

PROMOTED TiO₂ (ANATASE)-SUPPORTED VANADIUM OXIDE CATALYSTS. TPR STUDY AND ACTIVITY IN OXIDATION OF TOLUENE

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Vanadium oxide doped with K, Li, Bi, Sb, Te, U or Mo oxide, supported on TiO₂ – anatase, was studied by temperature programmed reduction (TPR). The influence of the addition of promoters (up to molar ratio M : V = 0.5) to 5 wt.% V₂O₅/TiO₂ catalyst on the TPR profile is presented in correlation with their catalytic activity in the vapor phase oxidation of toluene. All promoters, except Bi₂O₃, decrease the catalyst reducibility and decrease the rate of the toluene oxidation. A strong negative influence on the activity of the toluene oxidation have K, Li, and Te oxides. However, the presence of all tested promoters in the molar ratio M : V = 0.05 has a positive effect on the selectivity of benzoic acid formation. A further increase of this ratio leads to a decrease of the selectivity in the case of U, Mo and mainly K oxides, while with Li, Bi, Sb, and Te oxides, the selectivity remains almost unchanged. No correlation between TPR profiles of doped catalysts and their selectivity was found. The most effective promoter of vanadia catalysts for the benzoic acid production is Sb oxide, possessing a very high selectivity at high conversion of toluene.

Key words: V₂O₅; TPR; Oxidation of toluene; Vapor phase; Benzoic acid.

Vanadium oxide catalysts are well known as active catalysts in a number of oxidation reactions, including also oxidation of alkyl aromatics¹. From supported vanadium-based catalysts for the vapor phase oxidation, catalysts supported on low-temperature modified TiO₂ – anatase play an important role.

It is known and generally accepted that anatase-supported vanadia is the most active and selective catalytic system for the side-chain oxidation of methylbenzenes^{2,3}. Detailed activity measurements and spectroscopic studies of the toluene oxidation over this system were done by Jonson et al.⁴. The influence of the catalyst surface roughness on the selectivity to partial oxidation products was described by Mori et al.⁵. A possible reaction mechanism of the toluene oxidation, based on IR spectroscopy has been proposed⁶⁻⁸. Many authors described the modification of the catalytic activity of TiO₂ supported vanadia by the addition of a promoter to the active phase. The influence of potassium oxide^{9,10}, phosphorus pentoxide^{10,11}, potassium sulfate¹², Sb, Se and Te oxides¹³⁻¹⁵ and recently also molybdenum trioxide¹⁶ was described. In the most recent paper of Miki et al.¹⁷ results of the toluene oxidation over V₂O₅/TiO₂ catalysts pro-

moted with K_2SO_4 and W, Mo, Ag, Se, Sb, and Te oxides are presented. It is evident, that the influence of different additives on titania supported vanadia was tested in the oxidation of toluene. None of these studies, however, correlate the catalytic activity with catalyst reducibility, which is changed by the addition of the promoters.

EXPERIMENTAL

Catalyst Preparation

An impregnation method was used for the catalyst preparation. NH_4VO_3 and inorganic salts or oxides were added to an oxalic acid solution in deionized water. An appropriate amount of TiO_2 (100% anatase, verified by X-ray diffraction, specific surface area $7\text{ m}^2\text{ g}^{-1}$) was added under mixing. After evaporation of water at $80\text{ }^\circ\text{C}$, the catalysts were pelletized, crushed and sieved to a particle size fraction of 0.3–1.0 mm. All catalysts were dried for 15 h at $120\text{ }^\circ\text{C}$ and then calcined for 4 h at $450\text{ }^\circ\text{C}$ with heating rate $5\text{ }^\circ\text{C min}^{-1}$ in air, to prevent the formation of a solid solution of V^{4+} in the TiO_2 (ref.¹⁸) and the transformation of anatase to rutile¹⁹. The composition and the specific surface area of catalysts are given in Table I.

Catalyst Characterization

Temperature programmed reduction (TPR) experiments were performed in a conventional flow apparatus with a thermal conductivity detector using a heating rate of $10\text{ }^\circ\text{C min}^{-1}$ in the temperature range $25\text{--}600\text{ }^\circ\text{C}$ and a flow of 30 ml min^{-1} of H_2 . All experiments were done with a sample containing about 25 mg of V_2O_5 without any special sample pretreatment in the TPR reactor. The specific surface area of the catalysts was measured by the Pulse Chemisorb 2700 apparatus (Micromeritics) at $-196\text{ }^\circ\text{C}$ using the BET method with nitrogen as adsorption gas.

Oxidation of Toluene

Catalytic tests were run in a tubular stainless steel reactor with i.d. 8.4 mm in the temperature range $330\text{--}380\text{ }^\circ\text{C}$ and atmospheric pressure. Toluene and water were dosed by linear pumps, the flow of gases was controlled by mass flowmeters. In the upper part of the reactor, both toluene and water were evaporated and mixed with air and N_2 (total STP flow rate of gases $24\text{ dm}^3\text{ h}^{-1}$). The catalyst (3 g, particle size 0.3–1.0 mm) was diluted with 3 g of inert material (cordierite calcined at $1400\text{ }^\circ\text{C}$, specific surface area $<1.0\text{ m}^2\text{ g}^{-1}$) to avoid adverse thermal effects. Carbon oxides were analysed continuously using an Infralyt 4 apparatus. Unconverted toluene (PhMe) was analysed on line by a gas chromatograph equipped with TCD, using a column packed with 10% silicone UCW 982 on Chromatone NAW DMCS 0.125–0.16 mm. Benzaldehyde (BzH) and benzoic acid (BzOH) were collected in coolers, extracted by diethyl ether and analysed by gas chromatography with FID using a column packed with 10% of APIEZON L + 1% of H_3PO_4 on Chromosorb W AW 0.125–0.16 mm.

Axial temperature profiles in the catalyst bed were measured. The difference between the lowest and the highest temperatures in the catalyst bed did not exceed $10\text{ }^\circ\text{C}$. Maximal temperatures in the catalyst bed are given as reaction temperatures in Table II.

Under reaction conditions, almost no oxidation of toluene was observed on the catalyst support diluted with cordierite.

The toluene conversion X_T was calculated from the difference of the toluene signal in product mixture and in nitrogen stream. Selectivities of the reaction to benzoic acid S_{BzOH} and benzaldehyde S_{BzH} were calculated on the basis of analysis of condensed products, and selectivities to carbon oxides S_{CO}

and S_{CO_2} were obtained from the amount of CO and CO_2 present in the off-gas. Yields of the products were calculated from X_T and the selectivity.

RESULTS AND DISCUSSION

Temperature Programmed Reduction

Reported TPR data of supported V_2O_5 catalysts coming from different authors are not typical "fingerprints" of materials tested. As it was shown by Bosch et al.²⁰, the reduction of reducible species in the sample depends on a lot of parameters, as heating rate of the sample and its amount, flow rate and composition of the reducing gas. In our

TABLE I
Composition and surface area of 5 wt.% $\text{V}_2\text{O}_5\text{-MO}_x/\text{TiO}_2$ catalysts

Metal	M : V molar ratio	MO_x	wt. %	Area, $\text{m}^2 \text{g}^{-1}$	
				fresh	spent
	–		0	6.3	6.3
K	0.05	K_2SO_4	0.24	6.5	6.6
	0.1		0.49	7.1	5.8
	0.2		0.97	7.1	5.5
	0.5		2.43	5.1	5.4
K	0.05	K_2O^a	0.13	6.6	5.9
Li	0.05	Li_2O	0.04	5.7	5.5
	0.2		0.16	6.1	5.9
Te	0.05	TeO_2	0.44	6.7	6.9
	0.2		1.75	5.7	5.8
U	0.05	UO_3	0.79	6.3	6.5
	0.2		3.14	7.2	7.5
Mo	0.05	MoO_3	0.4	6.8	6.0
	0.2		1.58	7.6	7.8
Bi	0.05	Bi_2O_3	0.64	6.0	5.7
	0.2		2.56	6.6	6.4
	0.5		6.4	7.1	6.9
Sb	0.05	Sb_2O_3	0.4	7.1	6.0
	0.2		1.6	7.4	7.8
	0.5		4.0	7.2	7.4

^a K from K_2CO_3 .

paper we describe changes of the catalyst reducibility as a result of the addition of promoters. At first, a series of unpromoted V_2O_5/TiO_2 catalysts with different vanadia loading was prepared and measured. Many authors^{1,21} have expressed the amount of V_2O_5 on the catalyst surface as a "number of equivalent monolayers". A single lamella of V_2O_5 on the catalyst surface corresponds to 0.145 wt.% V_2O_5 per m^2 . On the basis, that the specific surface area of the used catalyst support is $7 m^2 g^{-1}$, the numbers in Fig. 1 express not only wt.% of V_2O_5 in TiO_2 but also directly the numbers of theoretical V_2O_5 monolayers present on the catalyst surface. From TPR profiles of unpromoted V_2O_5/TiO_2 catalysts, drawn in Fig. 1, the presence of two peaks is evident. The first one corresponds to the surface phase and the second one to the crystalline V_2O_5 , which is growing and shifted to higher temperatures with increasing V_2O_5 coverage. If less than about four theoretical monolayers are present, there exists only a single peak in the TPR profile. The observed results are in agreement with published data^{1,21}. TPR profiles of tested V_2O_5/TiO_2 catalysts doped with different types and amounts of promoters are shown in Fig. 2.

Oxidation of Toluene

The influence of V_2O_5 loading over TiO_2 on toluene oxidation was tested by varying the content of V_2O_5 from 0 to 20 wt.%. Over unpromoted V_2O_5/TiO_2 catalysts, the conversion of toluene increases with V_2O_5 loading up to ≈ 7 wt.% V_2O_5 . Maximal selectivity of the benzoic acid formation is observed at ≈ 3 wt.% V_2O_5 and maximal yield at ≈ 5 wt.% V_2O_5 in TiO_2 . On the bases of these results, the influence of promoters was studied with 5 wt.% V_2O_5/TiO_2 catalyst, doped with different promoters. Experimental results obtained over catalysts with optimal amount of promoters (at the highest S_{BzOH}) are summarized in Table II.

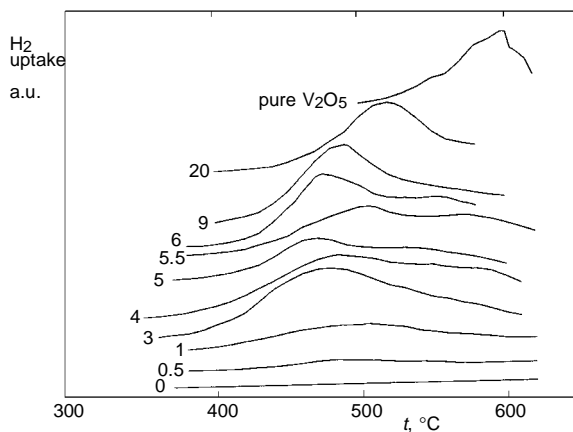


FIG. 1
Influence of V_2O_5 loading on TPR profiles of V_2O_5/TiO_2 catalysts. Numbers denote wt.% V_2O_5/TiO_2

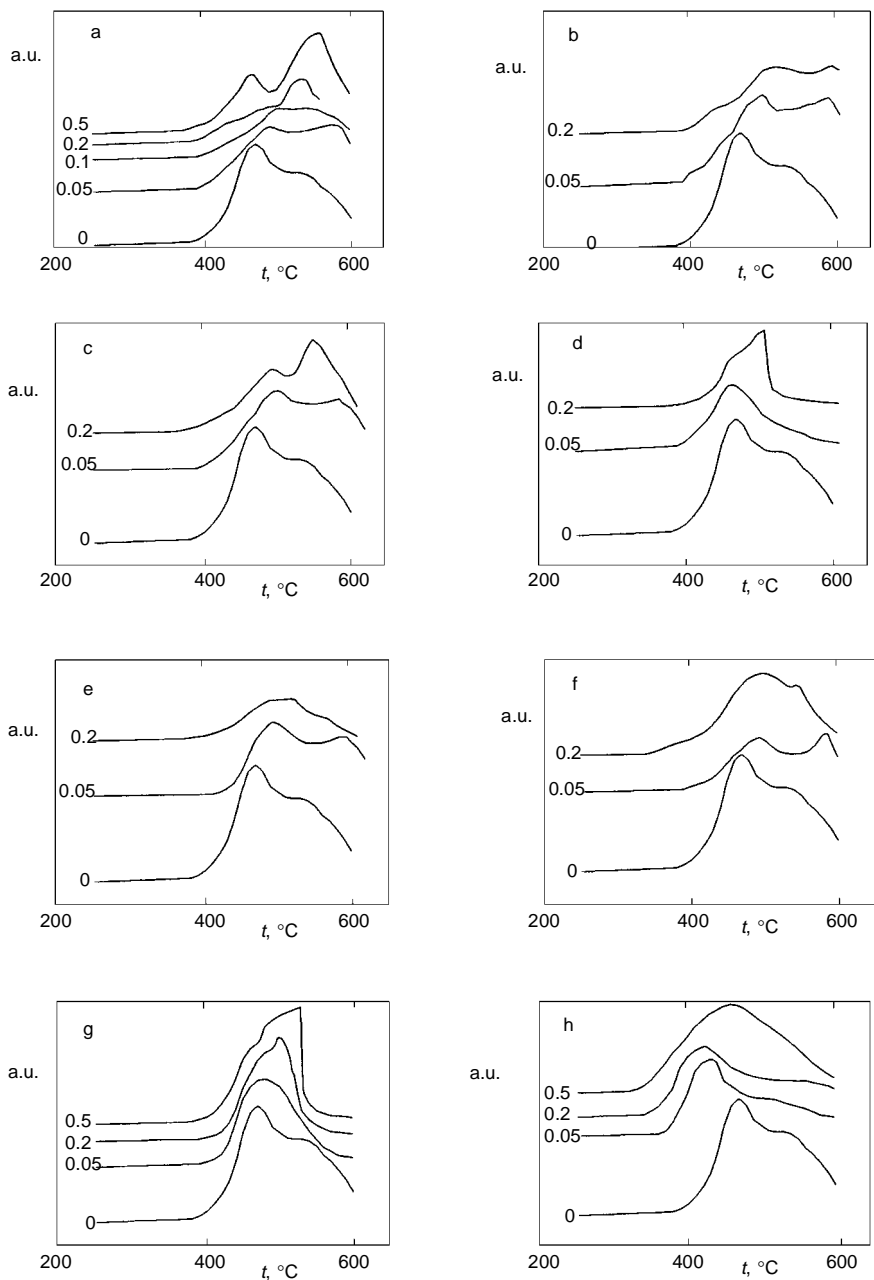


FIG. 2

Influence of promoters addition on TPR profiles of 5 wt.% V_2O_5/TiO_2 catalysts. Numbers denote $M : V$ molar ratio. a K_2SO_4 , b K_2O , c Li_2O , d TeO_2 , e UO_3 , f MoO_3 , g Sb_2O_3 , h Bi_2O_3

Effect of Promoters

From the first group of periodic table, potassium and lithium in the form of oxides were chosen for testing the influence of promoters on the catalyst reducibility and activity.

The effect of potassium on the reducibility of vanadium catalysts was tested using K_2SO_4 (molar ratio K : V = 0.05, 0.1, 0.2, and 0.5) and K_2O (from K_2CO_3 , molar ratio K : V = 0.05 and 0.2). From TPR experiments (Figs 2a and 2b) is evident, that an increase of the amount of potassium in the catalyst shifts the maximal reduction rate of vanadium to higher temperatures. This is in agreement with observations of Van Hengstum et al.¹⁰. These authors reported a decrease of the reducibility of the VO_x phase with increasing content of K_2O in VO_x/TiO_2 (anatase) catalysts, and also a large negative influence on the activity and maximal yield of benzoic acid in the oxidation of toluene. It is evident from Fig. 3, that the presence of potassium in both forms strongly decreases the catalytic activity of V_2O_5/TiO_2 catalyst. However, the influence of potassium on S_{BzOH} exhibits a maximum observed in the interval of the molar ratio of K : V = 0–0.2 (Fig. 4). At higher ratio, no benzoic acid was detected in the reaction mixture.

The presence of lithium, similar to the influence of potassium, shifts the maximal reduction rate of vanadium to higher temperatures (Fig. 2c). As it is evident from Figs 3 and 4, vanadium catalysts promoted with Li_2O at molar ratio Li : V = 0.05 and 0.2 obey higher selectivity to benzaldehyde and benzoic acid. This increase, however, is connected with a decrease in the catalytic activity expressed by the toluene conversion. A decrease of the catalytic activity of the toluene oxidation is linear as a function of temperature of the maximal reduction rate of vanadium (Fig. 5).

TABLE II

The effect of promoter addition on toluene oxidation over 5 wt.% V_2O_5/TiO_2 . Reaction conditions: 0.1 MPa, molar ratio PhMe : O_2 : water = 1 : 4 : 25, space velocity $10\,000\ h^{-1}$

Metal	M : V molar ratio	Reaction temperature °C	X_T %	Selectivity, %			
				BzOH	BzH	CO	CO ₂
–	–	375	89.6	53.1	2.5	24.2	20.2
K	0.05	379	79	71.9	2.5	12.8	12.8
Li	0.2	369	32.1	62.8	13.7	6.2	17.3
Te	0.2	367	39.1	76.7	7.8	5.1	10.3
U	0.05	374	74.3	74.6	5.7	8.8	10.9
Mo	0.05	376	90	63	2.6	18.5	15.9
Bi	0.2	377	80.5	62.7	3.6	17.1	16.6
Sb	0.5	376	65.3	73.5	3.9	9.1	13.6

For testing the *influence of tellurium*, two catalysts were prepared with molar ratio of $\text{Te} : \text{V} = 0.05$ and 0.2 . From the TPR profile in Fig. 2d. for the catalyst with a molar ratio of $\text{Te} : \text{V} = 0.05$, a shift of the maximal reduction rate of vanadium to lower temperature is evident in comparison with unpromoted 5 wt.% $\text{V}_2\text{O}_5/\text{TiO}_2$ catalyst. A further increase of the ratio $\text{Te} : \text{V}$ leads to a decrease of both the catalyst reducibility and activity of the toluene oxidation (Fig. 3). TeO_2 has a positive effect on the benzoic acid formation. Selectivity of benzaldehyde increases, as well.

Miki et al.^{14,17} reported higher S_{BzOH} and also toluene conversion over TeO_2 promoted catalysts in comparison with unpromoted 5 wt.% $\text{V}_2\text{O}_5/\text{TiO}_2$. They observed also a decrease of S_{BzH} on this type of catalyst. A decrease of the activity over our catalysts is probably connected with a decrease of the catalyst reducibility, similarly as it is observed for other promoters.

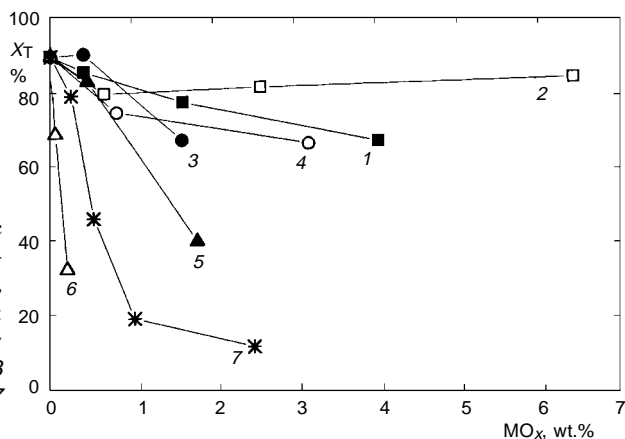


FIG. 3

Influence of promoters on catalytic activity of 5 wt.% $\text{V}_2\text{O}_5/\text{TiO}_2$ catalyst. Reaction conditions: $373\text{ }^\circ\text{C}$, 0.1 MPa , molar ratio $\text{PhMe} : \text{O}_2 : \text{water} = 1 : 4 : 25$, space velocity $10\ 000\ \text{h}^{-1}$. 1 Sb_2O_3 , 2 Bi_2O_3 , 3 MoO_3 , 4 UO_3 , 5 TeO_2 , 6 Li_2O , 7 K_2SO_4

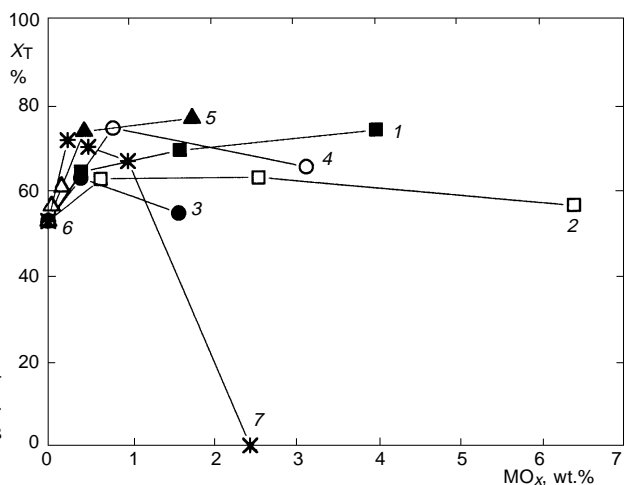


FIG. 4

Influence of promoters on selectivity of benzoic acid formation. Reaction conditions and symbols see Fig. 3

Uranium trioxide was tested as promoter at a molar ratio of $U : V = 0.05$ and 0.2 . TPR profiles of UO_3 promoted catalysts are given in Fig. 2e. The presence of UO_3 has a negative effect on the catalytic activity (Fig. 3) as a result of the shift of the maximal reduction rate of vanadium to higher temperatures (Fig. 5). Maximal selectivity to benzoic acid was observed at the molar ratio of $U : V = 0.05$ (Fig. 4).

Addition of MoO_3 shifts the maximal reduction rate of vanadium to higher temperatures (Fig. 2f). A catalyst with the molar ratio of $Mo : V = 0.05$ has almost the same activity for the toluene oxidation as the unpromoted 5 wt.% V_2O_5/TiO_2 catalyst. A further increase of $Mo : V$ to 0.2 leads to a slight decrease of the activity (Fig. 3). The results are in agreement with observations of Matralis et al.¹⁶ and Miki et al.¹⁷ reported for $V_2O_5-MoO_3/TiO_2$ catalysts. The presence of MoO_3 at the molar ratio $Mo : V = 0.05$ and 0.2 does not cause a strong change of S_{BzOH} (Fig. 4). On the other hand, a positive effect on S_{BzH} and decrease of CO and CO_2 formation was observed.

Sb_2O_3 is the most effective promoter of vanadium catalyst for benzoic acid production. Such catalysts obey very high S_{BzOH} at high conversion of toluene. TPR profiles of Sb-promoted 5 wt.% V_2O_5/TiO_2 catalysts are given in Fig. 2g. There is an evident decrease of reducibility with increased Sb_2O_3 content. This decrease is connected linearly with X_T decrease (Fig. 5). Results obtained during the toluene oxidation over catalysts with molar ratio of $Sb : V = 0.05, 0.2$ and 0.5 (Figs 3 and 4) demonstrate, that the selectivity to benzoic acid increases and X_T decreases with increasing $Sb : V$ molar ratio.

The effect of Bi_2O_3 was tested over catalysts with the molar ratio of $Bi : V = 0.05, 0.2,$ and 0.5 . The maximal reduction rate of vanadium is shifted to lower temperatures for all Bi_2O_3 promoted catalysts in comparison with unpromoted 5 wt.% V_2O_5/TiO_2 catalyst (Fig. 2h). In comparison with unpromoted 5 wt.% V_2O_5/TiO_2 catalyst, about 10% decrease of toluene conversion over all Bi_2O_3 promoted catalysts was observed

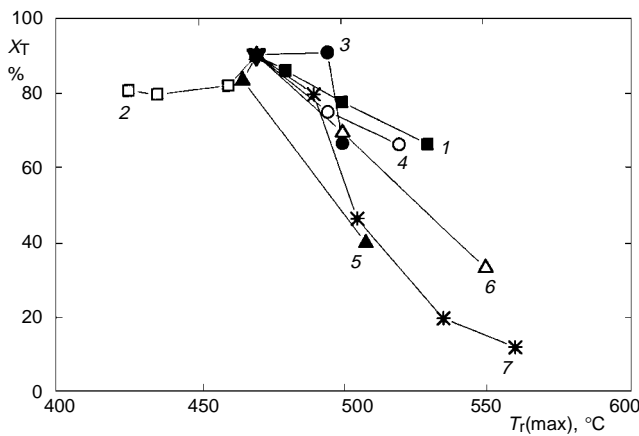


FIG. 5
Catalytic activity of toluene oxidation as a function of temperature of maximal reduction rate $T_r(max)$ of vanadium for promoted 5 wt.% V_2O_5/TiO_2 catalysts. Symbols see Fig. 3, \blacktriangledown denotes experiment without promoter

(Fig. 3). A positive effect on the selectivity is maximal in the range of Bi : V = 0.05–0.2 (Fig. 4).

Reducibility Versus Reactivity

According to the so called “Surface oxide–support interactions” theory (see for example paper of Deo and Wachs²²), the bond controlling the reducibility of supported vanadium oxide catalysts and reactivity in the oxidation of methanol is the bond between vanadium–oxygen–support V–O–S, and not the terminal V=O bond. The weaker V–O–S bond (lower $T_r(\max)$ in TPR experiments) leads to a higher number of active sites at steady-state conditions and greater turnover frequency compared to strong V–O–S bond. The $T_r(\max)$ determines the ease of the reduction or oxygen removal from the catalyst. Experimental results presented in Figs 2 and 5 show, that all promoters lower the reducibility of 5 wt.% V_2O_5/TiO_2 catalyst. The shift of $T_r(\max)$ to higher temperatures is connected with a decrease of activity of toluene oxidation. One exception from inverse relation of the oxidation activity to the $T_r(\max)$ was observed for Bi_2O_3 promoted catalysts. In comparison with unpromoted 5 wt.% V_2O_5/TiO_2 catalyst, an increase of reducibility and an about 10% decrease of the toluene conversion was observed.

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