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Oxidation of *o*-Xylene to Phthalic Anhydride over V_2O_5/TiO_2 Catalysts

II. Transient Catalytic Behaviour

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The transient phase of the oxidation of *o*-xylene and *o*-tolualdehyde, before establishment of the steady state, has been studied over V_2O_5/TiO_2 (anatase). At lower temperatures, an initial decrease in conversion and phthalic anhydride selectivity were observed, accompanied by an increase in selectivity to involatile products; at higher temperatures, the steady state was rapidly attained and no strong variations of conversion and selectivity were detected. For *o*-tolualdehyde oxidation, lower selectivities to involatile products were obtained, indicating that the adsorbed *o*-xylene molecules can lead more effectively to the formation of heavy organic compounds. Results obtained for selectivity to involatiles, time to reach steady state, and conversion indicate that catalyst deactivation can be ascribed to the formation of an organic residue on the catalyst surface. Such a residue can also desorb or undergo oxidation to CO_2. © 1995 Academic Press, Inc.

INTRODUCTION

Phthalic anhydride is an important organic chemical used mainly in the preparation of plasticizers for PVC (1). It has been commercially produced since 1872 and the first process was based on the liquid-phase oxidation of naphthalene with sulfuric acid in the presence of mercuric sulfate (2, 3). However, it was the development of the gas-phase air oxidation process that led to the commercial production of a high-quality product (1). Initially, phthalic anhydride manufacture was based on the oxidation of naphthalene in the presence of vanadium oxides (4), the process consisting of passing a stream of vaporized hydrocarbon at about 1 mol% concentration in air through a catalyst bed at a temperature between 673 and 773 K (5). Increasing demand for phthalic anhydride and decreasing availability of naphthalene has stimulated the search for alternative raw materials, *o*-xylene being the preferred feedstock since 1963 (3, 4). *o*-Xylene is available in large quantities from petroleum refineries and has, as a starting material, advantages compared with naphthalene (lower cost and ease of transportation).

Vanadium pentoxide supported on TiO_2 (anatase) exhibits better activity and selectivity for *o*-xylene oxidation compared with other catalysts (6–8); several explanations have been suggested for this superior behaviour (9–15).

o-Xylene oxidation has been the subject of several kinetic studies and some reaction mechanisms have been proposed (16–21); these are complex and include several successive and parallel steps, involving different products and intermediates. In spite of such studies, there are still some contradictory views about the reaction mechanism and active sites involved.

Deactivation, which is an important problem in catalysis, has been also observed for V_2O_5/TiO_2 (anatase) catalysts (2, 22, 23) and has been mainly associated with the transformation of the anatase support into rutile (a crystalline modification of TiO_2). In fact, it is known that the presence of rutile in V_2O_5/TiO_2 catalysts used for *o*-xylene oxidation can cause lower selectivities and activities (6, 7). According to the literature (24), anatase is the stable crystallographic form for temperatures below 973 K; however, it is known that the presence of vanadia promotes the anatase–rutile transformation (10, 12, 25–28), which can start at temperatures as low as 773 K (28). Due to the high exothermicity of the reaction a characteristic temperature profile with a pronounced maximum (hot spot) is formed along the catalyst bed (29, 30), leading to locally very high temperatures and enhancing the anatase–rutile transformation.

The work reported here is part of a complete study of the oxidation of *o*-xylene to phthalic anhydride and deals with the transient phase that precedes the steady state. *o*-Tolualdehyde, considered an important intermediate for *o*-xylene oxidation, was also used as a reactant, in order to obtain more information about the influence of the step *o*-xylene → *o*-tolualdehyde on the formation of heavy organic products. Kinetic tests performed at different tem-

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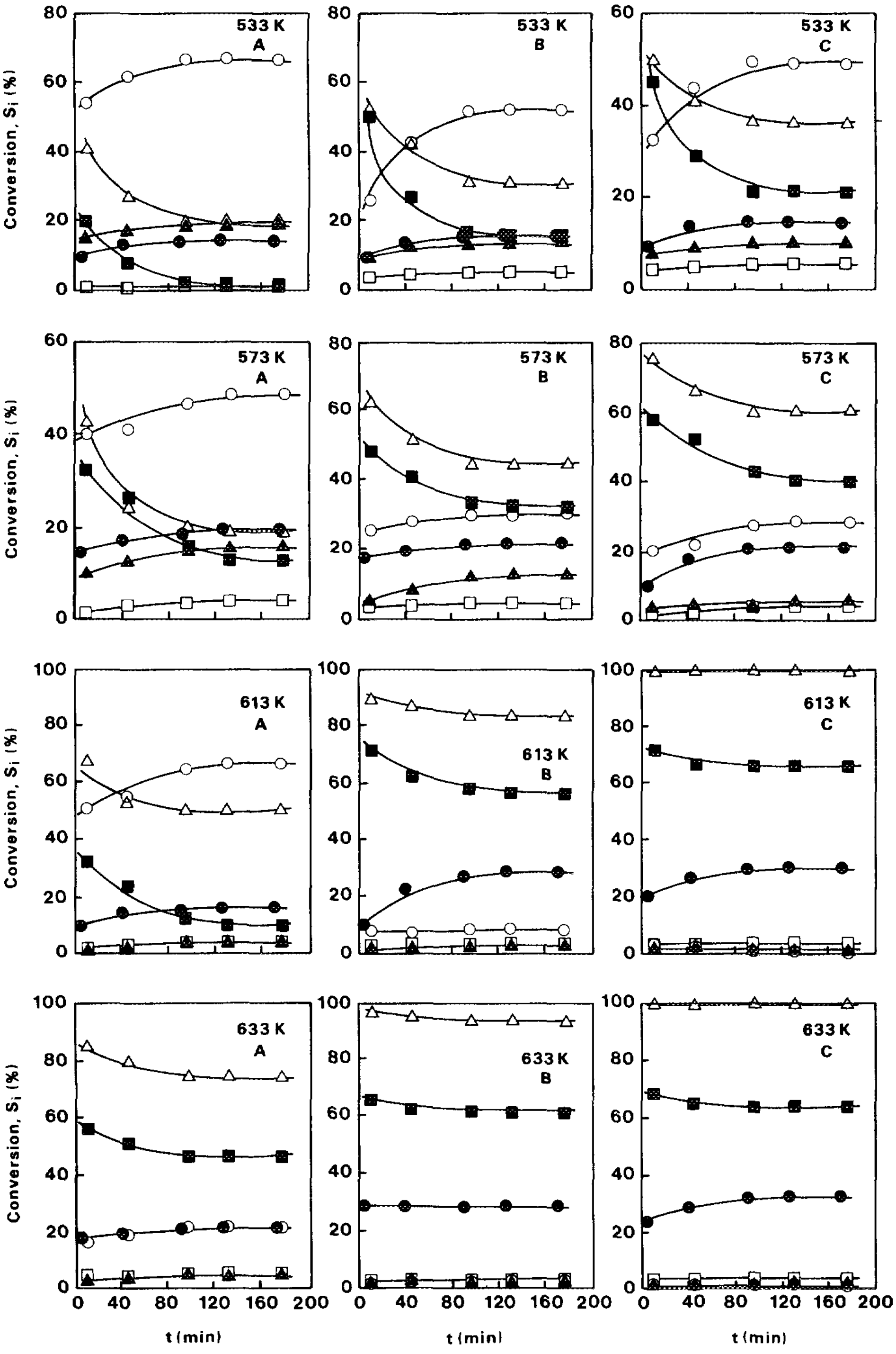

FIG. 1. *o*-Xylene oxidation, conversion and product selectivities for transient period at different temperatures (T_R) and contact times (W/F). Conversion (△), *o*-tolualdehyde (▲), phthalide (□), phthalic anhydride (■), carbon dioxide (●) and residual (○) selectivity. $C_{\text{xylene}} = 0.7$ mol%. $W/F = 2.5 \times 10^{-5}$ $\text{kg}_{\text{cat}}\,\text{dm}^{-3}$ h (A), 1.3×10^{-4} $\text{kg}_{\text{cat}}\,\text{dm}^{-3}$ h (B), 2.3×10^{-4} $\text{kg}_{\text{cat}}\,\text{dm}^{-3}$ h (C).

peratures, organic reactant concentrations, and contact times provided results that help to further the understanding of *o*-xylene to phthalic anhydride oxidation.

EXPERIMENTAL

Catalyst Preparation and Characterization

The catalyst (1 wt.% V_2O_5/TiO_2 (anatase)) was prepared by wet impregnation, using an aqueous solution of ammonium metavanadate (Fluka) in oxalic acid (1 *M*); it was characterized by XRD, BET analysis, laser Raman and FTIR spectroscopy, XPS, and TPR. The first two techniques were also used for the characterization of samples previously kept under reaction conditions.

The preparation and characterization procedures have been described in Part I (31).

Catalytic Measurements

o-Xylene and *o*-tolualdehyde oxidations were carried out in a conventional flow apparatus at atmospheric pressure. Kinetic results were obtained under transient and steady state conditions. Before each experiment, the catalyst was kept for 1 h at 673 K under flowing air, after which it was cooled to the reaction temperature. The organic reactant was fed to the system after stabilization of the temperature. The apparatus, the product analysis, and the calculation procedure have been described in Part I (31).

RESULTS AND DISCUSSION

Characterization of Catalysts

The characterization of fresh samples was reported in Part I (31). XRD analysis of the catalyst samples after reaction showed only the anatase peaks; those corresponding to the rutile modification were not detected, indicating that the anatase → rutile transition did not occur. BET measurements showed that fresh and used catalyst samples had similar surface areas (7.5 and 7.6 $m^2\ g^{-1}$, respectively). Results suggest that no major structural modifications occurred during the course of the reaction.

Catalytic Measurements

For *o*-xylene oxidation, *o*-tolualdehyde, phthalide, phthalic anhydride, and carbon dioxide were detected as products. The changes in conversion and selectivities as a function of time-on-stream are plotted in Figs. 1 and 2. The residual selectivity (S_R), corresponding to the fraction of reactant feed not recovered as a product detected by chromatography, has been associated with the formation of heavy organic compounds (16, 18). At lower temperatures (T_R) and lower contact times (W/F), S_R attained quite high values, whereas under the opposite conditions superior yields of desired products were obtained. For some operating conditions, the formation of such heavy by-products can cause considerable difficulties by blocking exit lines from the reactor.

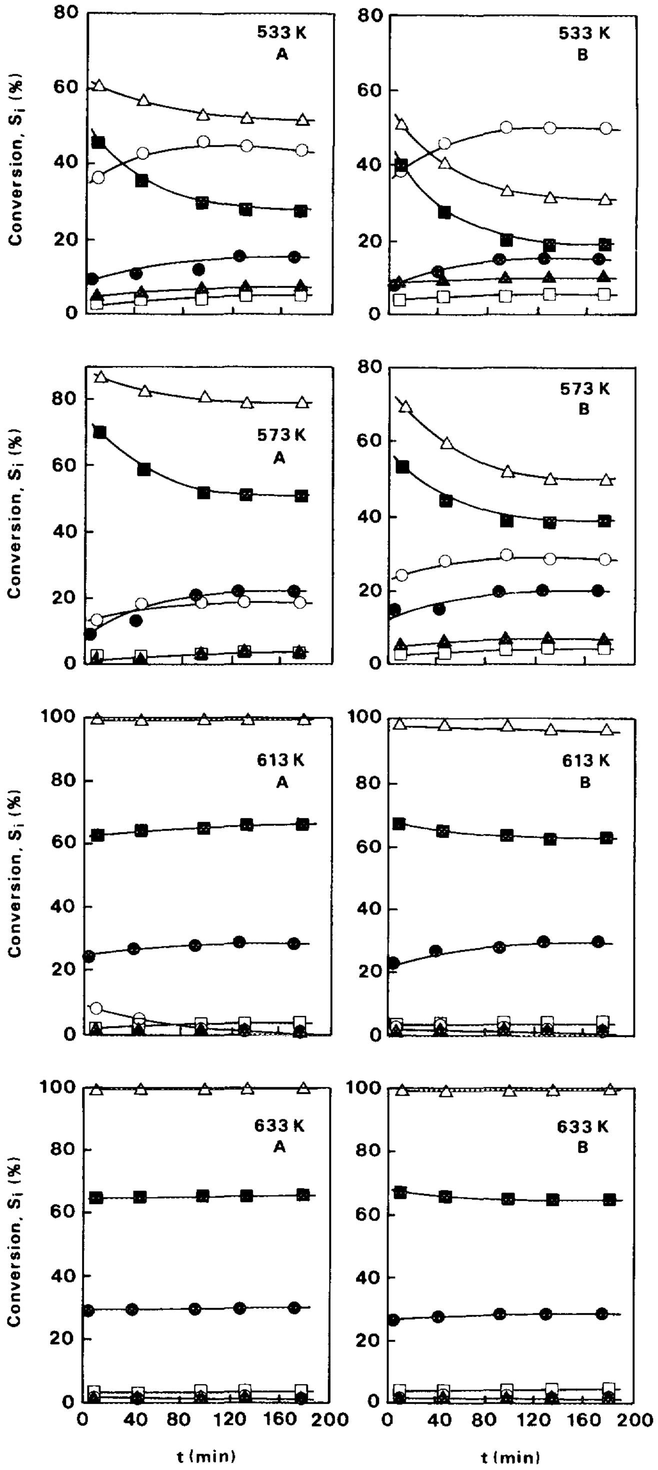

FIG. 2. *o*-Xylene oxidation, conversion and product selectivities for transient period at different temperatures (T_R) and reactant concentration. $W/F = 2.3 \times 10^{-4}$ kg_{cat} dm^{-3} h. C_{xylene} = 0.3 mol% (A), 1 mol% (B). Symbols are as in Fig. 1.

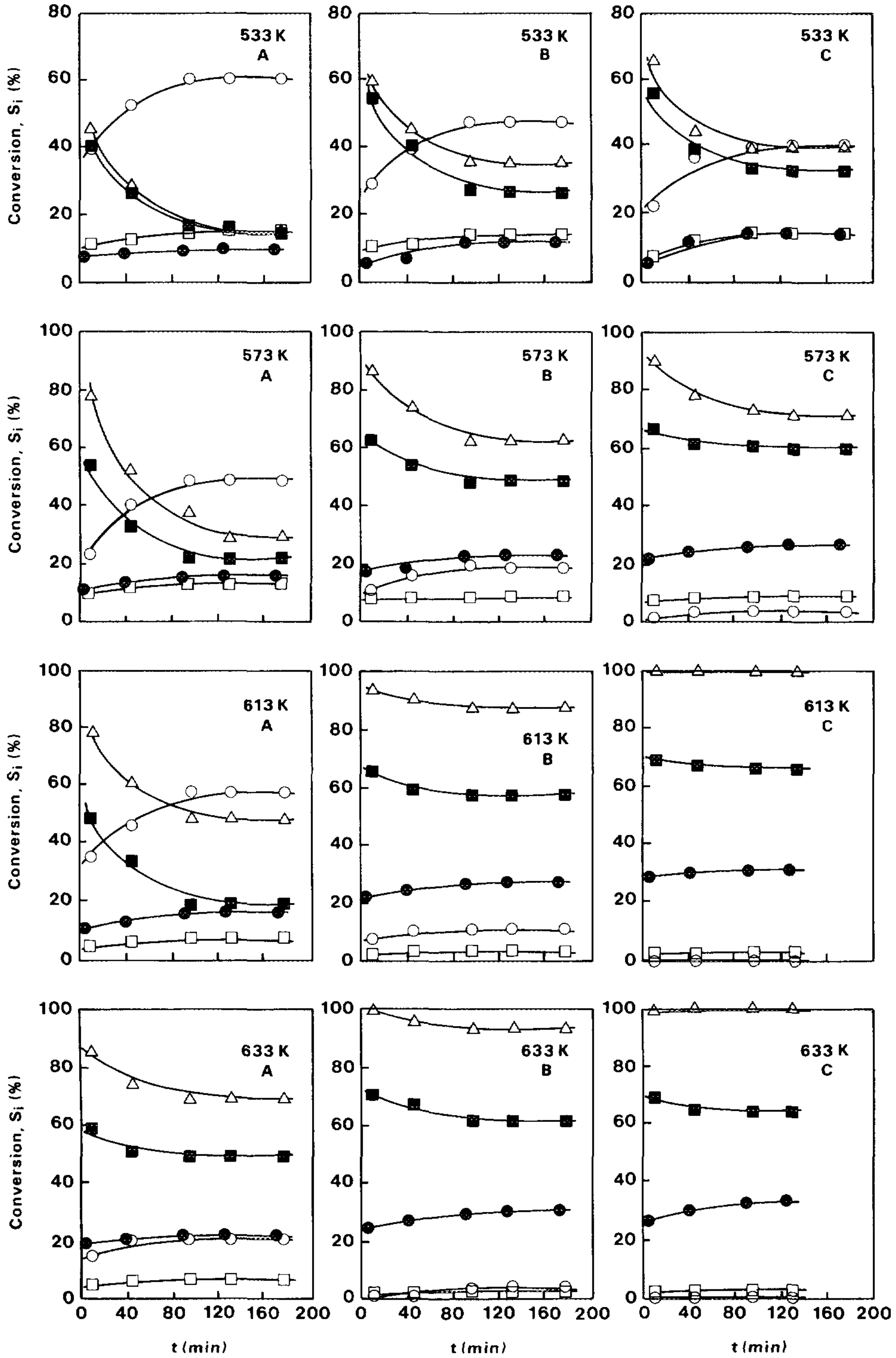

FIG. 3. o-Tolualdehyde oxidation, conversion and product selectivities for transient period at different temperatures (T_R) and contact times (W/F). $C_{\text{tolualdehyde}} = 0.5$ mol%. $W/F = 2.5 \times 10^{-5}$ kg$_{\text{cat}}$ dm^{-3} h (A), 1.3×10^{-4} kg$_{\text{cat}}$ dm^{-3} h (B), 2.3×10^{-4} kg$_{\text{cat}}$ dm^{-3} h (C). Symbols are as in Fig. 1.

At lower temperatures, conversion decreased strongly until a constant value, corresponding to the steady state, was reached. This decrease became less important as T_R increased. In fact, for the highest temperatures, the conversion decrease was negligible, the steady state being rapidly attained. Taking into account the characterization mentioned above, this decrease can be ascribed neither to the anatase → rutile transformation nor to modifications of the surface area.

The conversion decrease is always accompanied by an increase in S_R; moreover, stronger decreases in conversion are associated with higher S_R values (Fig. 1). The same opposing behaviour between conversion and S_R was also observed in the steady state (31). Since S_R has been ascribed to the formation of heavy compounds, the results suggest that their formation plays an important role in the loss of activity detected. In fact, the heavy organic compounds formed may stay on the catalyst surface, blocking active sites and leading to a decrease in conversion.

It should be emphasized that total deactivation was never observed. Since heavy products were constantly formed, processes involving residue consumption must also be considered. These may include desorption from the catalyst surface, since condensation of polymeric products has been detected at the reactor outlet by various authors (18, 22). Indications that the residue is a significant source of CO_2 come from Figs. 1 and 2, where it is seen quite clearly (especially at highest W/F) that S_{CO_2} increases as S_R decreases.

For the transient regime, an increase in S_R is always accompanied by a decrease in S_{PA} (Figs. 1 and 2); the same behaviour has been observed for the steady state (31). As the heavy compounds are not precursors of selective oxidation products (31), active sites involved in phthalic anhydride formation must be also important for the residue formation.

At lower temperatures, an initial variation in product selectivities occurred (Figs. 1 and 2). o-Tolualdehyde selectivity (S_T) increased slightly with time-on-stream, higher values of S_T being obtained at lower T_R, lower W/F, and higher reactant concentrations. Very low values were observed for phthalide selectivity (S_P). Carbon dioxide selectivity (S_{CO_2}) increased with time-on-stream, higher S_{CO_2} values corresponding to higher T_R and higher W/F. At lower T_R and W/F, higher selectivities for the formation of heavier by-products, which may result from reaction between less oxidized species, could be observed. At higher T_R and W/F, the variation of selectivity with time-on-stream became less pronounced.

For o-tolualdehyde oxidation (Figs. 3 and 4), the catalyst behaviour is similar to that observed when o-xylene was used as reactant. For the transient regime, at lower T_R, a strong conversion decrease occurred, this variation being absent when S_R is negligible. In the same way, an opposite variation can be observed between conversion and S_R and between S_R and S_{PA}. However, at lower T_R, higher conver-

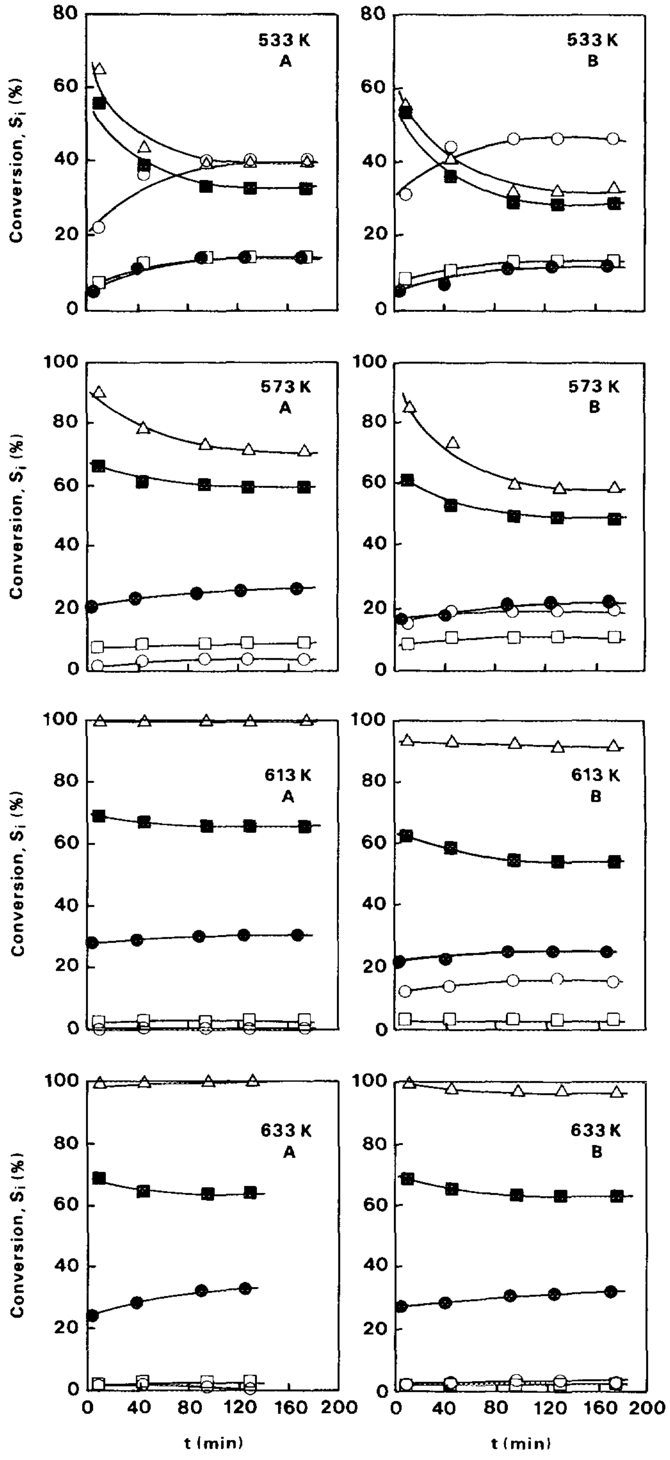

FIG. 4. o-Tolualdehyde oxidation, conversion and product selectivities for transient period at different temperatures (T_R) and reactant concentration. $W/F = 2.3 \times 10^{-4}$ kg_{cat} dm^{-3} h. $C_{tolualdehyde}$ = 0.5 mol% (A), 1 mol% (B). Symbols are as in Fig. 1.

sions, higher S_{PA}, and lower S_R than those for *o*-xylene oxidation were recorded, showing that the adsorbed *o*-xylene molecules must be considered as an important source of heavier products. *o*-Xylene adsorption on the catalyst surface is believed to occur by hydrogen abstraction from a -CH_3 group (32, 33). Results show that before subsequent oxidation it can react with other molecules or adsorbed species, leading to the formation of heavier molecules.

CONCLUSIONS

The study of the transient regime of *o*-xylene oxidation over V_2O_5/TiO_2 (anatase) has shown that an important variation of the catalyst activity and product distribution can occur in the first hours of reaction. For the experimental conditions used, this cannot be ascribed to structural modifications of the catalyst such as formation of rutile or decrease of surface areas. The experimental evidence points to a relation between deactivation and formation of an organic residue on the catalyst surface. This is enhanced at lower T_R and lower W/F and its amount influences the time necessary to reach steady state.

Therefore, the oxidation of *o*-xylene can lead to the formation of selective and total oxidation products and heavy organic compounds. These heavier products can stay on the surface and lead to a decrease in the number of active sites, or can undergo deep oxidation or simply desorb, yielding free active sites. The comparison of *o*-xylene and *o*-tolualdehyde oxidation results shows that adsorbed *o*-xylene can contribute to the formation of such compounds. For the experimental conditions used, a dynamic process involving formation and consumption of these species seems to occur even when the steady state is reached.

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