

# Gas phase partial oxidation of toluene over modified $V_2O_5/TiO_2$ catalysts in a microreactor

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Received 27 June 2006; received in revised form 22 September 2006; accepted 23 September 2006

## Abstract

The influence of different additives to  $V_2O_5/TiO_2$  catalyst for the gas phase partial oxidation of toluene was investigated in a microchannel reactor, where well-controlled reaction conditions were provided without heat and mass transfer influence. It was found that K-doping decreased the catalyst selectivity for benzaldehyde and benzoic acid. The addition of Sb promoted the selectivity but inhibited the catalyst activity greatly. The modification with Ag remarkably improved the catalyst performance in terms of increasing benzaldehyde and benzoic acid selectivity along with an increased activity. With Ag modified  $V_2O_5/TiO_2$  as catalyst and pure oxygen as oxidant, the total selectivity of benzaldehyde and benzoic acid reached over 80% with the toluene conversion above 10%. The maximum space–time yield of  $4.82 \text{ kg h}^{-1} \text{ L}^{-1}$  has been achieved, calculated on the basis of the channel volume.

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**Keywords:** Toluene; Partial oxidation; Microreactor; V/Ti oxides catalysts; Modification

## 1. Introduction

Gas phase partial oxidation of toluene has many competitive advantages over existing liquid phase reaction to obtain benzaldehyde (BA) and benzoic acid (BAC). To make the process commercially feasible, many efforts have been made to improve the selectivity of the partial oxidation products. Most research work on the process is focused on the study of catalysts [1–7]. Some researchers investigated the mechanisms, kinetics and process optimization [8–11], and some novel techniques have been developed to improve the catalyst performance, such as microwave [12], membrane reactor [13], woven fibrous catalyst [14] and microreactor [15].

For catalytic reactions, developing an effective catalyst is the foundational and critical step to promote the research and development of the process. It is generally accepted that supported vanadium oxide is suitable for the partial oxidation of toluene [1,2] and anatase  $TiO_2$  is the best support found by now [3,4]. It was reported that the two-dimensional vanadia layer showed higher activity and selectivity than bulk  $V_2O_5$  crystallites [5–7].

The concentration of vanadia, the properties of support, the pretreatment conditions of catalysts and the presence of additives are the main factors that influence the structure of vanadia species. Great deal of studies have been carried out to adjust and control the performance of catalysts via doping different additives, in an attempt to find more effective catalysts to satisfy the demands of industry.

Some research found elements with negative effects or no obvious influence on the catalyst capability, e.g. V/Ti oxides catalysts doped with  $MoO_3$  [16],  $MgO$  [17],  $WO_3$  [18] or phosphorus [19,20] were found to be less active and selective. Positive results were also reported. Miki et al. [18] found that the addition of  $SeO_2$ ,  $TeO_2$  and  $Sb_2O_3$ , especially the latter two oxides, to a  $V_2O_5/TiO_2$  catalyst greatly improved the BAC yields. Yan and Andersson [21] found that activity for toluene oxidation was enhanced with the addition of silver or cerium. Selectivity increased with the addition of silver mainly for BA while cerium further increased selectivity for both BA and BAC. The work of Zhang et al. [22] also showed that the selectivity of toluene oxidation to BA was improved by the addition of silver. However, there are some reverse results observed by others [18]. As for alkali metals, mainly potassium doping, there are various opinions. It was reported that alkali metal-containing vanadia catalysts revealed significant better performance and the

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increasing alkali cation size and basicity in the order of Li to Cs led to an increase in the BA selectivity [23]. Kiwi-Minsker et al. [24] believed that addition of potassium to surface vanadia led to increased oxygen nucleophilicity and surface basicity, resulting in higher selectivity towards BA and decreased activity. In some cases, both increased activity and selectivity were obtained with small addition of potassium [25]. But Zhu and Andersson [26] found a decrease in activity and BA selectivity, and a relatively small decrease in selectivity for BA with increasing potassium loading. van Hengstum et al. [20] also found potassium had a significant negative influence on the activity and maximum yield.

Up to the present, with all kinds of improved catalysts built, the selectivity and yields of BA and BAc are still rather low. There is little remarkable advancement but many inconsistent opinions on the modification of V/Ti oxides catalysts. In some cases relatively high selectivities (around 70%) were obtained, but inevitably large amount of inert gas or steam were introduced and the space–time yield was fairly poor. A possible reason is that the catalysts cannot perform well and show their intrinsic behaviors in the traditional reactors with hot spots and unsteady reaction environment. For a complex reaction system composed of numerous parallel and consecutive reactions with strongly exothermic processes, better heat and mass transfer conditions must be provided to make the reaction perform in a well-controlled manner. Microreactor is a competent alternative. When applied in chemical reactions, microreactors possess many fundamental advantages [27–29]. Due to their high specific surface areas, good heat and mass transfer capability and so on, microreactors have been widely applied in the field of heterogeneous catalytic reactions [30–35]. In our previous work [15], it has been proved that with V/Ti oxide as catalyst and pure oxygen as oxidant, remarkable improvement of partial oxidation product selectivity can be obtained in the microreactor. The operating conditions can be easily controlled and maintained steady and favorable to the process in a very wide range. With no heat and mass transfer limitations, the intrinsic reaction characteristics can be understood better.

Therefore, our present work aims at investigating the modification effects of different additives that possibly improve the catalyst performance in the microreactor, so as to further increase the selectivity of BA and BAc. Potassium, silver and antimony were selected as additives. The catalysts modified with the three additives, respectively, were compared with the undoped one in reaction performance. After choosing an appropriate catalyst and optimal reaction conditions, remarkably higher yield of desired products of toluene partial oxidation could be obtained.

## 2. Experimental

### 2.1. Catalyst preparation

The TiO<sub>2</sub> particle support was prepared by hydrolysis of Ti(SO<sub>4</sub>)<sub>2</sub> with ammonia solution added up to pH=7. The obtained hydrosol was washed to eliminate SO<sub>4</sub><sup>2-</sup>, and then

Table 1

Specific surface areas (SSA), pore volume (PV), average porous diameter ( $d_p$ ) and composition of the catalysts

Sample	SSA (m <sup>2</sup> /g)	PV (cm <sup>3</sup> /g)	$d_p$ (Å)	M <sup>a</sup> :V <sub>2</sub> O <sub>5</sub> :TiO <sub>2</sub> (wt. ratio)
Ti	79.39	0.254	128	0:0:100
V/Ti	51.08	0.211	148	0:4.99:100
K-V/Ti	41.34	0.193	154	–
Ag-V/Ti	48.82	0.205	173	3.60:5.11:100
Sb-V/Ti	47.33	–	–	–

<sup>a</sup> M is the oxide added as additive.

dried in a refrigerant drier and calcined at 823 K for 3 h. The material was proved to be pure anatase by analysis of XRD (Rigaku D/Max-rb, Japan). After forming, crushing and sieving, the particles were impregnated with aqueous solution of NH<sub>4</sub>VO<sub>3</sub> (0.171 mol/l) in appropriate amounts, followed by drying at 393 K and calcining at 773 K for 3 h. The amount of V<sub>2</sub>O<sub>5</sub> loading was kept at 5% in weight. The additives K, Ag and Sb were added to the catalysts by consecutive impregnation of aqueous solution of KNO<sub>3</sub> (0.107 mol/l) and AgNO<sub>3</sub> (0.085 mol/l) and hydrochloric acid solution of Sb<sub>2</sub>O<sub>3</sub> (0.033 mol/l), respectively. The atomic ratio of added metals to vanadium was kept at 0.5. Specific surface areas (SSA) of the catalysts were determined by nitrogen physisorption using the BET method in Quantachrome instruments (NOVA 4000, USA). The final composition of the catalysts was analyzed by X-ray fluorescence spectroscopy (Magix 601, Philips, Japan). The results are listed in Table 1. The elements represent their corresponding oxides.

### 2.2. Experimental set-up and procedure

The configuration of the microchannel reactor used in the experiments is shown in Fig. 1. The channels were made in a stainless steel plate (75 mm × 75 mm) by micro-precision-machining. Both the width and depth of the channels are 1 mm. Catalyst particles were packed within the 12 parallel channels. Quartz wool was set at each end of the catalysts to keep them from moving with the stream flow. A graphite sheet covered the plate to seal the channels. With an average deformation of 0.05 mm of the graphite compressed into the channels caused by press, the total volume of the channels packed with catalyst was 0.342 ml. Four grooves were made across in the back of the plate, where a thermocouple could be inserted and moved smoothly to measure the temperature of different regions of the reaction plate. The plate was firmly sandwiched between two stainless steel housings, which integrate four columnar heaters, a thermocouple and inlet and outlet. The heaters were inserted into both the top and bottom plates to keep the channels of the reaction plate at a certain temperature. A thermocouple for temperature control was inserted in the housing part beside the heaters. Stainless bolts were used to hold the different parts.

The studies were performed in the experimental set-up described in [15]. Toluene was injected with an isocratic pump (SSI series II, America), and pure oxygen (99.95%) as oxidant

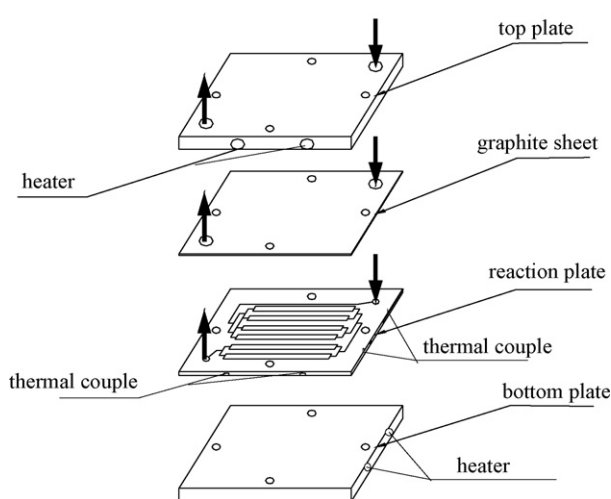
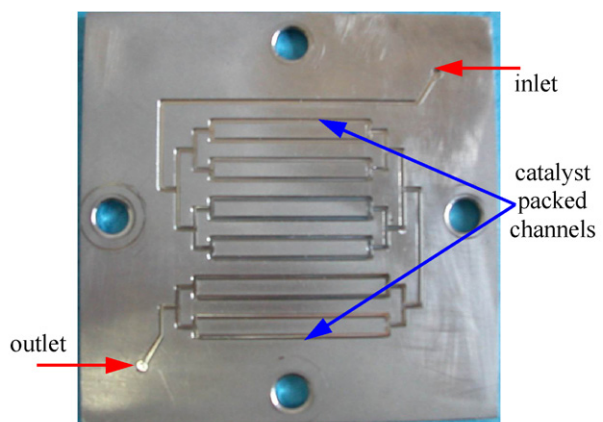
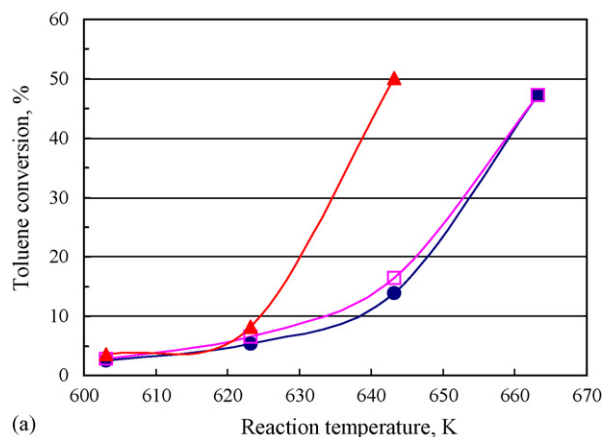


Fig. 1. Microchannel reactor configuration.

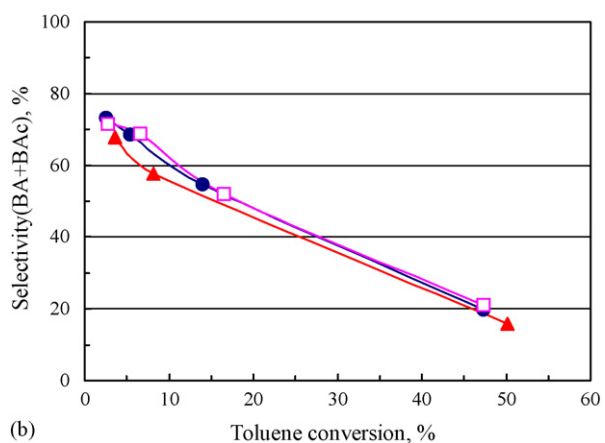
was regulated through a mass flow controller (SevenStar D08-1D/ZM, Beijing, China). A gas chromatograph (FULI 9790, Zhejiang, China) equipped with a TDX-01 packed column was used to analyze the gaseous products online. The organic products were collected in 273 K acetone and successive 253 K salt-ice bath cold trap system, then separated by a capillary column (PEG-20 M) and analyzed by FID in another gas chromatograph (Agilent 4890D, USA).

The catalyst activity test was also carried out in a fixed bed reactor packed with granular catalyst for comparison. The reactor is made of a 12 mm i.d. quartz tube and is heated by an oven. The catalysts have the same composition and same granularity as those used in the microreactor. The catalysts were diluted by quartz and nitrogen was introduced to avoid the formation of hot spots.

The data collections began after the reactions had come into steady conditions and under each certain condition the reaction continued for more than 2 h. The conversion and selectivity are calculated with the method proposed in literature [36]. Conversion is defined as the ratio of mole number of toluene converted to the toluene injected into the reactor. The product selectivity is calculated on the basis of converted toluene, with only BAc, BA, CO and CO<sub>2</sub> taken into account.



(a)



(b)

Fig. 2. Influence of catalyst particle size. Space velocity = 31,000 h<sup>-1</sup>; O<sub>2</sub>/toluene (mol) = 3.9; (●) 30–50 mesh; (□) 50–70 mesh; (▲) 70–90 mesh.

### 3. Results and discussions

#### 3.1. Effect of particle size of V/Ti catalyst

The influence of catalyst particle size on the microreactor performance was evaluated over the undoped V/Ti catalysts. It can be seen in Fig. 2 that when the particle size increased from 30–50 mesh to 50–70 mesh, the catalyst activity (Fig. 2a) did not change much and the total selectivity (Fig. 2b) under certain toluene conversions was almost the same. There might be a little reactant bypass occurring with larger catalyst size, but its effect on the catalyst performance was slight. Fig. 3 shows the relationship between the calculated internal effectiveness factor ( $\eta$ ) and Thiele Modulus ( $\varphi$ ) of the V/Ti catalyst, according to the function:

$$\eta = \frac{3}{\varphi} \left( \frac{1}{\tanh \varphi} - \frac{1}{\varphi} \right) \quad (1)$$

while  $\varphi$  was obtained from the equation:

$$\varphi = R_p \sqrt{\frac{k}{D_e}} \quad (2)$$

in which  $R_p$  (m) is the radius of the catalyst particle,  $k$  (s<sup>-1</sup>) the intrinsic rate coefficient got from kinetic experiments and

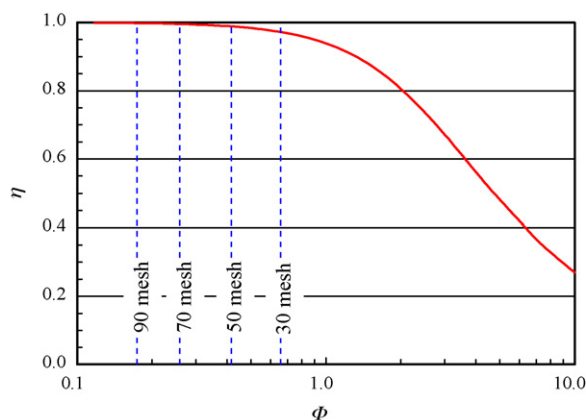


Fig. 3. Relationship between the calculated internal efficiency factor and Thiele Modulus of V/Ti catalyst.

effective diffusion coefficient  $D_e$  ( $\text{m}^2 \text{s}^{-1}$ ) is estimated using the relationship:

$$D_e = 48.5d_p \frac{\varepsilon}{\tau} \sqrt{\frac{T}{M}} \quad (3)$$

where  $d_p$  (m) is the pore diameter,  $\varepsilon$  the porosity of the catalyst,  $\tau$  the curvature coefficient of the pore inside the catalyst,  $T$  (K) the temperature and  $M$  is the molecular weight of toluene. The corresponding values of the different particle sizes were marked in the figure with dashed lines. It can be seen that  $\eta$  of catalyst of 30–50 mesh is above 0.97 and the value can exceed 0.99 with particle size being 50–70 mesh. The figure indicates that catalysts with particle size smaller than 30 mesh can be efficiently used in the reaction. When the particle size changed to 70–90 mesh, the toluene conversion increased much, especially under higher temperature, and the BA and BA<sub>c</sub> selectivities were much lower than those of the larger sized catalysts. It is suspected that because of the increased pressure drop, the exothermal process was accelerated in a limited space range. As a result, it was found that the upstream region of the catalyst channels was overheated, where combustion of the reactants took place. With the consideration of mass transfer, pressure drop and the possibility of blockage, particles of 50–70 mesh were chosen for further studies.

### 3.2. Effect of additives

The BET surface area decreased slightly with addition of both Ag and Sb, while it decreased severely with K-doping (see Table 1). It was reported [16] that the addition of vanadium brought about a drastic diminution of the SSA as well as the pore volume because the incorporation of vanadium onto anatase carrier has a dramatic effect in its texture, destroying the pore structure of the anatase and sharply decreasing the SSA. As for the further reduction of SSA with K addition, the similar results have been reported elsewhere [24–26], and it might be due to the support pore blocking by added compounds or to the increase wetting of the titania surface by supported vanadia upon K doping.

Table 2

Influence of additives on catalyst activity and selectivities in the traditional fixed bed reactor

Additives	Conversion (%)	Selectivity (%)		
		CO <sub>x</sub>	BA <sub>c</sub>	BA
	32.6	73.0	11.4	10.7
Sb	34.2	72.1	12.5	12.2
Ag	34.4	79.3	8.5	12.2
K	31.3	83.6	3.2	9.4

Catalyst = 0.5 ml, diluted with quartz by 1:10 in weight; toluene:O<sub>2</sub>:N<sub>2</sub> = 1:2.3:18.4 (mol); space velocity = 13,500 h<sup>-1</sup>; temperature = 643 K.

In our previous experiments carried out in the traditional fixed bed reactor, the addition of K and Ag or Sb decreased and increased the total selectivity, respectively, but differences of only several percent at most were detected between the modified and undoped catalysts (the comparison results are shown in Table 2). In the fixed bed reactor, although inert gas was introduced and the catalysts were diluted to avoid the formation of hot spots, large temperature gradient still existed. The reactions tended to be out of control, resulting in poor selectivity, temperature run-away and even catalyst deactivation caused by overheating. The microreactor provided uniform and steady temperature distributions. The temperature has been well controlled in the microreactor. No detectable temperature fluctuation was found. In all cases, whenever a certain temperature is fixed, it varies just within 1 K at different time of the reaction or at different parts of the reactor. Running in steady and accurate temperature windows, the catalysts can exhibit their intrinsic characteristics and best performances. In the microreactor, it was found that the activity of the catalysts decreased in the initial 180 min and after that no deactivation was observed all through our study. The running time added up to over 200 h, during which the catalysts showed no changes in their performance.

Fig. 4 shows the influence of additives on the catalytic activity (Fig. 4a) and total selectivity (Fig. 4b). It can be seen in the Fig. 4a that with the addition of K, the toluene conversion is a little higher than the undoped V/Ti catalyst in the lower temperature range. When temperature becomes higher (exceeding a value between 640 and 650 K), the activity of catalyst doped with K is low. Catalyst modified with Ag exhibits higher activity in a wide reaction temperature range, but the addition of Sb decreases the catalytic activity significantly. The data from the microreactor can fit the Arrhenius function well (see Fig. 5; the correlation coefficients are above 0.99). It can be deduced that all the additives decrease the apparent activation energy ( $E_a$ ) of toluene oxidation (the estimated  $E_a$  values over different catalysts are as these: V/Ti, 156.6 kJ/mol; AgV/Ti, 109.9 kJ/mol; KV/Ti, 126.5 kJ/mol; SbV/Ti, 133.7 kJ/mol). The effect of Ag is more obvious. The activity of AgV/Ti will be close to the V/Ti under rather high temperature. The crossing point of lines of KV/Ti and V/Ti appears in the moderate temperature range. With the Sb addition, the activity is expected to be the lowest unless under very low temperatures that is out of our experimental range.



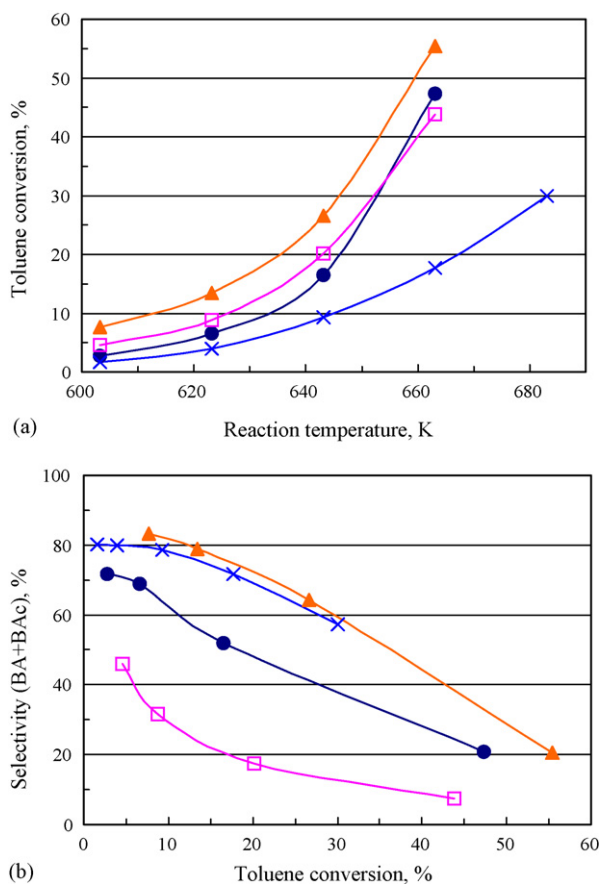


Fig. 4. (a and b) Influence of the additives on the catalyst activity and total selectivity. Space velocity =  $31,000 \text{ h}^{-1}$ ;  $\text{O}_2/\text{toluene (mol)} = 3.9$ ; (●) V/Ti; (□) KV/Ti; (▲) AgV/Ti; (×) SbV/Ti.

The comparison of total selectivities with conversions and the product distributions in different temperature ranges are showed in Figs. 4b and 6. In all cases, initial selectivities to BA and BAc are relatively high but decrease with increasing conversion, indicating that BA and BAc are intermediates of the consecutive reactions with  $\text{CO}_x$  as final products. Obviously, the addition of Ag or Sb can improve the total selectivity and the yield of partial

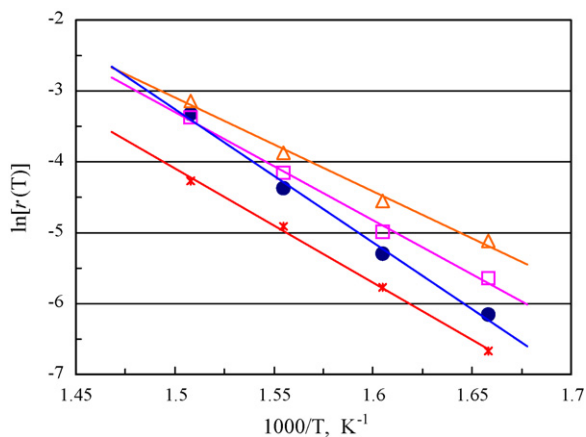


Fig. 5. Arrhenius plots for reaction rates in toluene oxidation over different catalysts.  $r_T$  = reaction rate of toluene oxidation ( $\text{mmol g}_{\text{cat}}^{-1} \text{ h}^{-1}$ ); (●) V/Ti; (□) KV/Ti; (Δ) AgV/Ti; (×) SbV/Ti.

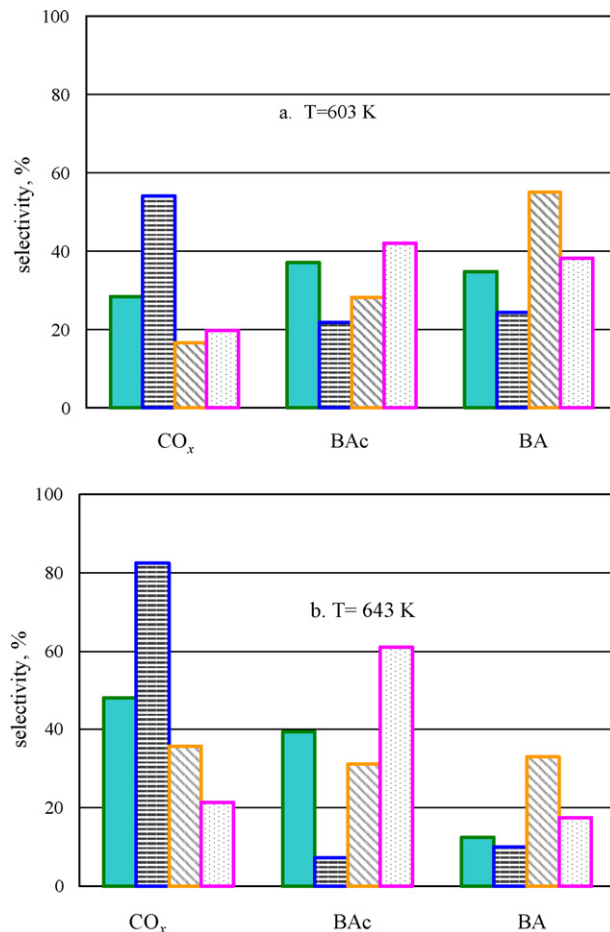


Fig. 6. Comparison of product distribution of toluene oxidation over different catalysts. Space velocity =  $31,000 \text{ h}^{-1}$ ;  $\text{O}_2/\text{toluene (mol)} = 3.9$ ; (■) V/Ti; (▨) KV/Ti; (▩) AgV/Ti; (□) SbV/Ti.

oxidation products. With the Ag addition, the total selectivity can amount to over 80% and remains nearly 20% higher than that of the unmodified catalyst until rather high conversions. However, the selectivity of the K-doped catalyst is much poorer comparatively. It can be seen in Fig. 6 that as an additive, Ag is more efficient in improving the BA selectivity, but Sb-doped catalyst favors the BAc formation. Addition of K dramatically decreases the BAc selectivity, with a relatively minor influence on the BA selectivity, especially under higher temperatures.

The conclusion can be drawn that the differences in catalytic activities are not caused by the change of specific surface areas after the addition of the second metals (see Table 1). The additives might have changed the amount or property of the active sites. The basicity caused by K addition [24] might lead to a strong adsorption of acid product (here BAc) and thus a higher probability of its destruction. It was also reported [26] that K produces new reactive sites for the further oxidation of BAc and other intermediates to  $\text{CO}_x$ . As for Sb, it is conceived to have inhibited the direct oxidation of toluene to  $\text{CO}_x$ , and therefore BA and BAc selectivity increased but toluene conversion decreased.

Ag might accelerate the side chain oxidation of toluene to produce BA, as reported in Ref. [22], because the silver promotes the

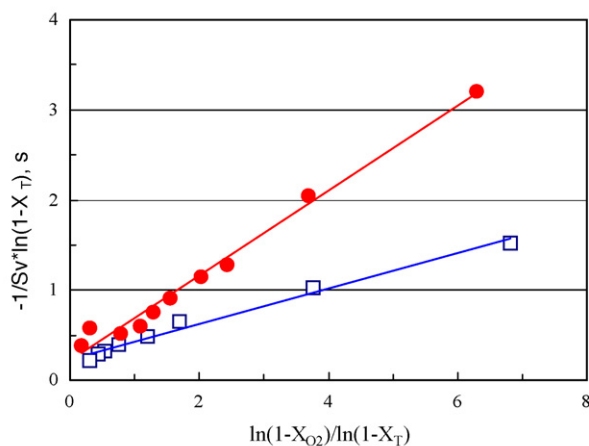


Fig. 7. Plot according to Mars and van Krevelen model as presented in Eq. (4). Reaction temperature = 638 K; (●) V/Ti; (□) AgV/Ti.

supplemental velocity of lattice oxygen and re-oxidative velocity of reduced vanadia species. At the same time, further oxidation of BA to BAc and ultimately  $\text{CO}_x$  might be suppressed by the presence of Ag. According to the Mars and van Krevelen model [37], the reaction of toluene oxidation composes of two steps, i.e., the oxidation of toluene by the oxidized catalyst and the re-oxidation of reduced catalyst. According to the model, the reaction rate of toluene was given by:

$$r_T = -\frac{1}{(1/k_1 p_T) + (\beta/k_2 p_{O_2})} \quad (4)$$

in which  $\beta$  is the average number of moles oxygen consumed by 1 mol of toluene,  $k_1$  ( $\text{s}^{-1}$ ) and  $k_2$  ( $\text{s}^{-1}$ ) the rate constants for toluene oxidation and catalyst re-oxidation reactions, respectively, and  $p_T$  and  $p_{O_2}$  are the partial pressures of toluene and oxygen. After integration, rearrangement and application of  $dp_{O_2} = \beta dp_T$ , the rate equation of toluene oxidation can be expressed as:

$$-\frac{1}{Sv \ln(1 - X_T)} = \frac{1}{k_1} + \frac{1}{k_2} \frac{\ln(1 - X_{O_2})}{\ln(1 - X_T)} \quad (5)$$

where  $Sv$  is the space velocity ( $\text{s}^{-1}$ ) and  $X_T$  and  $X_{O_2}$  are the conversions of toluene and oxygen. Then, the data from the experiments under certain temperature can fit a linear regression. In Fig. 7, the result of the reactions over AgV/Ti oxides catalyst is compared with the data from V/Ti oxides catalyst [15] in the same microreactor. It is noticed that  $k_1$  does not vary much over the two different catalysts, but over Ag modified catalyst,  $k_2$  is obviously increased. In another word, the addition of Ag influences the toluene oxidation over the catalyst surface mainly in accelerating the step of catalyst re-oxidation. Another interesting change caused by Ag addition is that the average ratio of  $\text{CO}_2$  to  $\text{CO}$  formed in the reaction over AgV/Ti oxides catalyst is 5.8, but that of the V/Ti oxides is 2.6 under the same reaction temperature. The change of the surface structure and redox potential should be responsible for the phenomenon.

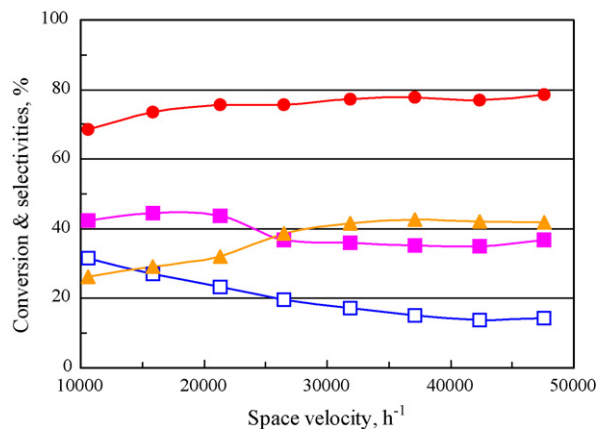


Fig. 8. Influence of space velocity on conversion and selectivities over AgV/Ti catalyst. Reaction temperature = 633 K;  $\text{O}_2/\text{toluene}$  (mol) = 3.6; (□) toluene conversion; (●) total selectivity; (▲) selectivity of BA; (■) selectivity of BAc.

### 3.3. Effect of operation conditions on the performance of AgV/Ti oxides catalyst

Ag modified V/Ti oxide catalyst is more efficient for toluene partial oxidation according to the experiments above. In order to find out the optimal operation conditions and to study the performance of the catalyst, the influence of the different reaction conditions was investigated.

Fig. 8 shows the influence of space velocity. The toluene conversion decreases with increasing space velocity. At the same time, the selectivity to BA increases and BAc the reverse. This can be explained by that shorter residence time leads to the depression of the reactions occurring on the catalyst surface, especially the further oxidation of the products. When the space velocity reaches to over  $30,000 \text{ h}^{-1}$ , all the items are almost independent of the variable. It seems that the addition of Ag makes the reaction over the modified catalyst not so sensitive to residence time compared to the V/Ti oxides catalyst (see Ref. [15]). It is suspected that the reaction rate of slow steps such as the formation of BA is increased.

The influence of molar ratio of  $\text{O}_2$  to toluene is shown in Fig. 9. The total space velocity was fixed and the  $\text{O}_2/\text{toluene}$  ratio was adjusted by varying the flow rate of toluene and  $\text{O}_2$  simultaneously. With  $\text{O}_2/\text{toluene}$  ratio increasing, toluene conversion gradually increases but the total selectivity decreases. After  $\text{O}_2/\text{toluene}$  ratio is higher than about 5, the influence is much weaker. Since the rate of re-oxidation reaction is greatly increased by Ag addition, as we have concluded in Section 3.2, higher  $\text{O}_2$  proportion becomes not so crucial in enhancing the total reaction rate of toluene oxidation. The BA selectivity goes down at first and then goes up slowly to pass through its maximum before dropping at high  $\text{O}_2/\text{toluene}$  ratios (above about 7). The BAc selectivity transforms in an almost reversed style.

The influence of reaction temperature is expressed in Fig. 10. With temperature increasing, the toluene conversion keeps going up but the total selectivity decreases continuously, and the trend becomes more remarkable over about 630 K. The selectivity of BA declines constantly with higher temperature while the selec-

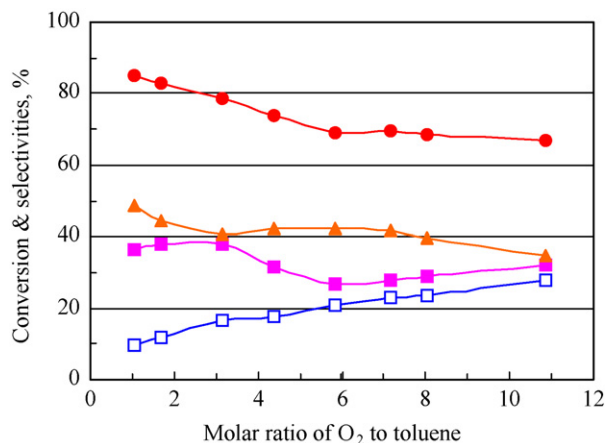


Fig. 9. Conversion and selectivities depending on O<sub>2</sub>/toluene ratios over AgV/Ti catalyst. Reaction temperature = 633 K; space velocity = 31,000 h<sup>-1</sup>; (□) toluene conversion; (●) total selectivity; (▲) selectivity of BA; (■) selectivity of BAc.

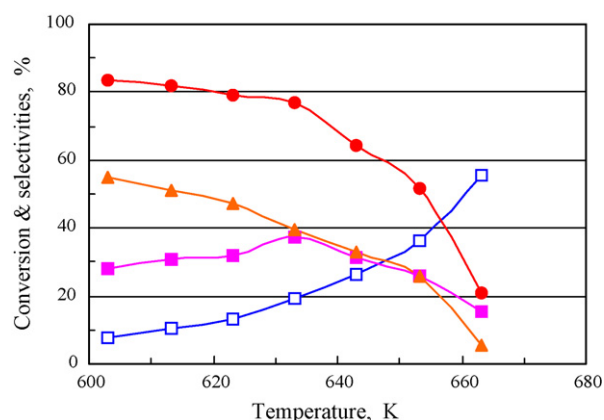


Fig. 10. Dependence of the conversion and selectivities on the reaction temperature over AgV/Ti catalyst. Space velocity = 31,000 h<sup>-1</sup>; O<sub>2</sub>/toluene (mol) = 3.9; (□) toluene conversion; (●) total selectivity; (▲) selectivity of BA; (■) selectivity of BAc.

tivity of BAc passes through a maximum. It is suggested that the reaction should be carried out under lower temperature range to get higher selectivity for partial oxidation products. To obtain higher space–time yield or more BAc, an optimal temperature range exists.

#### 4. Conclusions

The influences of additives to V/Ti oxides catalyst on activity and selectivity of gas phase toluene partial oxidation were studied in a microreactor. It is concluded that for improving the catalytic performance and investigating the catalyst intrinsic characteristics, the microreactor is a better choice than the traditional reactor. It is found that the addition of K decreases the catalytic selectivity and depresses the activity under higher temperatures. Sb promotes the selectivity obviously but decreases the activity. The presence of Ag can improve both the selectivity and activity of the catalyst. It accelerates the re-oxidation of the catalyst and decreases the apparent activation energy of the reaction. With Ag modified V/Ti oxides as catalyst and pure oxygen

as oxidant, the maximum space–time yield of 4.82 kg h<sup>-1</sup> L<sup>-1</sup> has been obtained in the microreactor.

#### Acknowledgements

We gratefully acknowledge the financial supports for this project from National Natural Science Foundation of China and China National Petroleum Corporation (No. 20176057 and No. 20490208), Key Program for International Cooperation of Science and Technology (No. 2001CB711203).

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