

Vapor-phase Oxidation of Alkylaromatics over V/TiO₂ and VSb/Al₂O₃ Catalysts: Effect of Alkali Metals

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Oxidation of alkylaromatics including toluene and *p*-methoxytoluene has been carried out over alkali metal (AM)-containing catalysts such as AM-V/TiO₂ and AM-VSb/Al₂O₃ in vapor-phase using oxygen as an oxidant. The selectivity for partial oxidations increases with incorporation of an alkali metal or with increasing the basicity of alkali metals (from Na to Cs), irrespective of the supports or reactants. However, the conversion is nearly constant or slightly decreasing with the addition of alkali metals in the catalyst. The increased selectivity may be related with the decreased acidity even though more detailed work is necessary to understand the effect of alkali metals in the oxidation. The AM-VSb/Al₂O₃ may be suggested as a potential selective catalyst for vapor-phase oxidations.

Key Words : Alkali metal, Vapor-phase oxidation, Partial oxidation, V/TiO₂, VSb/Al₂O₃, Catalyst

Introduction

p-Substituted benzaldehydes or benzoic acids are important intermediate chemicals in the specialty and pharmaceutical chemistry. The substituted benzaldehydes or benzoic acids are prepared by several methods, mainly in liquid-phase. Vapor-phase oxidations have been conducted to overcome the disadvantages of corrosion and environmental problems in the liquid-phase reactions. Several catalysts, especially supported vanadia catalysts, have been investigated as catalysts for selective partial oxidations.

Alkali metals have been used as promoters in various oxidation catalysts not only for vapor-phase reactions but also for liquid-phase reactions. The effect of the alkali metal (AM) in the partial oxidation reaction (to *p*-substituted benzaldehydes or benzoic acids) has been widely studied. Bentrup *et al.* reported that the aldehydes selectivity increases with decreasing the acidity of catalysts due to the alkaline metals.^{1,2} It is also said that selectivity to aldehydes is related with the basic properties of the catalyst, whereas the activity strongly depends on the amount and strength of acid sites.² Kiwi-Minsker *et al.* also reported that increase in basicity decreases catalytic activity for toluene oxidation, but at the same time the catalyst deactivation is suppressed.³ They also stated that the selectivity towards benzaldehyde is high with the addition of potassium onto surface vanadia. Bulushev *et al.*⁴ reported that not only the selectivity for partial oxidations but also activity was increased by the doping of K in the V/TiO₂ catalyst.

However, the positive effect of alkali metals on the selectivity for partial oxidations has not been agreed on completely. For example, very recently, Ge *et al.* reported that K-doping decreases the catalyst selectivity for benzaldehyde and benzoic acid.⁵ Zhu and Anderson had stated that a decrease in activity and selectivity for benzoic acid and

benzaldehyde occurred with potassium loading.⁶ Furukawa *et al.* reported that the addition of alkali metal to the lanthanum catalysts promoted the catalytic activity, rather than the selectivity, of the benzyl alcohol oxidation.⁷ Jhung and coworkers found that potassium, depending on the concentration, had a negative or positive effect on the activity of liquid-phase oxidation of *p*-xylene to terephthalic acid.⁸ Therefore, the effect of alkali metals on the oxidation of alkylaromatics needs further investigation.

Vanadium-antimony oxide catalysts, supported on alumina, have been used in a few oxidative dehydrogenation reactions such as for the preparation of styrene⁹ and light olefins.¹⁰ Moreover, this catalyst system has many advantages including noticeable stability in catalytic performances.⁹ However, this catalyst has not been applied in the vapor-phase oxidation of alkylaromatics to aldehydes or acids.

In this paper, the oxidation of *p*-methoxytoluene and toluene to aldehydes or acids was carried out over vanadia/TiO₂ and VSb/Al₂O₃ catalysts promoted with several alkali metals to understand the effect of alkali metals on the selectivity and conversion. The possible application of VSb/Al₂O₃ in the oxidation of alkylaromatics is also discussed.

Experimental

V/TiO₂ catalyst was prepared by impregnation of V on TiO₂ (P 25, 99.5%, Degussa, average primary particle 21 nm, BET surface area 50 ± 15 m²/g) using NH₄VO₃ (Aldrich, 99%) and successive calcination at 450 °C for 2 h. VSb/Al₂O₃ was prepared using NH₄VO₃, SbCl₃ and γ -alumina to follow the method reported earlier.¹¹ AM-V/TiO₂ and AM-VSb/Al₂O₃ catalysts were prepared using Na₂SO₄, K₂SO₄, Cs₂SO₄ similar to the syntheses methods of the catalysts without alkali metals. Unless otherwise stated, the concentration of V₂O₅ and Sb₂O₃ in VSb/Al₂O₃ and AM-

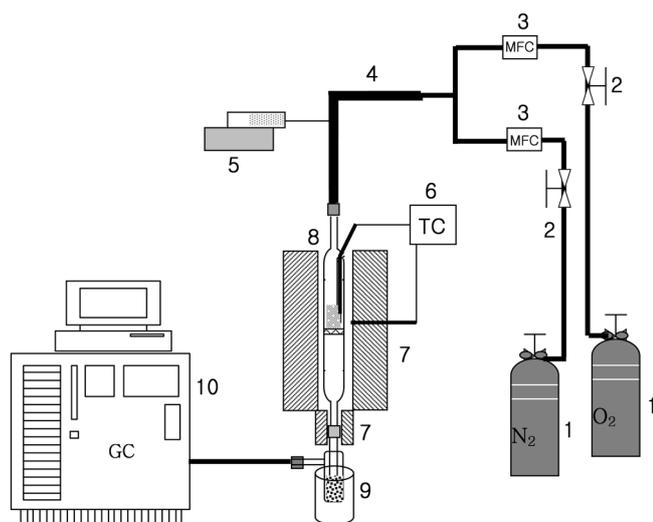


Figure 1. Experimental apparatus for the vapor-phase oxidation of toluene and *p*-methoxytoluene: 1. gas cylinder; 2. ball valve; 3. mass flow controller; 4. preheater; 5. syringe pump; 6. temperature controller and indicator; 7. heater; 8. reactor; 9. cold trap and 10. GC.

VSb/Al₂O₃ were 6.5 and 13.5 wt%, respectively. The V₂O₅ concentration in V/TiO₂ was 5.6 wt%. The concentrations of alkali metals corresponded to 0.5 wt% (based on metal) of the catalysts.

The catalysts were characterized by XRD (Rigaku, Miniflex diffractometer, CuK_α radiation) and NH₃-TPD (Micrometrics, Pulse Chemisorb 2705 system) for phase determination and acidity measurements, respectively.

The vapor-phase oxidation of toluene and *p*-methoxytoluene was carried out at 285 °C using a fixed bed reactor shown in Figure 1. Catalyst (0.5 g) was diluted with 5 g of quartz bead, and the reactant WHSV (weight-hourly space velocity) was 1 h⁻¹. Gas mixture of oxygen and nitrogen was fed with a mass flow controller and nitrogen was used as an internal standard. Gas products (CO, CO₂ and CH₄) and liquid products were analyzed by a TCD (equipped with CTR I column) and a FID (with HP-20M capillary column) GC, respectively. Gas products were analyzed using an on-line GC, whereas the liquid products were analyzed after trapping using solvent (water/ethanol = 1 wt/1 wt). Unless otherwise stated, the results were reported for the reaction time of 3 h.

Results

Figure 2 shows XRD patterns of the prepared AM-V/TiO₂ and AM-VSb/Al₂O₃ catalysts. All spectra are very similar to those of supports (TiO₂ and Al₂O₃), showing the vanadium and alkali metals species are well dispersed or amorphous phases and do not exist in crystalline or polymeric phases.

Figure 3 illustrates the NH₃-TPD patterns of the AM-V/TiO₂ and AM-VSb/Al₂O₃ catalysts. As the basicity of alkali metal increases from Na to Cs, the acid sites at high desorption temperature (about 300–400 °C) decreases with the steady increase in the intensity of low acidity, showing

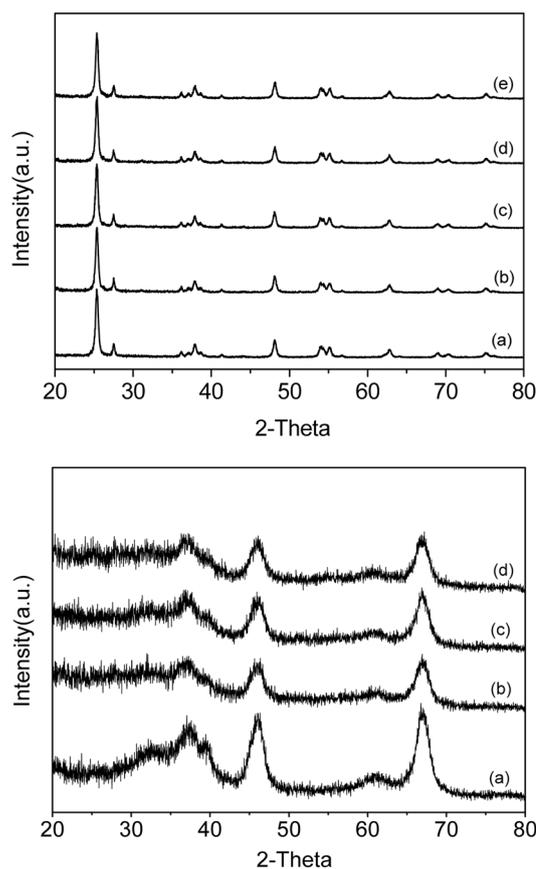


Figure 2. (Upper) XRD patterns of the TiO₂, V/TiO₂ and AM-V/TiO₂ catalysts: (a) TiO₂, (b) V/TiO₂, (c) Na-V/TiO₂, (d) K-V/TiO₂ and (e) Cs-V/TiO₂. (Lower) XRD patterns of Al₂O₃, VSb/Al₂O₃ and AM-VSb/Al₂O₃ catalysts: (a) Al₂O₃, (b) VSb/Al₂O₃, (c) K-VSb/Al₂O₃ and (d) Cs-VSb/Al₂O₃.

the reduction of the population of strong acid sites with the incorporation of alkali metals with high basicity such as Cs.

Figure 4 depicts the conversion and selectivities in the toluene oxidation over AM-V/TiO₂ catalysts. As the basicity or cation size of alkali metal increases (from Na to Cs), the selectivity for partial oxidations (benzaldehyde and benzoic acid) increases steadily, whereas, the conversion is relatively constant or slight decreasing.

Figure 5 shows the results of oxidation of toluene and *p*-methoxytoluene over the VSb/Al₂O₃ catalysts. The selectivity for benzaldehyde and benzoic acid, however, is too high (to compare the selectivity over catalysts containing alkali metals) with low toluene conversion in the vapor-phase oxidation of toluene. Therefore, we changed the reactant from toluene to *p*-methoxytoluene (Figure 5) to highlight the effect of alkali metals in VSb/Al₂O₃ for the vapor-phase oxidation.

Figure 6 illustrates the conversion of *p*-methoxytoluene and selectivity of *p*-methoxybenzaldehyde and *p*-methoxybenzoic acid over the AM-VSb/Al₂O₃ catalysts, and the effect of alkali metal is very similar to that of the toluene oxidation over AM-V/TiO₂ catalysts. The beneficial effect of alkali metals on the selectivity is noticeable even though the conversion is quite low of ~5%.

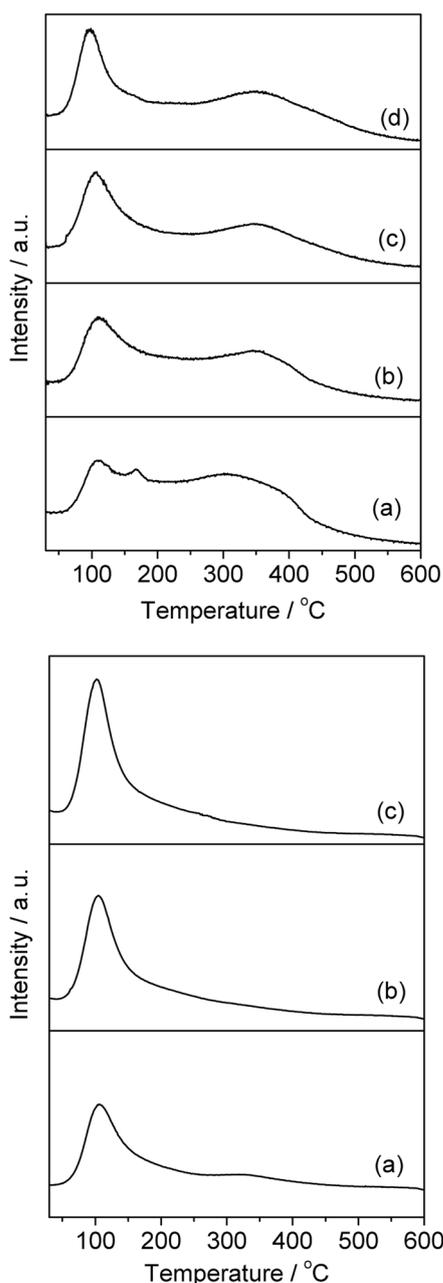


Figure 3. (Upper) NH_3 -TPD patterns of the V/TiO_2 and AM- V/TiO_2 catalysts: (a) V/TiO_2 , (b) Na- V/TiO_2 , (c) K- V/TiO_2 and (d) Cs- V/TiO_2 . (Lower) NH_3 -TPD patterns of the VSb/ Al_2O_3 and AM-VSb/ Al_2O_3 catalysts: (a) VSb/ Al_2O_3 , (b) K-VSb/ Al_2O_3 and (c) Cs-VSb/ Al_2O_3 .

Discussion

All the prepared catalysts show that the vanadium species are in the monomeric or well-dispersed states rather than polymeric states; therefore, the catalysts may be suitable for selective oxidations.^{4,12} As shown in Figure 4, the summed selectivity for aldehyde and acid is high even though the conversion is relatively low.

Alkali metals, as promoters, have been widely used in oxidation reactions to decrease total oxidations to carbon

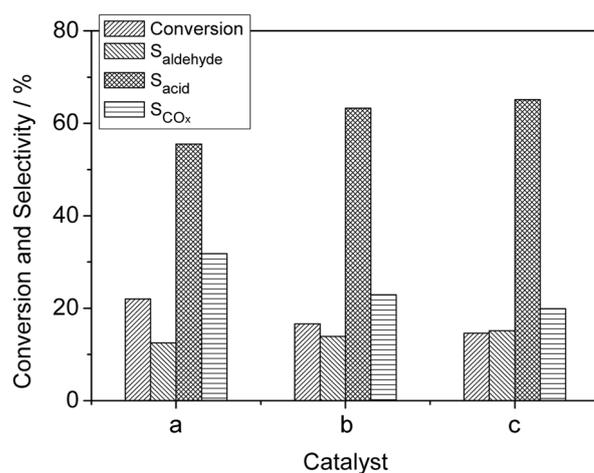


Figure 4. Toluene conversion and selectivity over AM- V/TiO_2 catalysts: (a) Na- V/TiO_2 , (b) K- V/TiO_2 and (c) Cs- V/TiO_2 .

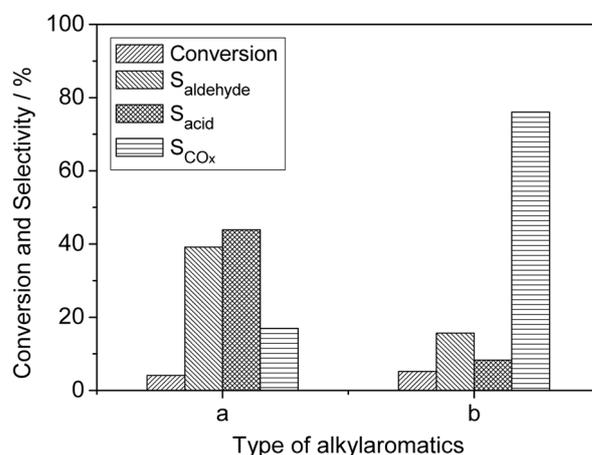


Figure 5. Oxidation of *p*-methoxytoluene and toluene over VSb/ Al_2O_3 catalyst: (a) toluene and (b) *p*-methoxytoluene.

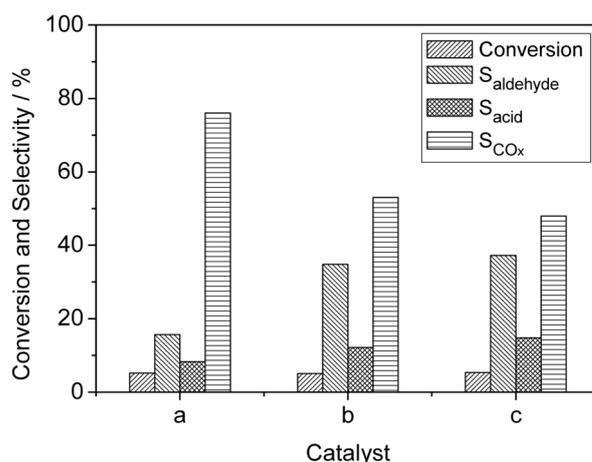


Figure 6. Oxidation of *p*-methoxytoluene over VSb/ Al_2O_3 and AM-VSb/ Al_2O_3 catalysts: (a) VSb/ Al_2O_3 , (b) K-VSb/ Al_2O_3 and (c) Cs-VSb/ Al_2O_3 .

monoxide and carbon dioxide. In a special case, an alkali metal can increase both the activity and selectivity for partial oxidation.⁴ However, the positive effect in selectivity is not

always observed, leading to the decrease of activity and selectivity for some cases.⁵ It is also stated that the concentration of alkali metal is also very important for the promoting role of alkali metals.⁸

In this study, it has been confirmed that the selectivity for partial oxidations (to aldehyde and acid) increases with increasing basicity or cation size (or in the order of from Na to Cs) of the alkali metals, irrespective of supports (TiO₂ and Al₂O₃) or substrates (toluene or *p*-methoxytoluene). So, the selectivity is highest with Cs-V/TiO₂ and Cs-VSb/Al₂O₃. However, the activity is nearly constant or slightly decreasing with increasing the basicity of alkali metals.

Several reasons have been suggested to explain the increased selectivity of partial oxidation with the addition of alkali metals. For example, the facile desorption of intermediate aldehydes or acids, by the decrease of the acidity of catalysts, can lead to the recovery of partial oxidation products.¹ Because of the electron-donating alkali metals, the concentration of nucleophilic oxygen species in the catalysts can also be increased, leading to the improvement of selective oxidations.⁴ It is also stated that nucleophilic oxygen species may be increased for the case of monomeric vanadium species.²

The reason to increase the selectivity by the addition of basic alkali metals cannot be explained at the moment. However, the decreased acidity is very important for the selective oxidations considering the acidity measured by NH₃-TPD (Figure 3). At this moment, the contribution of monomeric vanadia cannot be estimated because all the vanadium species in the catalysts exist in monomeric or amorphous states as determined by XRD (Figure 2). More detailed studies including 1) the effect of increasing the basicity of supports or addition of basic materials such as pyridine, 2) evaluation of vanadium states (monomeric and polymeric species) by UV-Vis and 3) measurement of desorption energy of aldehydes are necessary to understand the effect of alkali metals in selective oxidations. Moreover, the effect of alkali metals should be studied in wide concentrations because the effects are still debating¹⁻⁷ and the effects depend strongly on the concentration in the liquid-phase oxidations.⁸

The alkali metal-VSb/Al₂O₃ catalyst may be used in selective oxidations, after adding suitable promoters and optimizing process conditions, because the selectivity for

partial oxidation of benzene is very high even though the activity is quite low (Figure 5a). These studies for characterization and applications will be pursued.

Conclusions

The effect of alkali metal in the vapor-phase oxidation of alkylaromatics has been studied over AM-V/TiO₂ and AM-VSb/Al₂O₃ catalysts using oxygen as an oxidant. The selectivity for partial oxidation increases with the basicity or cation size of alkali metals, whereas the conversion is nearly constant or slight decreasing with the changing from Na to Cs. The beneficial role of alkali metal in the selective oxidation may be explained with the decreased acidity of the catalysts. The AM-VSb/Al₂O₃ may be suggested as a potential catalyst for selective oxidation of alkylaromatics.

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