

INFLUENCE OF ALKALINE PROMOTERS ON THE SELECTIVITY
OF VANADIUM CATALYSTS IN THE OXIDATION OF o-XYLENE
TO PHTHALIC ANHYDRIDE

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Received January 31, 1975

The influence of the alkali metals Na, K, Rb, and Cs on the catalytic properties of the system $V_2O_5-TiO_2$ has been studied in the oxidation of o-xylene. When introducing the promoter into the catalyst, and as the alkaline nature of the metals increases, the initial selectivity to partial oxidation products increases. A correlation is observed between the selectivity and the acidity of the surface, which was determined in a model reaction of cumene cracking. The most acidic sites of the surface are assumed to be responsible for the destructive oxidation of o-xylene. The rate of oxidation of phthalic anhydride remains constant when the nature of the additive varied.

Изучено влияние добавок щелочных металлов Na, K, Rb и Cs на каталитические свойства системы $V_2O_5-TiO_2$ в реакции окисления о-ксилола. При введении в катализатор промотора и с ростом щелочности металла начальная селективность по продуктам парциального окисления увеличивается. Наблюдается корреляция между селективностью и кислотностью поверхности, определенной по модельной реакции крекинга кумола. Предположено, что за деструктивное окисление о-ксилола ответственны наиболее кислые места поверхности. Скорость окисления фталевого ангидрида при вариации природы добавки оставалась постоянной.

In the oxidation of o-xylene to phthalic anhydride, catalysts on vanadium pentoxide basis are used /1/. Non-promoted vanadium pentoxide has a rather low selectivity. In order to improve the selectivity, compounds of transition and alkali

metals are often introduced into the catalyst/2/. The most selective catalysts were obtained using titanium dioxide as an additive and a support. In order to obtain higher yields of phthalic anhydride, salts of alkali metals are often introduced into the vanadium-titanium oxide system /3, 4, 5, 6/.

In the literature there are no systematic data on the influence of alkaline additives on the catalytic properties of these catalysts.

The aim of this work is to study the influence of alkaline promoters on the catalytic properties of vanadium-titanium oxide catalysts in the oxidation of o-xylene and to elucidate the nature of their action.

The catalyst preparation procedure was as follows. The alkali metal nitrate and titanium dioxide of special purity, having the structure of anatase and a surface area of $20 \text{ m}^2/\text{g}$, were introduced into a solution of vanadyl oxalate obtained from V_2O_5 (S. P.) and oxalic acid. The resulting suspension was evaporated under stirring, dried at 80°C and calcined at 450°C for 2 hrs. The V_2O_5 content in the final catalyst was 5 wt.%. The Me_2O to V_2O_5 mole ratio was 1:8. The specific surface areas of the catalyst samples were approximately equal and amounted to 18 to $22 \text{ m}^2/\text{g}$.

The oxidation of o-xylene was carried out in a flow-circulation apparatus at 325°C , using catalyst grains 0.25 to 0.5 mm in size. Calculations showed that the reaction over the catalyst of such grain size proceeded in the kinetic region. The composition of the starting reaction mixture was 1 vol.% o-xylene in air. Under these conditions, the homogeneous non-catalytic oxidation of o-xylene was not observed. The reaction products were analyzed chromatographically.

Figure 1 gives typical curves of the selectivity to individual products against the degree of conversion. Analysis of these curves shows that the oxidation of o-xylene follows a consecutive-parallel scheme.

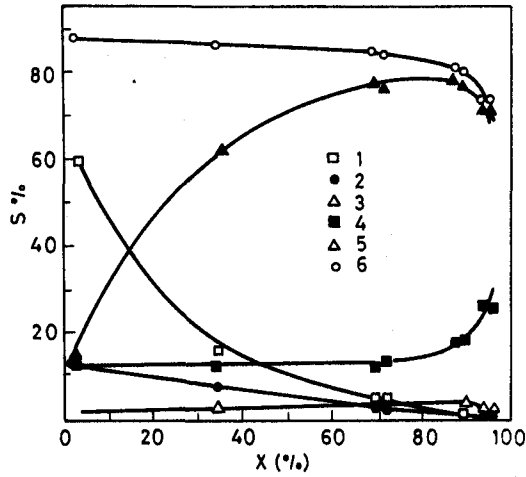
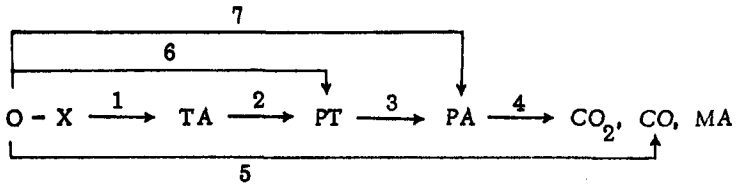


Fig. 1. Selectivity as a function of conversion, at 325°C, catalyst with K additive
 1 - o-TA, 2 - PT, 3 - PA, 4 - CO₂ + CO, 5 - MA, 6 - C₈

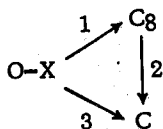


where O-X, TA, PT, PA and MA are o-xylene, o-toluic aldehyde, phthalide, phthalic anhydride and maleic anhydride, respectively. The rates of each route were satisfactorily described using equations of the form:

$$W_i = k_i \frac{C_i}{1 + a C_{OX}} \quad (1)$$

where C_i is the concentration of the starting material of the i -th route; C_{OX} the concentration of o-xylene and k_i the rate constant of the i -th route.

From Fig. 1 it is seen that the sum of the selectivities to partial oxidation products (S_{C_8}) at low conversions determines the maximum selectivity to PA. The variation in S_{C_8} is small over a wide range of conversions. This is due to a low selectivity of the oxidation of TA and PT to combustion products via the parallel route and to a very low value of k_4 as compared with k_1 , k_2 and k_3 . The decrease in S_{C_8} becomes appreciable at high conversions where the selectivities to TA and PT are low. For the determination of the catalytic properties of the catalyst, it is therefore convenient to consider the group of products TA, PT and PA as one product C_8 . In this case one may assume a triangular scheme for the process:



where C is the sum of the products of destructive oxidation (CO, CO₂, MA).

If the rate of each route is given by an equation of type (1), after rearrangement and the introduction of S_0 and b for $\frac{k_1}{k_1+k_3}$ and $\frac{k_2}{k_1+k_3}$, respectively, one obtains /8/

$$S_{C_8} = S_0 - bS_{C_8} \frac{x}{1-x} \quad (2)$$

where x is the conversion, S_0 is the selectivity at $x = 0$, representing the extent of the parallel oxidation of O-X to partial oxidation products.

From the above equation, the values of S_0 and b can be determined graphically. The value of S_{C_8} as a function of $S_{C_8} \frac{x}{1-x}$ is given in Fig. 2 for several samples, while the values of S_0 and b are in Table 1.

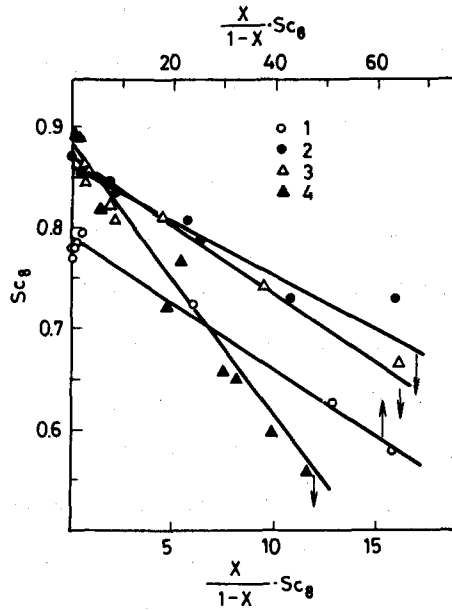


Fig. 2. S_{C_8} vs. $S_{C_8} \frac{x}{1-x}$ for catalysts with Na (1), K (2), Rb (3), Cs (4) additives

Table 1

Influence of the nature of the alkaline promoter on the kinetic characteristics at 325°C

Additive	S_0	$b \times 10^2$	$(k_1+k_3) \times 10^2$	$k_1 \times 10^2$	$k_2 \times 10^4$	$k_3 \times 10^2$
			(nl/g sec)	(nl/g sec)	(nl/g sec)	(nl/g sec)
— —	0.70	0.3	8.1	5.7	2.4	2.5
NaNO ₃	0.79	0.4	9.8	7.6	3.9	2.0
KNO ₃	0.86	1.0	4.1	3.5	4.0	0.6
RbNO ₃	0.87	1.4	1.9	1.6	2.6	0.26
CsNO ₃	0.88	2.7	0.96	0.85	2.6	0.12

The vanadium-titanium oxide catalyst without additive has relatively low values of S_0 and b . The introduction of an alkaline promoter increases S_0 . The relative rate constant of the oxidation of partial oxidation products, b , remains small for the sample with Na additive but increases in the case of K, Rb and Cs. In the series of the alkaline promoters an increase in S_0 and b is observed.

It should be noted that not all of the catalyst samples studied are stable. The activity of the samples decreased during the experiments. At the same values of x the selectivity remained constant. The higher the degree of conversion, the more stable the catalyst. The samples without additive and with Na and K additives were stable at high degrees of conversion. The instability of the catalyst at low values of x may be due to the reduction of vanadium to an inactive state. The samples with Cs and Rb additives were stable over the whole range of x values.

At high values of x the rate can be described by an equation first order in *o*-xylene. The values of the rate constants for the total conversion ($k_1 + k_3$) and for the individual routes are given in Table 1. In the series of the catalysts a decrease in the rate constant for the total conversion and, accordingly, in k_1 and k_3 is observed. The decrease in k_1 is less pronounced than in k_3 . As a consequence, the initial selectivity increases. The value of k_2 is approximately constant. Small deviations from the given relationships appear to be due to the inaccuracy of the constants.

Derivatographic measurements show that during the preparation of the catalysts the alkali metals nitrates decompose to oxides. Therefore, alkali metal additives must decrease the acidity of the catalyst surface.

During destructive oxidation of *o*-xylene the cleavage of the carbon skeleton of the *o*-xylene molecule occurs as a result of interaction between the basic benzene

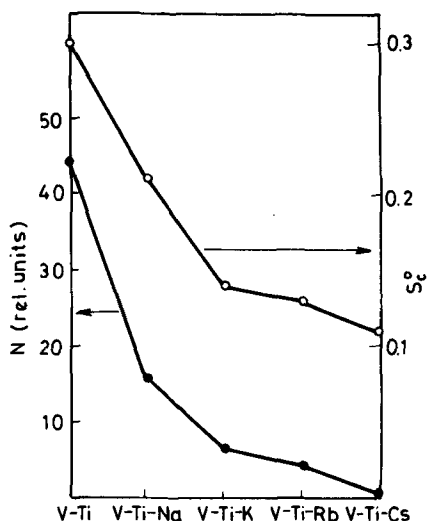


Fig. 3. Influence of the nature of additive on the acidity (N) and selectivity (S_{C_8}) of the catalyst

ring and the acidic surface sites. Therefore, one can expect that the rate of destructive oxidation of o-xylene will decrease with the decrease in the acidity of the catalyst surface, which must lead to an increase in S_0 . The introduction of alkaline promoters decreases the surface acidity, and the selectivity increases as evidenced by the results. The effect of the additive on the value of S_0 increases as its alkaline nature becomes more pronounced.

In order to verify the assumption on the influence of the acid-base properties of the catalyst on the selectivity, the acidity of the catalyst samples was measured in the model reaction of cumene cracking known to occur on the acid sites /7/. Measurements were made by a pulse technique at 350°C. The degree of cumene conversion did not exceed 1%. Figure 3 represents the dependence of the catalyst acidity and the initial selectivity to the products of destructive oxidation of S_0 on

the nature of the additive. The satisfactory correlation between these values confirms the above assumption.

The increase in the value of b in the series of the catalysts results from a decrease in the total reaction rate constant ($k_1 + k_3$). The absolute value of the rate constant of oxidation of partially oxidized products k_2 remains approximately the same. This leads one to suggest that the oxidation of phthalic anhydride occurs on sites different from those responsible for the oxidation of o-xylene.

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