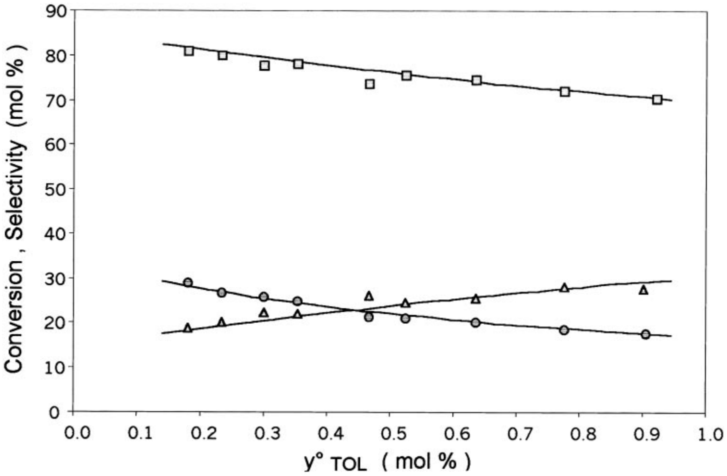


Fig. 4. Conversion and selectivity vs. toluene molar fraction in the feed: reaction temperature = 713 K; $Y_{O_2} = 19.9$ mol%; nitrogen balance; space–time = 0.59 g-cat min/ml. (●) Toluene conversion; (▲) benzaldehyde selectivity; (■) CO_x selectivity.

the surface increases the formation of partial oxidized products ($\theta < 1$).

The kinetic parameters of the rate expressions were determined by minimizing the sum of the squares of the deviations between measured and calculated molar fraction of reactants and products. A specific optimization routine for multivariable non-linear regression developed by Quiroga and Gottifredi [14] coupled with a standard routine of numerical integration of the differential equations was used.

The best value of the objective function and the best fitting of the experimental values were achieved with "$m = 1$" and "$n = 1$". The estimated parameters (the preexponential factors and the activation energies) are presented in Table 2. The goodness of the correlation between experimental and calculated toluene molar fractions is showed in Fig. 2.

The steps involving toluene oxidation were found to have similar values of apparent activation energies ($E_{a_1} = E_{a_2}$). A similar behavior was found by Van

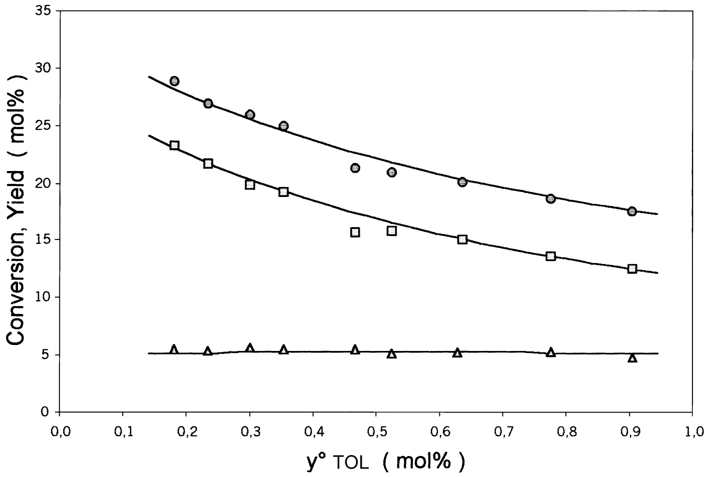


Fig. 5. Toluene conversion and product yields vs. toluene molar fraction in the feed: reaction temperature = 713 K; $Y_{O_2} = 19.9$ mol%; nitrogen balance; space–time = 0.59 g-cat min/ml. (●) Toluene conversion; (▲) benzaldehyde yield; (■) CO_x yield.

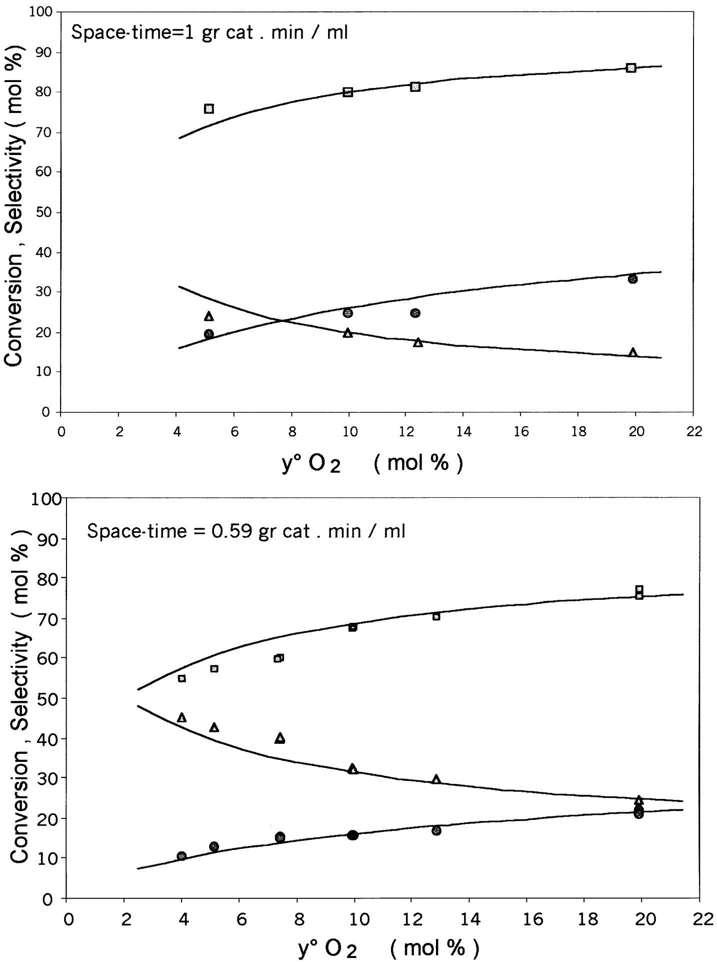


Fig. 6. Conversion and selectivity vs. oxygen molar fraction in the feed: reaction temperature = 713 K; $Y^0_{\mathrm{Tol}} = 0.49$ mol%. (●) Toluene conversion; (△) benzaldehyde selectivity; (□) CO_x selectivity.

der Wiele and Van den Berg [9] in the oxidation of toluene over bismuth molybdate catalysts.

This fact points out that the same intermediate is involved in both processes. In analogy with the mechanism proposed in many hydrocarbon oxidations [8], this intermediate could probably be related with the hydrogen abstraction and the formation of the benzyl radical. However, detailed mechanistic theories are beyond the scope of the present investigation.

3.5. The influence of the space–time

In Fig. 3, toluene conversion and the selectivities for the formation of carbon oxides and benzaldehyde are plotted as functions of the space–time at different reaction temperatures. The carbon oxides selectivity increases and the benzaldehyde selectivity decreases as space–time increases, as a result of benzaldehyde oxidation to carbon oxides. This fact implies the existence of consecutive reactions for these products at longer residence times The extrapolation to zero contact time indicates that toluene is also oxidized directly to carbon oxides.

3.6. The influence of the reaction temperature

In Fig. 1, the selectivities are plotted as a function of toluene conversion at 673 and 713 K. The catalytic

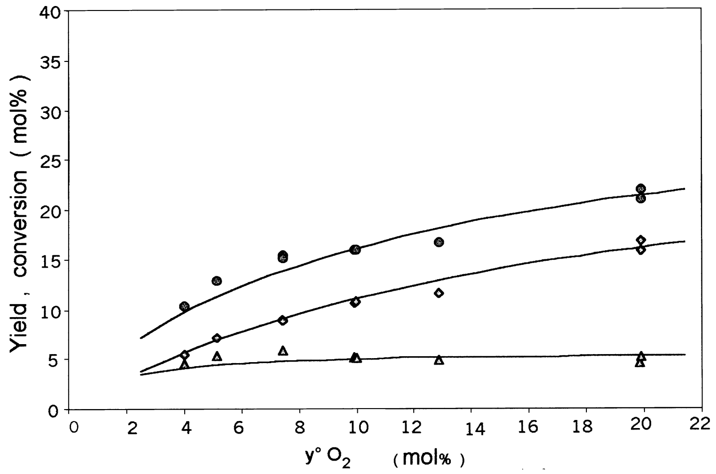


Fig. 7. Toluene conversion and product yields vs. oxygen molar fraction in the feed: reaction temperature = 713 K, $Y_{\mathrm{Tol}} = 0.54$ mol%, space–time = 0.59 g-cat min/ml. (●) Toluene conversion; (▲) benzaldehyde yield; (■) CO$_x$ yield.

experiments were carried out varying the space–time, keeping constant the feed composition, and the temperature. At a constant value of toluene conversion, benzaldehyde selectivity increases and carbon oxides selectivity decreases while reaction temperature increases. These data suggest that the activation energy for benzaldehyde oxidation is lower than the one for its formation. Besides, the results obtained for toluene conversion (Fig. 3) indicate that the conversion of toluene increases as temperature increases. Therefore, at high temperatures, one could expect greater yield to benzaldehyde, since the yield is obtained as the product between the selectivity and the conversion.

3.7. The influence of partial pressures of reactants

Toluene conversion, CO$_x$ and benzaldehyde selectivities and yields are plotted in Figs. 4 and 5, as a function of the toluene molar fraction in the feed. From Fig. 4, it is clear that greater toluene conversions are

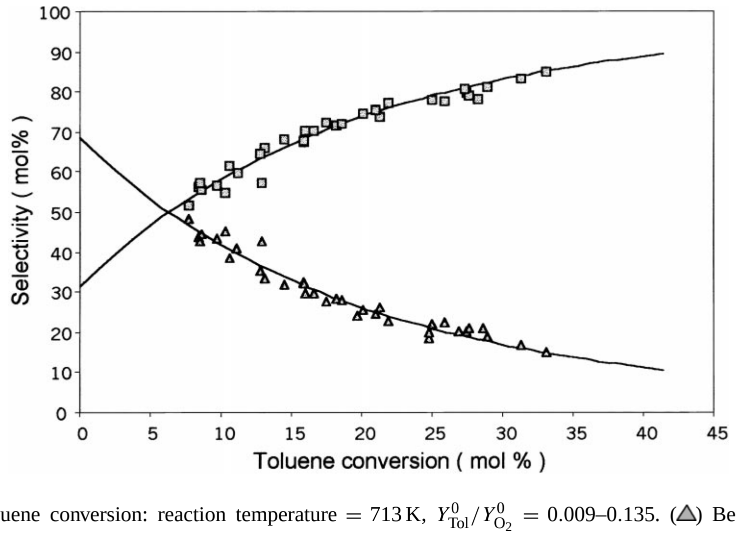


Fig. 8. Selectivities vs. toluene conversion: reaction temperature = 713 K, $Y^0_{\mathrm{Tol}}/Y^0_{\mathrm{O_2}} = 0.009$–$0.135$. (▲) Benzaldehyde selectivity; (■) CO$_x$ selectivity.

achieved at lower toluene molar fraction in the feed. In concordance, the results obtained for benzaldehyde and carbon oxides selectivities show the trend corresponding to an intermediate and final products, respectively. It means that lower benzaldehyde selectivity and higher carbon oxides selectivity are achieved at greater toluene conversion. On the other hand, benzaldehyde yield remains constant independent of the reactant concentration in the feed.

In Figs. 6 and 7, the effect of the oxygen molar fraction in the feed over conversion, selectivities and yields is shown. Greater toluene conversions are achieved at greater oxygen molar fraction, indicating that increasing the oxygen concentration in the reaction mixture increases the reaction rate. The selectivities of partial and final products follow the trend mentioned above, in accordance with toluene conversion.

In Fig. 8, CO_x and benzaldehyde selectivities are plotted as a function of toluene conversion at different toluene/oxygen molar ratio in the feed. Benzaldehyde and carbon oxides selectivities remain constant while the toluene/oxygen molar ratio changes. This means that selectivities at isoconversion are not affected by the feed composition, pointing out that there is no competition between the reactants for the active sites. Then, the hydrocarbon oxidation and the catalyst reoxidation involve different active sites.

4. Conclusions

The present study of the vapor-phase oxidation of toluene has shown that the formation of CO_x by direct oxidation of toluene must be considered. The proposed kinetic scheme has three steps: the partial oxidation of toluene to benzaldehyde, a consecutive oxidation of benzaldehyde to carbon oxides and a parallel oxidation of toluene to carbon oxides. The reaction network was modeled assuming the redox mechanism proposed by Mars and van Krevelen. The approach is oversimplified with respect to the true reaction mechanism, but provides a better description of the experimental data than the empirical approaches (power-law equations). The oxidation of toluene and benzaldehyde was found to be first order in the reactant partial pressure. The reoxidation of the catalyst was found to be first order in oxygen partial pressure.

Toluene conversion and products selectivities values were strongly influenced by the reaction temperature. An important effect of the reaction temperature is that the selectivity to benzaldehyde at isoconversion increases as the temperature increases. This behavior corresponds with the fact that the activation energy for the formation of the benzaldehyde is greater than the one for its oxidation (Table 2). Therefore, at high temperatures one could expect greater yield to benzaldehyde. Besides, benzaldehyde selectivity has the same maximum value at different temperatures. This value depends on the k_1/k_2 ratio that is independent of the temperature since the two activation energies involved have equal values.

For a specific value of toluene conversion, yields and selectivities of the products are independent of the feed composition. This suggests that there is no competition between the reactants for the active sites. The hydrocarbon oxidation and the catalyst reoxidation take place at different active sites, as it is proposed by the redox mechanism.

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