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V_2O_5/TiO_2 Catalysts for the Vapor-Phase Oxidation of β-Picoline: Influence of the TiO_2-Carrier

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The heterogeneously catalyzed vapor-phase oxidation of β-picoline to nicotinic acid over a series of V_2O_5/TiO_2 was investigated. Characterizations of the catalysts were carried out using X-ray diffraction, temperature-programmed desorption, and N_2-adsorption. It was found that the use of an anatase type of TiO_2-carrier with a higher BET surface area enhances the activity of the V/Ti-oxide catalyst enormously. TiO_2-materials with different BET surface areas (between 10 and 270 m^2/g) were used. Since these different materials originate from different processes, namely, the chloride and the sulfate process, the influence of the sulfate content was investigated. Additionally, the use of different TiO_2 crystalline structures (anatase vs rutile) was evaluated, and a sulfate-free TiO_2-material was modified with sulfate and cerium oxide during vanadia impregnation. The results of these experiments verified that the sulfate content itself did not have a strong influence on the catalyst activity. XRD-characterization of the catalysts demonstrated that only the TiO_2 and the V_2O_5 phase could be detected. This corresponds with other investigations in the literature and strengthens the assumption that there is a synergetic effect of a V_2O_5 layer supported by TiO_2 as a catalyst carrier. Therefore the increase of the interface between these two crystalline phases is the determining factor to improve the catalyst's activity. © 2000 Academic Press

Key Words: β**-picoline oxidation; V_2O_5–TiO_2; vapor phase.**

INTRODUCTION

The literature on the vapor-phase oxidation of organic compounds catalyzed by vanadium titanium oxide catalysts is quite numerous. Focussing on the selective oxidation of β-picoline to nicotinic acid, an important intermediate for pharmaceuticals and food additives, one can see three different groups of results. The first is marked by a high amount of deep oxidation (1–3). They operate around temperatures of 300 to 450°C with a molar oxygen/water/β-picoline ratio of around 40–50/80–110/1. Yields are around 35–45% with a conversion up to 100%. The second group (4) uses much higher dilution factors of water (470–670/1), which enhances the yield to 50–65%. In (5) it could be demonstrated with the same catalyst that this improvement is caused solely by the increase in water and oxygen excess. In all examples cited, air is used as the oxygen source. This is valid as well for the results of the third group, who have published yields of 82–86% with a simple V_2O_5/TiO_2-catalyst (6). The oxygen/water/β-picoline ratio is around 40/70/1 with temperatures between 250 and 290°C. This is an astonishing increase in product selectivity and therefore strongly reduces deep oxidation. But all authors describe a binary vanadia/carrier system as the essential basis for their catalysts. Further sources examining the vapor phase oxdiation of organic compounds confirm that anatase has a positive effect on the vanadia layer although it is not active in this reaction itself (7).

In the present work we studied the effect of the modification of the titania carrier on the performance of the V_2O_5/TiO_2-catalyst in this reaction. The chemical composition and the BET surface area of the titania have been examined. We showed how the differing results mentioned above with V_2O_5/TiO_2-catalysts in this vapor-phase oxidation interrelate.

EXPERIMENTAL

Catalyst Preparation

The catalysts used in this examination are vanadia/titania systems with TiO_2 as carrier and V_2O_5 as the active catalytic layer. The vanadium precursor (ammonia-meta-vanadate) was dissolved in water. The carrier TiO_2-material was then mixed with the aqueous vanadia solution and stirred. The water was vaporized during stirring at 100°C under vacuum. The dry material was dried for 3 h at 150°C and calcined in air for 4 h at 450°C. The heating rate was 1°C per minute.

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Characterization of Catalyst

The X-ray diffraction (XRD) was carried out on a Siemens D 5000 diffractometer using Cu $K\alpha$ radiation with a scanning range (2θ) from 3° to 90°.

The ammonia temperature-programmed desorption (NH_3-TPD) experiment was performed to scrutinize the difference between a TiO_2-supported V_2O_5-catalyst and bulk V_2O_5 with respect to acidic properties. Prior to adsorption with ammonia, the catalyst sample (150 mg) was pretreated for 8 h in a helium stream at 450°C. Then 30 ml/min of ammonia were conducted over the catalyst at 100°C. After adsorption, the gas stream was switched to helium (10 ml/min) to remove physically adsorbed ammonia from the catalyst surface. The ammonia desorption profile was detected by a pH-meter and titration with a 0.1 N HCl-solution at a heating rate of 10°C/min from 10 to 800°C under 10 ml/min helium flow.

The determination of the Hammett acid strength of the acid sites was executed as described by Tanabe *et al.* in (8).

BET specific surface areas of the catalysts were measured by N_2 adsorption using a Micromeritics ASAP 2010 in liquid nitrogen at 77 K.

Catalytic Testing

The catalytic tests were conducted in a conventional laboratory-scale fixed-bed reactor. The reactor was a coil made out of steel with 70-cm length by 0.6-mm I.D., which was in an electrically heated oven. The catalyst was filled in at the end of the tube. The air flow was controlled by a Krohne rotameter. Before entering the oven, the air flows through a temperature-controlled device and exits saturated with β-picoline. Water is pumped with a Telab pump through a steel tube with a 1.5-mm I.D. into the oven, where it is mixed with the air and β-picoline stream at the beginning of the catalyst bed. Right after the reactor, nicotinic acid is precipitated from the process gas in a steel tube heated at 160–200°C. The water, unreacted β-picoline, pyridine-3-carbaldehyde, and dissolved nicotinic acid are condensed, and samples are analyzed by HPLC. This renders it possibile to determine the absolute concentration of the components in the liquid. Therefore conversion and selectivities can be calculated without analysis of the vapor phase. Prior examinations confirmed that the vapor phase only consists of products of total oxidation, i.e., CO_2, CO, and HCN (9).

RESULTS AND DISCUSSION

Thermodynamics and Reaction Network

According to the literature, the side products of this reaction are pyridine-3-carbaldehyde as reaction intermediate and CO_2, CO, and HCN as deep oxidation products (10). The decomposition of β-picoline or nicotinic acid to gaseous substances (e.g., CO_2, CO, and HCN) is summarized as a single-product group. Therefore we propose the reaction network shown in Fig. 1. Referring to this network, a mathematic determination of the Gibb's free energy could be made according to the model of Chermin and van Krevelen (11). The results are published in (12). Obviously the deep oxidation is, in any case, the preferred route from the thermodynamic point of view. But the calculations in (12) depict as well that the desired oxidation of β-picoline to nicotinic acid via the pyridine-3-aldehyde is thermodynamically feasible. As experiments published in (5) demonstrate, the route from the pyridine-3-carbaldehyde to the deep oxidation products (r_5) can be neglected. As we can see from the experiments in (12), a parallel decomposition reaction of β-picoline takes place only in the presence of high excesses of water, but independently of the V/Ti-oxide catalyst (reaction r_3 in Fig. 1). Therefore for the published selectivities towards total oxidation products (CO_2, CO, HCN), one has to distinguish between the parallel and the consecutive path (r_3 and r_4). The precise control of residence time will be crucial for this reaction in order to avoid the consecutive oxidation of nicotinic acid. But in order to reduce the loss of β-picoline due to its direct decomposition, the deciding specification is the catalyst's activity. This parameter must be increased in order to reach complete conversion and reduce the necessary reactor volume.

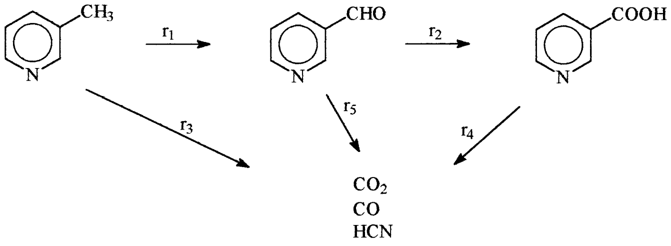

FIG. 1. Reaction network.

Variation of the BET Surface of the TiO_2-Carrier

The specifications for an oxidation catalyst with respect to its surface are dominated by two characteristic features of these reaction types. First, they are highly exothermic. Therefore it is necessary to reduce the catalyst's outer surface to a minimum in order to reduce the development of hot spots. Second, as already mentioned, the residence time of the organic molecules in the reactor has to be limited in order to avoid deep oxidation. Thus the catalyst must not have a pore system into which the substrate could diffuse. In most publications on V/Ti-oxide catalysts, such a catalyst has been synthesized by using TiO_2-carriers with a BET surface area of 10–50 m^2/g (5, 13). This carrier has been impregnated with amounts of 1–10 wt% V_2O_5, and the development of a vanadia monolayer could be observed (14, 15). Also, the BET surface of the catalyst stayed below 50 m^2/g.

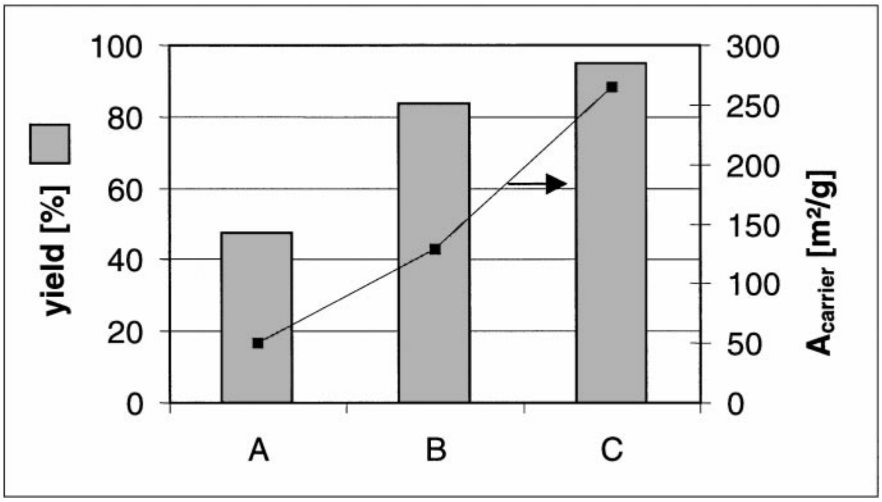

FIG. 2. Variation of BET surface. Reaction conditions: $T = 265$–275°C, WHSV = 0.04 g/(g_{Kat} h), $O_2/H_2O/\beta$-Pic = 35/55–70/1 (molar).

In our experiments we used a series of TiO_2-carriers of the anatase modification with different BET-surfaces, impregnating them with adequate amounts of vanadia. Table 1 presents the characteristic data of these materials. We compared them on the basis of their catalytic performance in the vapor-phase oxidation of β-picoline with respect to their yield of nicotinic acid. The results in Fig. 2 show clearly that the increase of TiO_2-surface enhances the activity and selectivity of the catalyst at identical reaction conditions. Nevertheless it has to be considered that other parameters of these catalysts were changed too. First, due to the higher surface area of the carrier material, a higher amount of vanadia was impregnated upon them. This resulted in a collapsing outer surface area of the catalyst, therefore making it suitable for application in an exothermic vapor-phase reaction. As further examinations in (17) show, the total amount of vanadia plays a secondary role with respect to a low amount of deep oxidation. Regarding the differing chemical compositions of the TiO_2-materials, the way they were produced has to be considered. The TiO_2-P25 material has been produced by the chloride-process, yielding an anatase material with a slight amount of rutile formation. In contrast, the TiO_2 materials Anatase B and Anatase C were synthesized by the sulfate process, yielding a higher surface area and a sulfate content of about 0.5%. As described in (18), the presence of sulfate in the TiO_2 changes the acid character of the material.

Characterization of Catalysts

We used the temperature-programmed desorption (TPD) of ammonia and the determination of acid strength with Hammett indicators in order to characterize the surface of the used materials. This examination shows that all of the used TiO_2 materials are only slightly acidic and do not show a difference with respect to their Hammett acid strength. The values in Table 2 are in accordance with examinations in (8). The TPD analysis of the Anatase C and the resulting catalyst (C) in comparison with bulk V_2O_5 gives a more detailed picture; see Fig. 3. While the Anatase C and a sulfur-free Anatase A (Aldrich; surface area = 10 m^2/g) show a peak at a temperature of around 200°C, the first has a long shoulder to higher temperatures, originating from more acidic sites. The higher amount of acidic sites might result from a higher surface area (270 m^2/g vs 10 m^2/g). But when it is impregnated with the vanadia (yielding the catalyst sample C), there remains only one distinct peak at 200°C. See Fig. 4. The TPD analysis of pure V_2O_5 shows one

TABLE 1

V/Ti-Oxide Catalysts with Differing Carrier Characteristics

Catalyst	TiO_2-carrier	BET-surface carrier (m^2/g)	V_2O_5-content (wt%)	BET-surface catalyst (m^2/g)
A	TiO_2-P25	50	2.3	25
B	Anatase B	130	17	65
C	Anatase C	265	19	40

TABLE 2

Hammett Acid Strength of the TiO_2-Carrier Materials

TiO_2-material	Hammett acid strength
TiO_2-P25	4.8–3.3
Anatase B	4.8–3.3
Anatase C	4.8–3.3

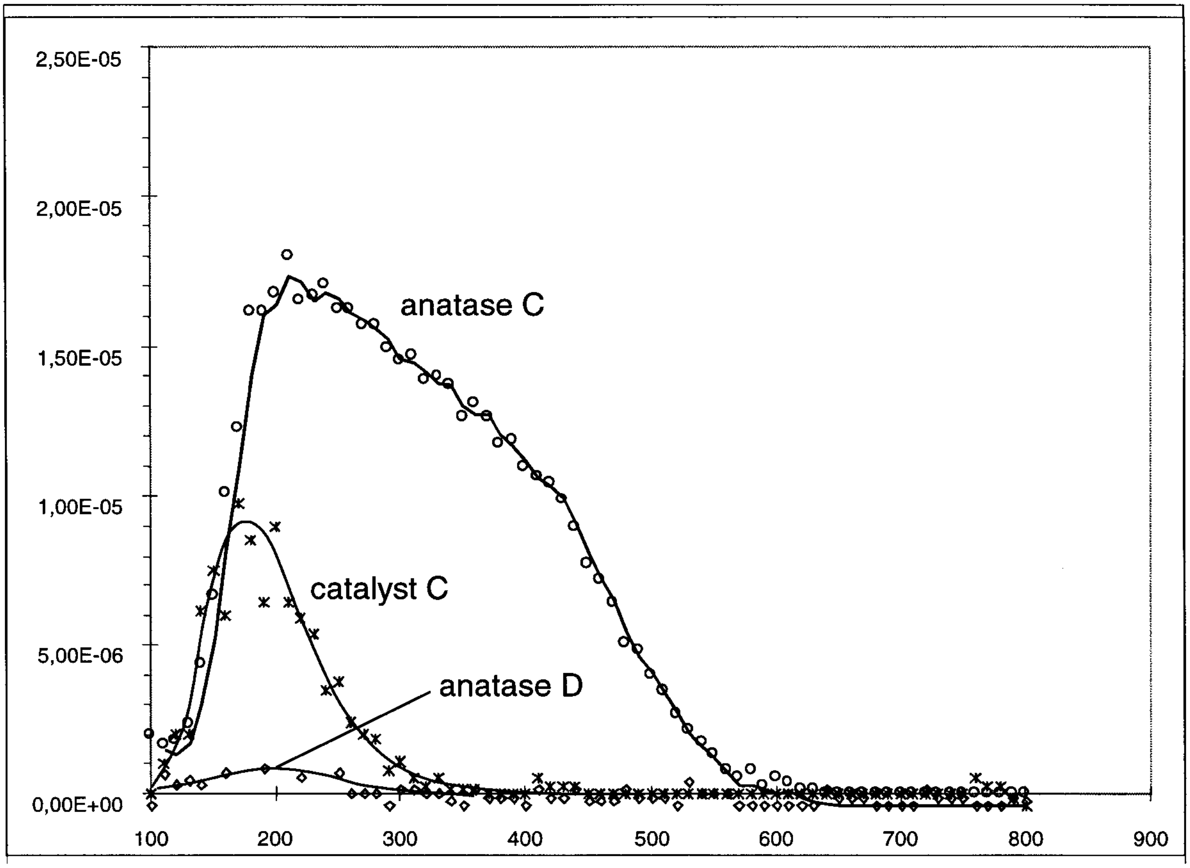

FIG. 3. NH_3-TPD.

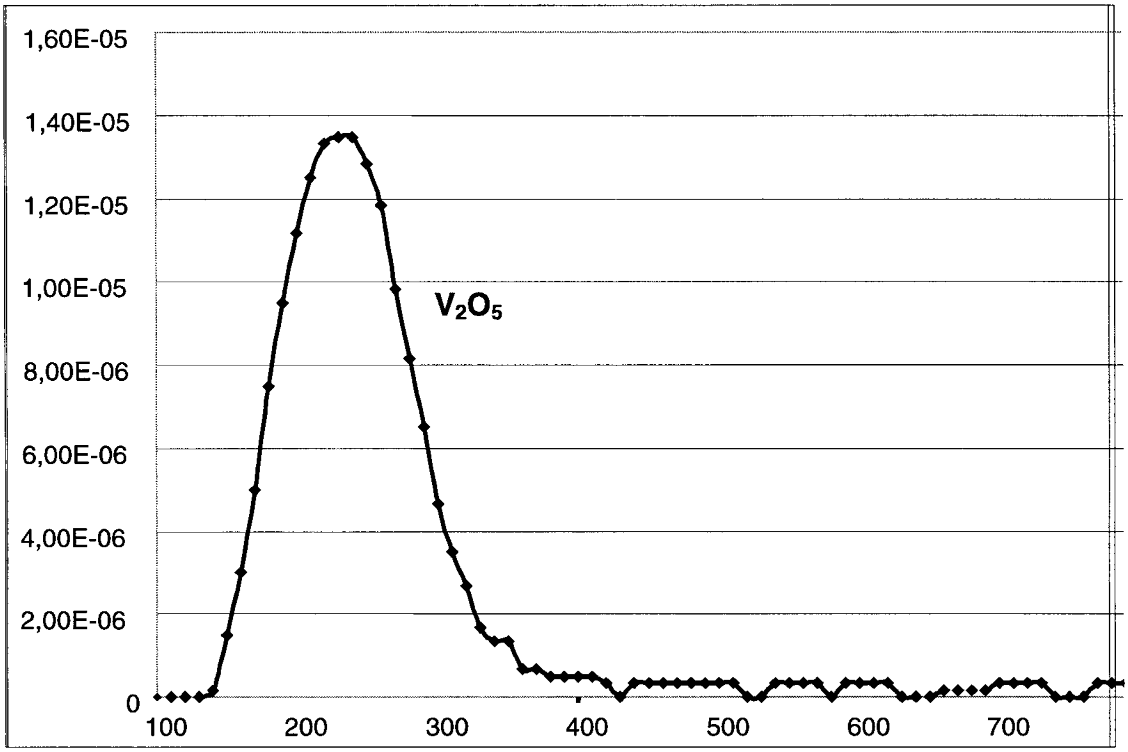

FIG. 4. NH_3-TPD of V_2O_5.

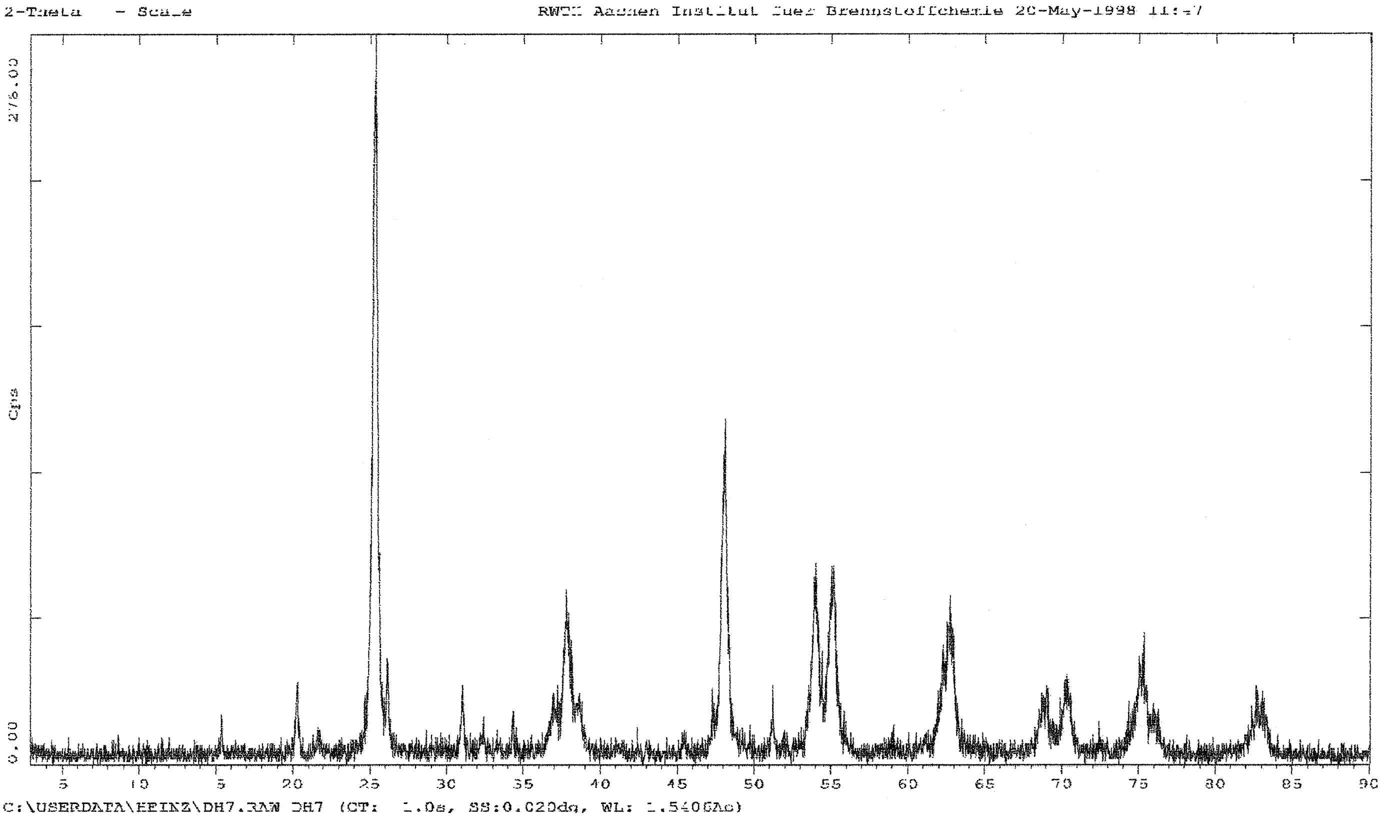

FIG. 5. X-ray diffractogram of C.

distinct peak at a temperature of around 235°C. Obviously the acidic strength of pure V_2O_5 is slightly stronger than that of the resulting catalyst. We assume that the change in acidic strength compared to the carrier and the pure V_2O_5 indicates that there is interaction between the two oxides. Also the total amount of acidic sites on the surface of the catalyst is reduced in comparison to bulk V_2O_5.

We additionally examined the X-ray diffractogram of the catalysts in order to find more hints as to their different behaviour in this oxidation. See Figs. 5 and 6. The diffractogram of the sample C shows smaller peaks at 2θ values of 15, 20, 26, 31, 34, 5, and 51. These can directly be related to the signals of V_2O_5. The remaining peaks represent the complete diffractogram of the anatase material. In the case of the catalyst A only the signals of the TiO_2-P25 material are detected. This is in complete accordance with the observations made in (14). Ruiz *et al.* report that XRD analyses of catalysts with a low V_2O_5 content on TiO_2 only show the peaks of the carrier TiO_2 material. Only at higher vanadia loadings can crystalline V_2O_5 be detected. They further confirm that no phases other than TiO_2 and V_2O_5 were detected (14).

The catalysts characterization generates the following picture. After impregnation, the catalyst still consists of the TiO_2-phase of its original carrier material and the pure V_2O_5-phase of the additional layer. With respect to the examination of the acidic sites, we can differentiate between catalyst A and catalyst C, the latter being responsible for over 90% yield. The quality of the acidic sites on the carrier materials is different, since Anatase C contains 0.5 wt% sulfate. After impregnation, catalyst C has a narrow distribution of acidic sites whose strength is influenced by carrier-active layer interaction. The quantity of acidic sites is lower on sample C than on its carrier Anatase C, while the amount of acidic sites on pure bulk V_2O_5 is slightly higher.

With respect to the difference in product yield of the two catalysts A and C in the vapor-phase oxidation of β-picoline, one can observe that the higher BET surface area of Anatase C might be the main parameter to induce the higher activity of catalyst C. As mentioned earlier, these two catalyst samples have further differences which can be attributed to their respective synthesis procedures (chloride vs sulfate process). Therefore the following examinations show to what extent other parameters influence the catalysts activity with respect to the vapor-phase oxidation of β-picoline.

Variation of the Crystalline Phase of TiO_2

As the XRD spectra of the catalysts A and C confirm, the TiO_2-P25 carrier of the first catalyst also contains a small

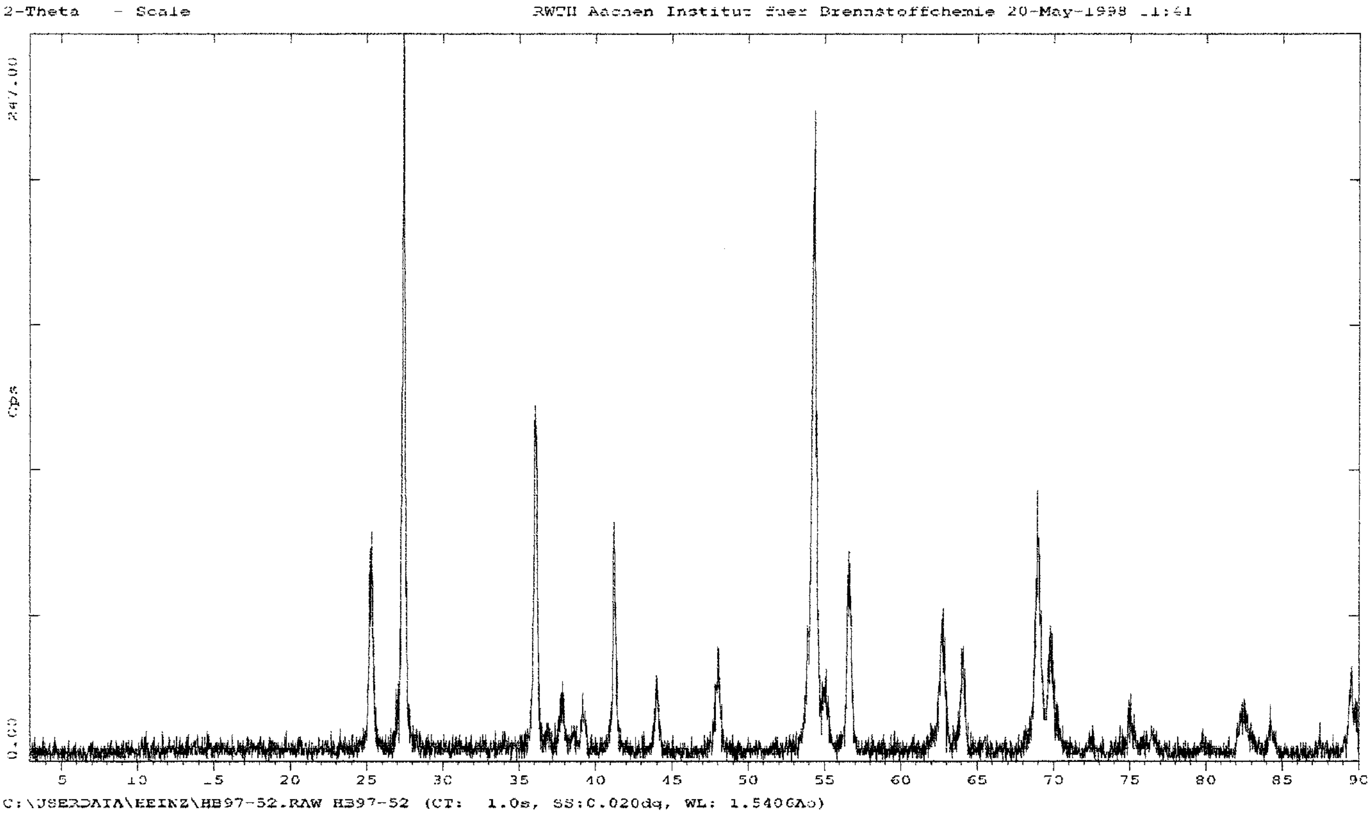

FIG. 6. X-ray diffractogram of A.

amount of rutile. According to (16) this might influence the development of the vanadia structure upon the TiO_2 carrier. In order to check the influence of the crystalline composition of the TiO_2-carrier in this reaction, we chose a pure anatase material from Aldrich (Anatase A) and a rutile TiO_2 from Aldrich (Rutile A), with BET surface areas around 10 m^2/g. Both were impregnated with 2.5 wt% V_2O_5. The impregnation procedures for all catalysts presented in this paper are identical. See Fig. 7.

As Fig. 8 depicts, the different crystalline TiO_2-phases do not have a substantial influence upon the product yield in these reaction conditions. The fact that the yields are rather

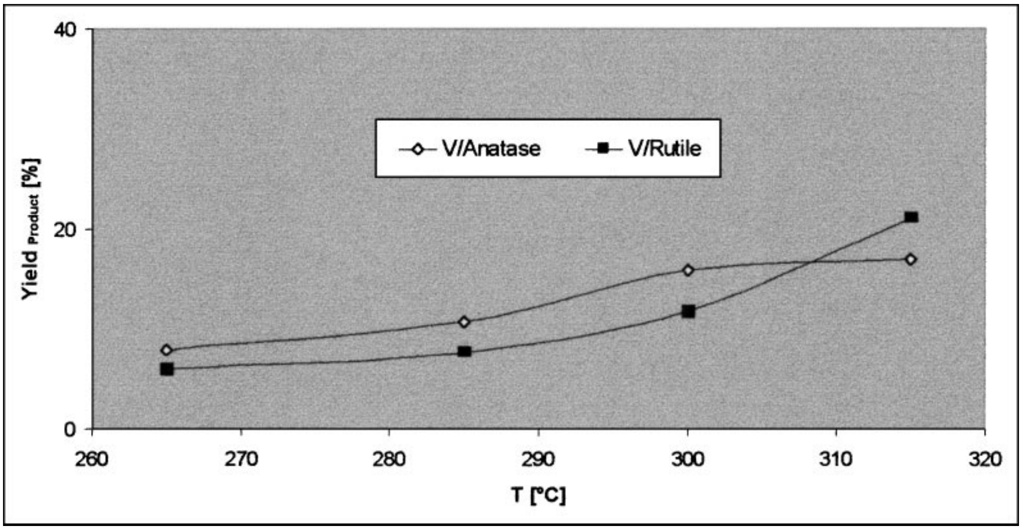

FIG. 7. Comparison of anatase and rutile TiO_2. Reaction conditions: $T = 265–315°C$; WHSV = 0.18 g/(g_{Kat} h); $O_2/H_2O/\beta$-Pic = 40/70/1; catalyst V/anatase, 2.5% V_2O_5 on Anatase A; catalyst V/rutile, 2.5% V_2O_5 on Rutile A.

TABLE 3

Variation of Sulfate Content

Catalyst	TiO_2-carrier	BET-surface TiO_2 (m^2/g)	Sulfate-content (%)	V_2O_5-content (wt%)	BET-surface cat. (m^2/g)
B	Anatase B	130	0.5	17	65
B*	Anatase B*	129	1.5	11	61
C	Anatase C	275	0.5	19	40
C*	Anatase C*	260	1.5	22	35

low can be related to the even smaller BET surface area of the anatase and rutile samples (10 m^2/g), strengthening the assumption that this is the important parameter for catalyst activity. Therefore we can exclude that the minor content of rutile in the TiO_2-P25 is responsible for the difference between the product yields of catalyst A (based on TiO_2-P25) and those of the other samples.

Variation of Sulfate Content

From the analyses we have received a hint that the sulfur content plays a minor role in the catalysts acidity, but in order to verify its influence on the oxidation of β-picoline we impregnated two more TiO_2-carrier materials containing higher amounts of sulfate. See Table 3. As the specific values confirm, we can compare the carriers with respect to their sulfate content only while the other relevant parameters remain constant. The diagrams in Figs. 8–11 demonstrate clearly that the total sulfate content within the limits mentioned in this paper does not have as strong of an influence on conversion and selectivity as the actual surface area of the TiO_2-carrier does. Comparing Figs. 10 and 11, one can observe that the reaction temperature where the maximum yield is obtained is shifted with a higher sulfate content from 275 to 265°C. Nevertheless one can state that the influence of the sulfate content on the total yield is rather low.

Modification of the Sulfate-Free TiO_2-Carrier

On the basis of the TiO_2-carrier which is sulfate free (TiO_2-P25, chloride process), we modified the impregnation procedure in order to add further components to the catalyst. For one, we added sulfate ions to the catalyst by stirring it during the impregnation procedure in diluted sulfuric acid. A second catalyst was impregnated with cerium oxide before impregnation with vanadia in order to verify the influence of further oxides between the TiO_2 and the V_2O_5 phases on the catalytic performance. See Table 4. Again, these catalysts were compared in terms of their activity in the vapor-phase oxidation of β-picoline under the current reaction conditions. See Fig. 12. The additional modification of the V/Ti-oxide system does not lead to a better catalytic performance in this reaction. The sulfate content itself is not necessary to improve the catalyst.

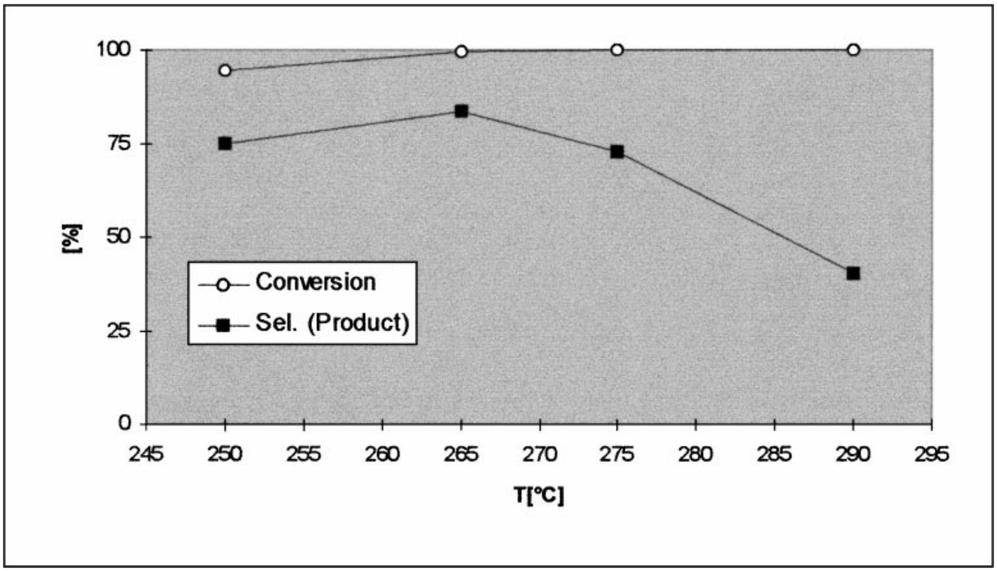

FIG. 8. Catalyst B: 20 wt% V_2O_5 on TiO_2-carrier with 0.5% sulfate; BET surface area = 130 m^2/g.

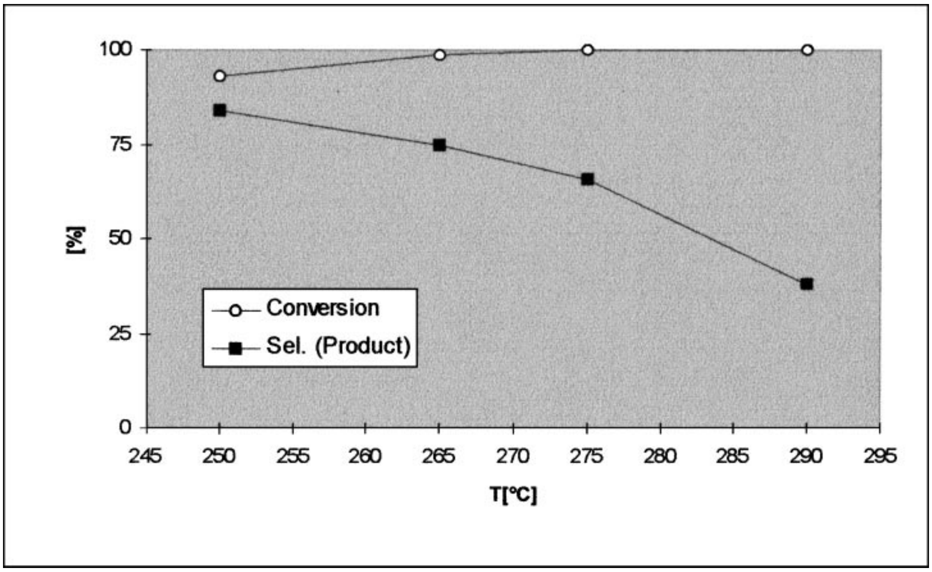

FIG. 9. Catalyst B*: 20 wt% V_2O_5 on TiO_2-carrier with 1.5% sulfate; BET surface area = 130 m^2/g.

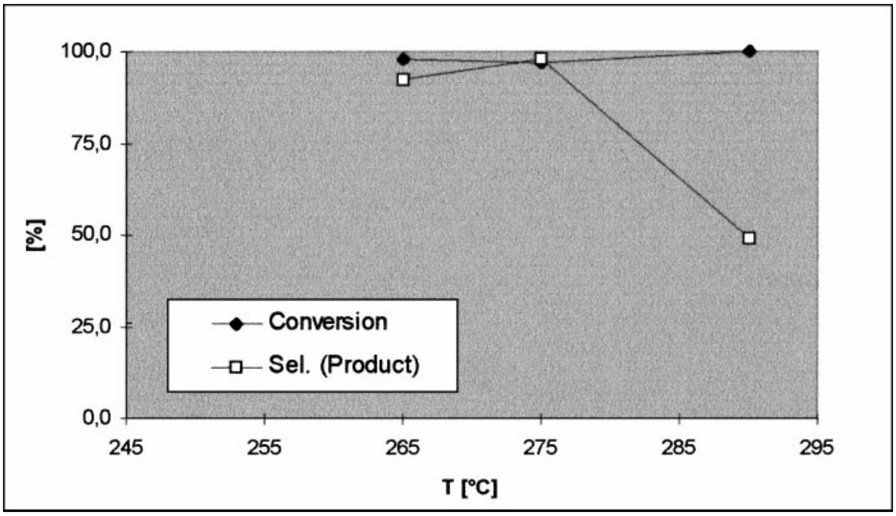

FIG. 10. Catalyst C: 20 wt% V_2O_5 on TiO_2-carrier with 0.5% sulfate; BET surface area = 270 m^2/g.

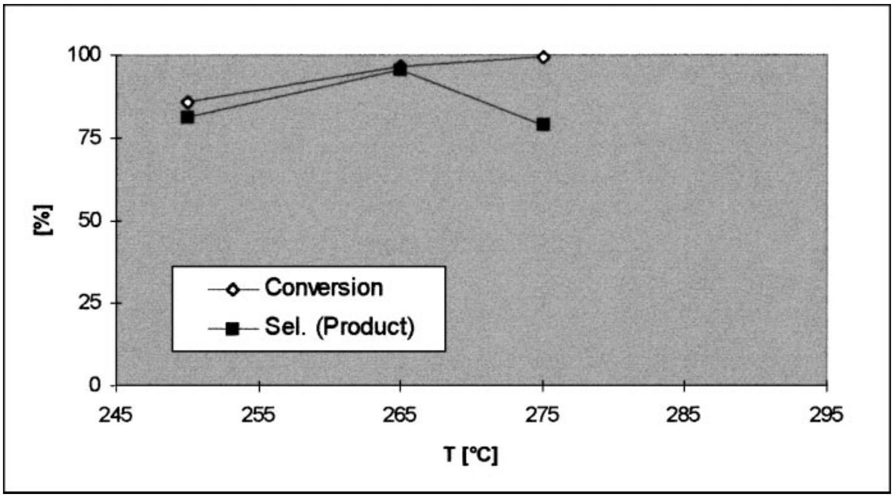

FIG. 11. Catalyst C*: 20 wt% V_2O_5 on TiO_2-carrier with 1.5% sulfate; BET surface area = 270 m^2/g. Reaction conditions (Figs. 8–11): WHSV = 0.04–0.05 g/(g_{Kat} h), $O_2/H_2O/\beta$-Pic = 35/55/1.

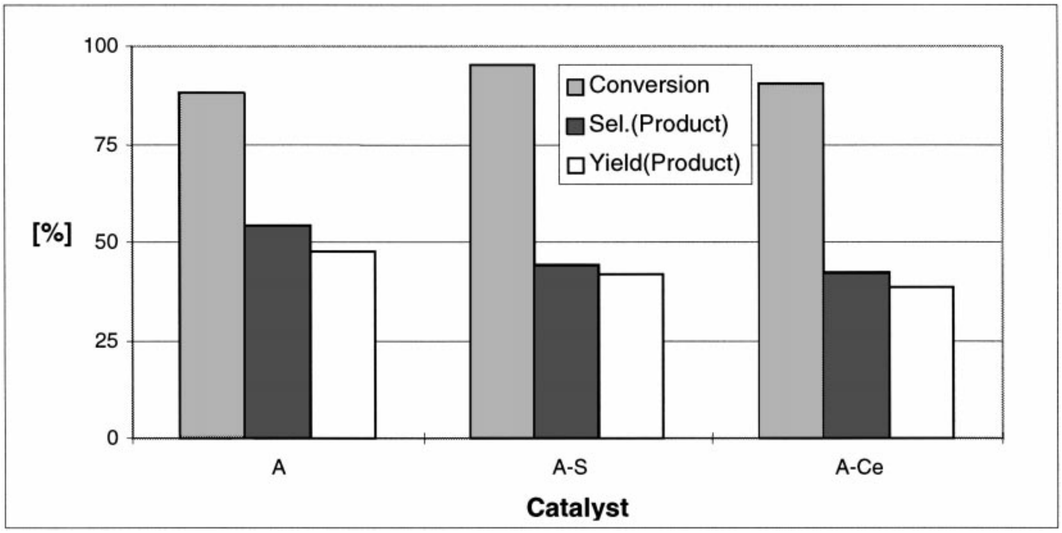

FIG. 12. Modification of sulfate-free TiO_2-carrier. Reaction conditions: WHSV = 0.04 g/(g_{Kat} h), $O_2/H_2O/\beta$-Pic = 35/70/1, $T = 275°C$.

According to (19) the addition of alkali metals on TiO_2-P25 improves the carrier's surface capacity for vanadia impregnation. This can be supported for the addition of CeO_2, but despite the higher amount of vanadia the presence of CeO_2 on the surface of the titania seems to lower conversion and selectivity towards nicotinic acid. Therefore our experiments present a clear statement: The main parameter which improves the catalyst in this oxidation reaction is the surface area of the TiO_2-carrier. This might happen in combination with the sulfate content, although tripling the sulfate content renders little change. The roles of the V_2O_5 and its carrier can be related to the Mars/van Krevelen mechanism which is proposed for this type of reaction (20), including the following steps (21, 22):

- activation of the substrate,
- nucleophilic attack of the O^{2-} lattice ion,
- hydrogen abstraction and desorption of the product,
- adsorption of oxygen from the gas phase, transfer of electrons from the solid to the adsorbed oxygen molecule, and incorporation of oxygen ions into the lattive of the oxide.

According to (22) the oxidation of β-picoline to nicotinic acid necessitates three lattice oxide ions, the abstraction of two hydrogen atoms from the substrate, the insertion of two oxygen atoms, and the transfer of six electrons. Additionally the authors of (7) report that the crystal planes of V_2O_5 and TiO_2 in the anatase form have an excellent structural fit. This leads us to the assumption that V_2O_5 in combination with TiO_2 has better possibilities for balancing the manifold steps necessary in the Mars/van Krevelen mechanism over the entire crystal structure of both metal oxides. These synergies may lead to a higher catalytic activity, and the required reaction volume could be substantially reduced. Since the undesired deep oxidation results mainly from a parallel decomposition of the substrate, which is independent of the catalyst, the reduction of reactor volume also reduces this undesired reaction path. Therefore it is possible to improve the yield of nicotinic acid to values up to 90–97% in our experiments.

TABLE 4

Modification of Sulfate-Free TiO_2-Carrier

	A	A–S	A–Ce
V_2O_5-content (wt%)	2.3	1.2	4.8
Surface area (m^2/g)	24.9	50.0	47.7
Additives	—	0.5 wt% SO_4^{2-}	0.5 wt% CeO_2

CONCLUSIONS

The catalytic tests show that yields of 90–97% nicotinic acid can be achieved with a V_2O_5/TiO_2 system based on a TiO_2-carrier with a surface area of 270 m^2/g. The X-ray diffractograms show that it consists only of the anatase and the V_2O_5 phase. Ammonia TPD demonstrates that the catalyst's surface has acidic sites compared to pure V_2O_5. The sulfate content of these TiO_2-materials with higher surface areas does not have such a significant influence upon the catalytic activity after impregnation with vanadia. We observed that the catalyst's outer surface area is strongly reduced after the impregnation step, making this a suitable type of catalyst for exothermic vapor-phase oxidations. The crucial parameter for the optimization of a catalyst for this reaction is the area of the interface between the crystal phases of TiO_2 and V_2O_5.

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