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Catalysis Today 32 (1996) 265–272

CATALYSIS
TODAY

Selective oxidation of toluene on $V_2O_5/TiO_2/SiO_2$ catalysts modified with Te, Al, Mg, and K_2SO_4

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Abstract

The effect of the modification of vanadia catalysts supported on TiO_2/SiO_2 by the oxides of Al, Mg and Te, and K_2SO_4 on the selective oxidation of toluene in the vapor phase has been studied. The catalysts were prepared by successive impregnation and characterized by BET surface measurements, XRD, XPS, and TPR. Addition of the second component decreased specific activity in all cases, except Al, mainly due to the decrease of surface area. Intrinsic activity was increased with addition of Te and Al, and decreased by that of Mg, while K_2SO_4 had little effect. These differences could be explained by the observed changes in either vanadium surface dispersion or reducibility. Selectivity to benzaldehyde increased markedly with addition of Te or K_2SO_4, that caused the formation of new oxide phases, $V_3Ti_6O_{17}$ and TiV_2O_6, in which vanadium is in a partially reduced state.

Keywords: Toluene selective oxidation; Vanadia; Titania; Silica; Tellurium; Aluminium; Magnesium; Potassium sulfate

1. Introduction

In contrast to the selective oxidation of o-xylene, a well known industrial process based on V_2O_5/TiO_2 [1,2], practically no successful catalyst has been found for the selective oxidation of toluene in the gas phase. A number of metal oxide catalytic systems have been tested for this reaction, most of them based on vanadia [3–7], supported either on SiO_2 [3,5] or TiO_2 [3,4,6]. The coating of SiO_2 supports by a TiO_2 layer, initially developed for DeNOx reactions, increases the mechanical strength of supported vanadia catalysts, while keeping high surface area and high resistance to sintering. But at the same time, it modifies the properties of the supported vanadia [8]. Then, it has been applied in our group as a tool to modulate the catalytic properties of vanadia for several oxidation reactions [8–10]. In a previous work [9], the selective oxidation of toluene on monolayer vanadia catalysts supported on SiO_2 coated with various amounts of titania was studied at atmospheric pressure between 623 K and 773 K. Both activity and selectivity to partial oxidation products increased with the titanium content, the highest being obtained for an TiO_2 amount above one monolayer. However, in the reaction conditions studied, the main partial oxidation product on the V–Ti–Si samples was maleic anhydride.

Based on these results, we have explored the activity of the more active V–Ti–Si catalyst formulation in a lower temperature range, as well as the use of additives, as a way to increase the selectivity to benzaldehyde (BzA). In this

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PII S0920-5861(96)00174-5

work we study the influence of the additives on the physico-chemical properties of these catalysts for the selective oxidation of toluene to BzA. The oxides of Mg, Al and Te, and potassium sulphate were selected as additives.

2. Experimental

2.1. Preparation of catalysts

The preparation of the titania-coated silica support and its physico-chemical characterization has been described in detail elsewhere [9,10]. Briefly, support was prepared covering SiO_2 (Aerosil MOX 80) with TiO_2 by the method of Geus et al. [11] (hydrolysis of $TiCl_3$). The final analytical TiO_2 content was equivalent to a 1.6 theoretical monolayers (TML). The undoped catalyst, denoted here as VTS (cf. V-2TS in our previous work [9]) was prepared by impregnation with an ethanolic solution of vanadyl acetyl-acetonate, in an amount equivalent to 1 TML of V_2O_5, followed by solvent evaporation at 383 K and calcination at 773 K. Catalysts with additives (denoted *M*-VTS, where *M* is the additive) were prepared by successive impregnation of the same $V_2O_5/TiO_2/SiO_2$ precursor before the calcination step, with aqueous solutions of magnesium nitrate, telluric acid, potassium sulphate (KS), or an ethanolic solution of aluminum isopropoxide. The weight ratio V_2O_5 to additive was 3:2, except for mKS-VTS in which the ratio was 3:1. For comparative purposes, catalyst V/KS-Si was prepared by the method of Kumar Ray and Mukherjee [12] described in Ref. [13]: vanadium was impregnated on a support obtained from silica dissolved in a KOH solution, then diluted to a pH of 5–5.6 by addition of diluted H_2SO_4, and evaporated to dryness.

2.2. Characterization of catalysts

Surface areas and textural properties of the catalysts were determined by the BET method in a Micromeritics ASAP 2000 apparatus, and are summarized in Table 1 with their composition. Powder X-ray diffraction (XRD) patterns were obtained with a diffractometer Seifert 3000P by using the Ni-filtered Cu Kα radiation, scanning the 2θ range between 5 and 70° at a rate of 2°/min. X-ray photoelectron spectra (XPS) were obtained with a Leybold LHS 10 spectrometer provided with a hemispherical electron analyzer and a Mg anode X-ray exciting source (Mg Kα = 1253.6 eV), as detailed in Ref. [9]. Accurate binding energies (BE) were determined by reference to the C 1s and Si 2p lines to which arbitrary BE values of 284.6 and 103.4 eV were assigned [14]. Temperature programmed reduction (TPR) profiles were obtained with a microbalance Perkin Elmer TGS-2 (sensitivity = 1 μg). Prior to the experiment, the samples were heated in a N_2 flow up to 773 K to clean the surface. After cooling in N_2 flow down to 373 K, gas was switched to N_2/H_2 mixture (1:1 v/v) with a flow rate of 100 ml/min and the experiment began, heating at 4 K/min up to 900 K, while continuously recording the weight changes.

Table 1
Characteristics of the *M*-VTS catalysts

Catalyst	V (wt%)	*M* (wt%)	BET area (m^2/g)	Pore vol. (cm^3/g)	TPR weight loss (wt%)
VTS	3.84	–	102	0.47	1.10
Mg-VTS	3.70	2.66	71	n.d.	1.48
Al-VTS	3.70	2.36	97	n.d.	1.16
Te-VTS	3.80	n.d.	45	0.11	1.75
mKS-VTS	3.60	1.15 [a]	40	0.16	1.93
KS-VTS	3.64	2.25 [a]	15	0.05	2.46
V/KS-Si	5.67	15.5 [a]	33	0.24	14.7

[a] Expressed as K; n.d.: not determined.

2.3. Catalytic tests

The catalytic selective oxidation of toluene was tested in a fixed bed, down-flow tubular reactor in the temperature range 600–700 K, using a reactant mixture toluene:O_2:He in molar ratio 1:13:38, with a reciprocal of space velocity W/F = 15 g.h/mol toluene, as described in detail in Ref. [15]. Conversion and selectivity to products are expressed as mol% on a C atom basis. In all experiments carbon balances were within 100 ± 5%.

3. Results and discussion

3.1. Catalytic activity

In the conditions used here, benzaldehyde (BzA), benzoic acid (BzAc) and carbon oxides were the main products on each catalyst. At a variance of previous results on VTS [9], only minor amounts of maleic anhydride and benzene were detected in some experiments in this temperature range. Fig. 1 shows the variation of toluene conversion with reaction temperature on the catalysts supported on TiO_2-coated silica. The catalyst supported on K_2SO_4-modified silica, V/KS-Si, (not shown) was about 7.5 times less active than mKS-VTS. As can be seen, the addition of the second component decreased activity in all cases, except that of Al_2O_3. On this catalyst (Al-VTS) carbon balances tended to be deficient and when conversions were above those reported here, the connections downstream the reactor became clogged by deposit of solids, indicating that very high boiling point compounds were formed, probably polynuclear aromatics formed via oxidative coupling [16].

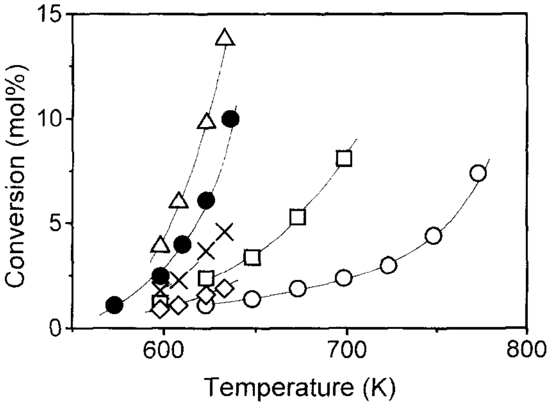

Fig. 1. Toluene conversion versus reaction temperature on: △ Al-VTS; ◇ Mg-VTS; ✕ Te-VTS; □ mKS-VTS; ○ KS-VTS; ● VTS. W/F = 15 g.h/mol toluene.

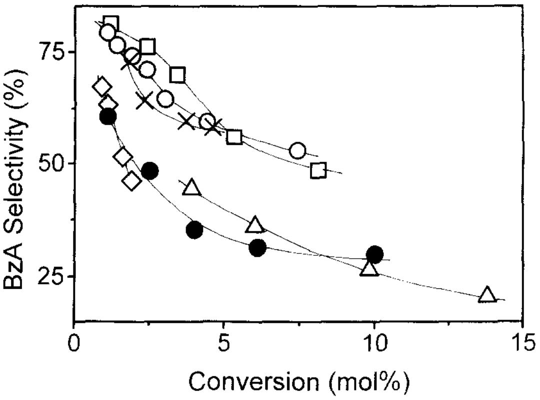

Fig. 2. Dependence of selectivity to BzA on total conversion. △ Al-VTS; ◇ Mg-VTS; ✕ Te-VTS; □ mKS-VTS; ○ KS-VTS; ● VTS. W/F = 15 g.h/mol toluene.

In all the cases, initial selectivities to BzA were rather high, but decreased with increasing conversion (Fig. 2). The catalysts modified by Al and Mg showed a behavior similar to that of VTS. On the contrary, addition of Te and K_2SO_4 increased markedly the selectivity of BzA, that reached initial values (at 1–3% conversion) close to 80 mol%, and remained ca. 20 mol% higher than that of the unmodified VTS sample at higher conversions. As also BzAc is of industrial importance, it is relevant to indicate that the addition of Al or Te did not change the selectivity to BzAc on VTS (between 18 and 30 mol%) at isoconversion, while this selectivity decreased on mKS-VTS and no BzAc was detected among the products of Mg-VTS and KS-VTS. This makes the total selectivity to partial oxidation products (POx = BzA + BzAc) to decrease in the order: Te-VTS > mKS-VTS > Al-VTS ≥ VTS ≫ Mg-VTS.

3.2. Bulk characterization

All XRD patterns of the catalysts (Fig. 3) showed a broad band at low 2θ values, due to the amorphous silica of the support. VTS pattern showed no peak attributable to V_2O_5 phase and only broad weak peaks assigned to the four

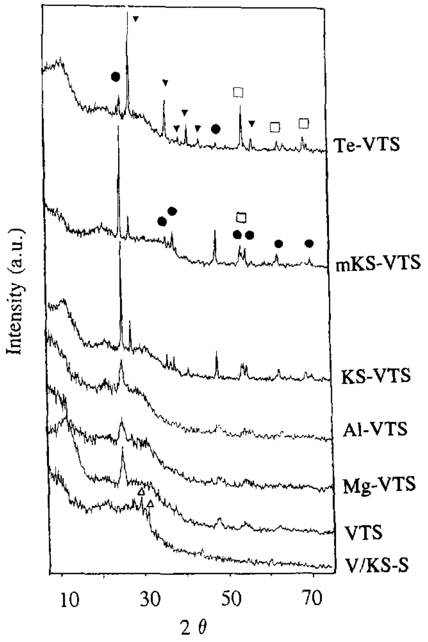

Fig. 3. XRD patterns of catalysts. Identified phases: ● TiO_2; ▼ $V_3Ti_6O_{17}$; □ TiV_2O_6; △ K_2SO_4.

strongest reflections of anatase [17], indicating a low crystallinity of this phase. This agrees well with its Raman spectrum [18], in which bands of anatase were weak and no band assigned to crystalline V_2O_5 was found. Addition of Al or Mg oxide did not modify the phase composition nor the crystallinity. On the contrary, addition of K_2SO_4 caused changes in the very similar patterns of both KS-VTS and mKS-VTS: (i) the intensity of the anatase peaks increased, with additional peaks not observed with VTS being detected; (ii) low intensity peaks at interplanar spacings $d = 3.00$ and 2.90 Å adscribed to K_2SO_4 were detected in the higher sulphate content sample (KS-VTS); and (iii) new peaks at $d = 3.25$, 2.48, 2.18, 1.68, and 1.65 Å, assigned to the most intense reflections of the complex oxides $V_3Ti_6O_{17}$ [19] and TiV_2O_6 [20] appeared. The strong increase of anatase peaks intensity, also found in the Raman spectra [18], indicates that probably K_2SO_4 promotes the sintering of anatase crystals and, in a lower degree, that of the mixed V–Ti oxides.

The strongest peaks in the Te-VTS pattern were those assigned to $V_3Ti_6O_{17}$ and TiV_2O_6; anatase peaks were also present, but less intense than for VTS. No peak assigned to tellurium compounds was detected. Thus, these binary oxide phases, which contain vanadium in oxidation states lower than 5 +, were well crystallized and predominant in this sample. The reason for this change should come from the preparation method: during the impregnation with aqueous solution of telluric acid, an acid attack to the surface of the precursor could take place, with partial disolution of vanadium and titanium oxides. This would favor the formation of the double oxides, leading to well crystallized phases after calcination.

3.3. Surface composition

The oxidation state and surface dispersion of component elements were analyzed by XPS. The measured BE values of orbitals Ti $2p_{3/2}$

Table 2
Bulk and surface atomic ratios of *M*-VTS catalysts

Catalyst	Bulk ratio		XPS surface ratio			
	V/(Ti + Si)	*M*/(Ti + Si)	V/(Ti + Si)	*M*/(Ti + Si)	Ti/Si	S/(Ti + Si)
VTS	0.051		0.061		0.090	
Mg-VTS	0.053	0.078	0.057	0.098	0.096	
Al-VTS	0.052	0.062	0.122	0.334	0.099	
Te-VTS	0.053	0.020	0.098	0.038	0.029	
mKS-VTS	0.049	0.021 [a]	0.076	0.031 [a]	0.059	0.016
KS-VTS	0.051	0.041 [a]	0.061	0.032 [a]	0.057	0.016
V/KS-Si	0.121	0.432 [a]	0.086	0.082 [a]	–	0.051

[a] Expressed as K.

(458.5 eV), V $2p_{3/2}$ (517.4 eV), Al 2p (517.4 eV), Mg 2p (50.4 eV), S 2p (74.3 eV), K $2p_{3/2}$ (168.9 eV) and Te 3d (576.4 eV) showed no meaningful differences among the catalysts. These values can be ascribed to the oxidation states Ti^{4+}, V^{5+}, Mg^{2+}, Al^{3+}, S^{6+} in sulphates, K^{+} in very ionic environments, and Te^{4+} in TeO_2, respectively. Table 2 summarizes the surface atomic ratios determined from the corresponding XPS peak intensities. Ti/Si ratio was not changed by Al or Mg addition but decreased by one third in Te-VTS, in good agreement with the decrease of the anatase phase shown by XRD. This seems to confirm the hypothesis of an acid attack to the precursor surface during the tellurium impregnation. As a similar, less marked effect was also observed in the K_2SO_4-doped samples, this can be related to the formation of the mixed V–Ti oxide phases.

Vanadium surface dispersion, calculated as XPS (V/(Ti + Si)) atomic ratio, increased markedly with addition of Al, and slightly with that of Te. Addition of Mg or K_2SO_4 had practically no effect. The good fit between the surface contents of S and K in samples KS-VTS and mKS-VTS indicates that both are present as K_2SO_4. By contrast, V/KS-Si (supported on K_2SO_4-modified SiO_2) showed a strong decrease of the surface content of S and K, which are unbalanced, and a slighter one in V. This means that most of the K_2SO_4 is retained at the core of the support in this sample, and vanadium becomes relatively less dispersed.

3.4. Reducibility

The TPR profiles of catalysts modified by oxides showed just one reduction peak (Fig. 4), alike the profile of VTS, although the maximum reduction rate peak temperature was decreased 20 K by addition of Te, increased 85 K by addition of Mg and addition of Al had little effect.

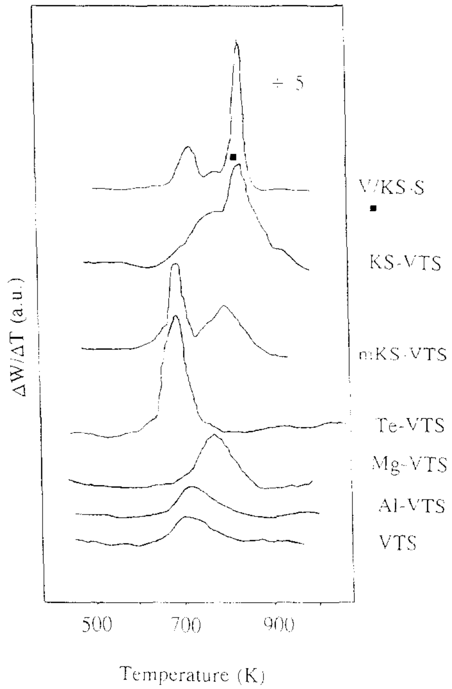

Fig. 4. TPR profiles of catalysts.

Table 1 summarizes total weight losses in the TPR experiments. That of Al-VTS corresponded to that calculated for the reduction of the vanadium from V^{5+} to V^{3+}, while that of VTS was slightly lower, indicating that probably vanadium was partially reduced in this sample. Weight loss of Mg-VTS was higher, but taking into account the temperature range of the peak, this could be interpreted as due to overlapping with the decomposition of surface carbonate species bonded to Mg. TPR profiles of catalysts modified by K_2SO_4 were more complex, showing at least two overlapping peaks. However, they can be interpreted by analyzing the TPR of sample V/KS-Si. It shows two well-defined peaks at 813 and 924 K, with a small intermediate shoulder. A similar profile was reported by Monti et al. [21] with bulk V_2O_5–K_2SO_4. Taking into account the sample composition, the weight losses in the two peaks (5.2 and 9.5 wt%) fit well with those calculated for the reduction of V^{5+} to V^{3+} and SO_4^{2-} to SO_3^{2-}, and for the reduction of SO_3^{2-} to S^{2-}, respectively. This allows to propose to interpret the low temperature peak as due to simultaneous reduction of v^{5+} and SO_4^{2-} to V^{3+} and

SO_3^{2-}, and the high temperature peak to reduction of SO_3^{2-} to S^{2-}.

TPR profile of mKS-VTS is similar to that of V/KS-Si, with maxima shifted to lower temperatures (687 and 786 K), and the ratio between areas of both peaks is reversed, as expectable from its lower bulk K_2SO_4/V_2O_5 ratio. In the KS-VTS profile, the first peak shifted to higher temperatures, overlapping the second one. This means that the higher amount of K_2SO_4 stabilized vanadium against reduction. Nevertheless, in both cases the total weight loss was lower than that calculated for the reduction of all the sulfur and vanadium present. This could indicate that vanadium may be partially reduced in these samples, in good agreement with the presence of $V_3Ti_6O_{17}$ and TiV_2O_6, phases where vanadium is in oxidation states lower than V^{5+}.

3.5. General discussion

Except of Al, which increased activity of VTS, the addition of a second component caused a detrimental effect in the total conversion of toluene but also a decrease of the specific surface area, more marked in the case of Te and K_2SO_4, due to pore blocking as revealed by the pore volume values (Table 1). So, the decrease in specific activity is mostly due to the loss of surface area during the second impregnation. Taking into account this factor, a different picture emerges: the intrinsic activity (i.e., per unit surface area) for each catalyst was not so different [18] and decreased in the order: Al-VTS > Te-VTS > VTS ≥ mKS-VTS ≥ KS-VTS ≫ Mg-VTS. Jonson et al. [22] correlated the activity of metal oxides in the oxidation of toluene with the IR frequency of its M–O bond stretching vibration, and postulate a higher activity for those oxides whose υ(M–O) allows a resonance with the vibration of the toluene molecule. The free molecule of toluene shows an IR band at 1040 cm^{-1}, attributed to the rocking of the methyl group. This must be the vibration which allows the interaction of catalyst surface with the toluene molecule by modifying the space arrangement of the methyl group towards a planar configuration of the molecule. Recently, Ramis et al. [23] found that the band of the vanadyl groups observed at 1035 cm^{-1} in the undoped V_2O_5–TiO_2 sample was shifted to 1040 cm^{-1} by Al addition and to 1032 cm^{-1} by that of Mg. This suggests, according to the analysis by Jonson et al., that Mg addition should have a detrimental effect and that of Al a beneficial one. Our results agree well with this approach.

However, addition of Al had also a strong effect in vanadium surface dispersion, what could cause the observed increase. In fact, the ratio between intrinsic rates of VTS and Al-VTS (1:2) was close to that of their XPS surface dispersion of vanadium (1:1.7). Given the precision of the techniques involved, it becomes evident that the activity per surface vanadium atom is practically equal in both catalysts. The high surface concentration of Al (fivefold the bulk content) may be responsible of the observed change of the surface vanadium species, with formation of isolated vanadyl species (Raman band at 1035 cm^{-1} [18]). This seems to indicate that, at least in supported catalysts, the observed increase of activity is probably due more to the increase of the number of active centers than to the increase of intrinsic activity of the active center, as suggested by Jonson et al.

The increase of activity of Te-VTS could be explained in a similar way, as the vanadium surface dispersion increased. Besides, TPR peak shifted to lower temperatures; however, the overlapping of simultaneous reductions of Te and V makes uncertain to assign this change to an increase of the vanadium reducibility. On the other side, the formation of new V-containing phases, $V_3Ti_6O_{17}$ and TiV_2O_6, may also involve the presence of new vanadium species with the same or higher activity that those on the VTS surface.

The decrease of intrinsic activity of K_2SO_4-containing samples with sulphate content may be due to the better vanadium dispersion and reducibility in sample mKS-VTS. It is noteworthy that the activity of these catalysts supported on the TiO_2–SiO_2 support was almost one order of magnitude higher than that of V/KS-Si, in spite of their similar BET areas. This may be due to either to the surface impoverishment in V in the latter or to the presence of the V–Ti mixed oxides in the former.

Besides activity, the key criterion for the selection of a catalyst is selectivity. The improvement of selectivity to total partial oxidation products (POx = BzA + BzAc) at isoconversion should be explained by the inhibition of the consecutive oxidative degradation of BzA and/or BzAc, which may be achieved when desorption of these products is favoured before further interaction with oxygen species. Both Te and K_2SO_4 increased POx selectivity and reduced severely the surface area. This may lead to think that the increase of selectivity is mostly to the reduction of area by disappearance of microporosity, a known effect in the oxidation of alkylaromatics. However, it this was true one should expect a higher selectivity for KS-VTS than for mKS-VTS, which area is double. We found just the opposite, what allow to discard this as the main cause of the promotion. Besides, the different trends in BzAc selectivity show that each dopant plays a different role to produce its promoting effect: the increase of BzA selectivity by K_2SO_4 is due to the inhibition of its oxidation to BzAc (inhibition that increases with the sulphate content), while that caused by Te is due to the inhibition of the degradation of POx to carbon oxides, as it does not change the BzAc formation. The different product distribution on the K_2SO_4 containing catalysts (similar selectivity to BzA on both but higher selectivity of mKS-VTS to BzAc) should be due to the different reducibility shown by the two samples.

To our knowledge, the selectivity to BzA and POx of catalysts Te-VTS and mKS-VTS are very high, among the higher maximum selectivities reported in the literature on vanadia-based catalysts for reaction in the absence of water in the feed: 40–60% BzA on low V-content V_2O_5/SiO_2 [5], 40% to BzA and 25% to BzAc on V_2O_5/TiO_2 [6], 60% BzA on V_2O_5/K_2SO_4–SiO_2 [13]. Very recently, Miki et al. [24] reported that addition of TeO_2 to V_2O_5/TiO_2 catalyst greatly improved the activity in the vapor phase oxidation of toluene to selectively form BzAc. A very high selectivity (74.4%) at high conversion (79.8%) is reported. However, these results are obtained using an extremely high steam content in the feed (toluene/O_2/H_2O/N_2 molar ratio = 1/2/55/10) and a rather low space velocity (15000 h^{-1}); so, no comparison can be made with our results.

Finally, it is noteworthy that the most selective catalysts studied here have in common the presence of mixed oxide phases of Ti and V in which vanadium is in a partially reduced state. Further work is needed to clarify the role of such phases.

4. Conclusions

The combination of a TiO_2-coated silica support and the use of the Te and K_2SO_4 as additives leads to an increased selectivity to BzA formation, among the highest reported in the literature when using feeds *in the absence of water*. Thus, $V_2O_5/TiO_2/SiO_2$ catalysts modified by Te or K_2SO_4 could constitute the basis for a suitable catalyst formulation. However, as promoter addition produced a strong decrease of surface area, and hence of specific activity, further studies are needed to reduce this drawback and to obtain a practical catalyst.

Acknowledgements

This work was financed by Spanish Comisión Interministerial de Ciencia y Tecnología (CICYT) under Project MAT92-0189. We thank Prof. J.L.G. Fierro for the XPS measurements.

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