Alkylation of aldehydes with methanol over titanium oxide catalysts

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The methylation of various aldehydes, such as acetaldehyde, propionaldehyde, and phenylacetaldehyde over titanium oxide-supported vanadium oxide was studied under atmospheric pressure and temperatures of 250–400°C. The catalyst properties of titanium oxide can be enhanced only by addition of a fairly small amount of vanadium. High-temperature treatment transforms titanium oxide, the support, from anatase to rutile, which causes the catalysts to lose their catalytic properties. The reactivity of these can be ranked in the following order: acetaldehyde > propionaldehyde > phenylacetaldehyde. The steric effect of the substituted groups in propionaldehyde or phenylacetaldehyde may prevent self-condensation to form oligomers and to give a high selectivity of alkylated products.

Keywords: alkylation; acetaldehyde, propionaldehyde; phenylacetaldehyde; methanol, V/TiO$_2$

1. Introduction

In recent years, numerous attempts have been made to develop synthesis methods for fine chemicals based on the utilization of C$_1$ chemicals such as CO, methanol, and CH$_4$, instead of olefins [1–4]. Some of the methanol-based processes have been already industrialized, and some other processes are technologically ready for commercialization [5–8]. An interesting example is the alkylation of compounds, such as aromatics, nitriles, ketones, and esters of carboxylic acids, by the addition of methanol as a carbon source [9–12]. We have recently developed a type of reaction in which methanol may add to ethanol and *n*-propanol skeletons for the formation of isobutyraldehyde in one step over titanium oxide-supported vanadium oxide (V/TiO$_2$), where isobutyraldehyde is formed via an aldehyde intermediate formed from the corresponding alcohol [13,14]. These results prompted us to study the alkylation of aldehydes over V/TiO$_2$ using methanol as the methyl group source.

In this work, the reactivities of a series of aldehydes, such as acetaldehyde, propionaldehyde, and phenylacetaldehyde, with methanol over V/TiO$_2$ were examined. The influences of contact time and of reaction temperature were also studied in these reactions.

2. Experimental

2.1. Catalyst

The V/TiO$_2$ catalyst was prepared by impregnating titanium oxide (TiO$_2$) with a solution of oxalic acid containing ammonium vanadate (NH$_4$VO$_3$). The vanadium content (wt%) was based on the concentration of the vanadate anion in the processing solutions. After impregnation, the catalysts were dried in air at 383 K for 24 h. All the catalysts were heated in air for 6 h at 773 K before the reaction. TiO$_2$, the support, is of the anatase type and has a BET surface area of about 11 m^2 g^{-1} before and after calcination at 773 K. All the V/TiO$_2$ catalysts are characterised by a BET surface area close to that of TiO$_2$ and have a packing density of about 0.9 g ml^{-1}.

2.2. Apparatus and procedures

The reactions under atmospheric pressure were performed using a fixed-bed system equipped with a reactor and a tubular furnace. The reactor was a 12 mm inner-diameter quartz glass tube. The reaction was conducted at 350°C by using a 1 g portion of V/TiO$_2$ as a catalyst. All starting materials were reagent grade. The reactant mixture (substrate/methanol = 1/10) was fed by a syringe pump and vaporized in an evaporator. The vapor was adjusted to a constant rate of 15 ml/min and then diluted with nitrogen. The total flow rate was controlled at 45 ml/min. Except where otherwise noted, these conditions were employed for all experiments. The products were identified by gas chromatography–mass spectrometry and analyzed quantitatively with a gas chromatograph attached to the reaction system through a gas-sampling valve. The columns used in the gas chromatography were a Porapak Q column (3 m) at 90–190°C (10°C/min ramp) and Carbosieve S-II column (3 m) at 25°C for H$_2$, CO, and CH$_4$ analysis.

3. Results and discussion

The reaction of various aldehydes, i.e. acetaldehyde, propionaldehyde, and phenylacetaldehyde with metha-

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nol over V/TiO_2 yields methylated aldehydes selectively, with minor amount of other hydrocarbons. Almost all the excess methanol was recovered, together with a small amount of methane, after the reaction. The general reaction scheme is described as follows:

$$RCH_2CHO + CH_3OH \rightarrow R(CH_3)CHCHO + H_2O \quad \text{(main reaction)}$$
$$\rightarrow RCH_2CH_3 + R(CH_3)CHCH_3 \quad \text{(byproducts)},$$

where $R = H, CH_3$ or phenyl group.

In this study, catalyst performance will be expressed according to the following formulas:
aldehyde conversion:

$$C\,(\%) = \frac{\text{aldehyde}_{\text{inlet}} - \text{aldehyde}_{\text{outlet}}}{\text{aldehyde}_{\text{inlet}}} \times 100,$$

product selectivity:

$$S_i\,(\%,\text{mol}) = \frac{\text{product}(i)}{\text{aldehyde}_{\text{inlet}} - \text{aldehyde}_{\text{outlet}}} \times 100,$$

product yield:

$$Y_i\,(\%,\text{mol}) = \frac{\text{product}(i)}{\text{aldehyde}_{\text{inlet}}} \times 100 = CS_i.$$

3.1. Effect of catalyst composition

The activity of V/TiO_2 catalysts strongly depends on the concentration of vanadium. The dependencies of aldehyde conversion and main product selectivity on the vanadium content are shown in fig. 1. The catalyst properties can be enhanced by addition of a small amount of vanadium; excess addition of vanadium, however, results in a decrease in activity and selectivity of alkylated aldehyde (except acetaldehyde conversion). The optimum results of aldehyde conversion and selectivity of the alkylated products were obtained for V(2.5 wt%)/TiO_2. The XRD patterns of V/TiO_2 with various vanadium contents are shown in fig. 2. As the concentration of vanadium increases, the characteristic peaks of V_2O_5 become significant, indicating that addition of excess vanadium results in multilayers and/or crystallites of vanadium oxide. According to the results of the partial oxidation of toluene over V/TiO_2 catalysts [15] and other studies of V/TiO_2 catalysts [16], V(2.5 wt%)/TiO_2 appears to be a V-monolayer catalyst. This suggests that vanadium oxide is an essential constituent for the reaction, but must be present in a particular state of dispersion.

The DSC spectra of V/TiO_2 catalysts show an absorption peak at about 700°C, which indicates that phase transformation will happen at a high temperature. The XRD studies show that a high temperature (> 600°C) transforms TiO_2 from anatase to rutile, as shown in fig. 3. The anatase-into-rutile transformation has also been reported in other studies [17,18]. For the V(2.5 wt%)/TiO_2 catalyst, the dependencies of the conversion of aldehyde and the yields of the desired products on the reaction temperature are shown in fig. 4. A significant drop in activity of these reactions is observed when they occur at a temperature of 650°C. By analogy to the results in o-xylene oxidation over V_2O_5–TiO_2 catalysts [17], the anatase-into-rutile transformation seems to be the reason V/TiO_2 catalysts lose their catalytic activity.

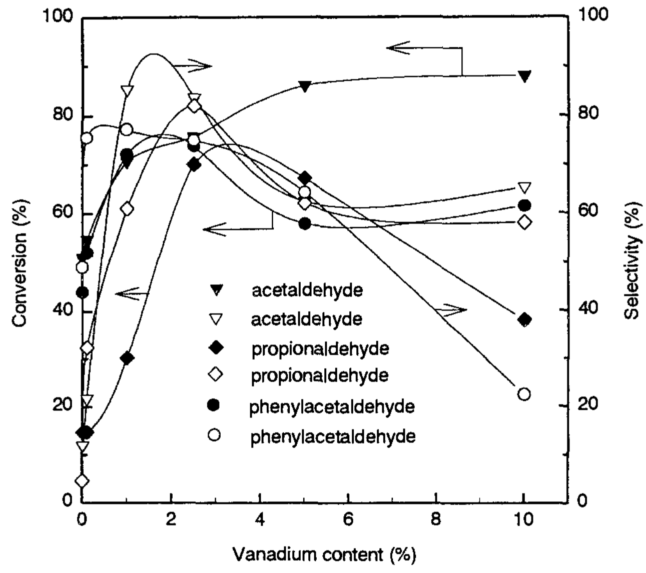

Fig. 1. Addition effect of V_2O_5 to TiO_2 on the reactions of various aldehydes with methanol (1 : 10).

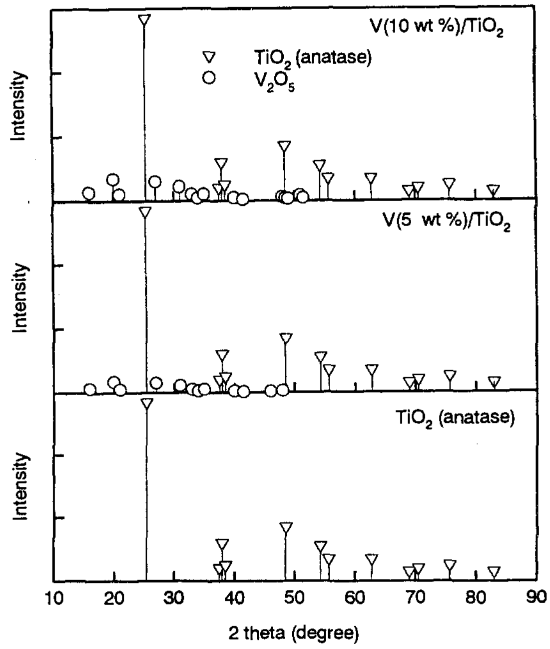

Fig. 2. Addition effect of V_2O_5 to TiO_2 on the XRD patterns of various V/TiO_2 catalysts.

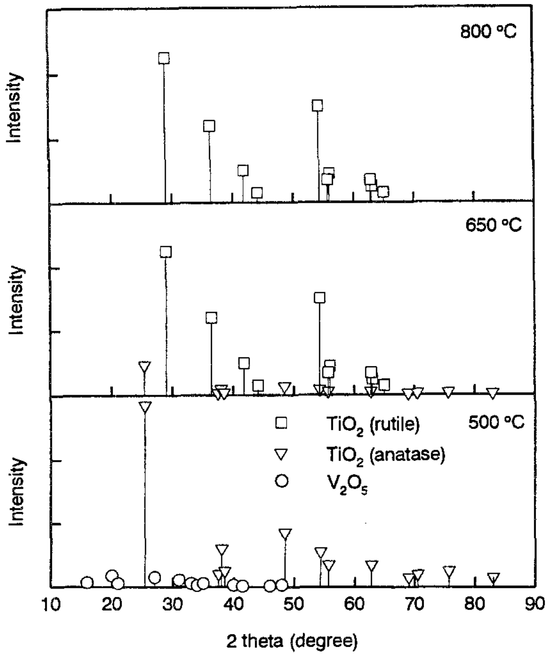

Fig. 3. Effect of calcination temperature on the XRD pattern of V(5 wt%)/TiO$_2$ catalyst.

3.2. *Effect of contact time and feed composition*

3.2.1. *Reaction of acetaldehyde and methanol*

The reaction of acetaldehyde and methanol over V/TiO$_2$ catalysts yields propionaldehyde (PA) selectivity and isobutylraldehyde (IBA) with minor amounts of by-products, such as ethyl ether (EE), C$_3$ and C$_4$ hydrocarbons (HC), crotonaldehyde (CA), and some oligomers of acetaldehyde (OG). Fig. 5 illustrates the yields of products vs. acetaldehyde conversion in the reaction of acetaldehyde and methanol (mole ratio = 1 : 10) over V(2.5 wt%)/TiO$_2$ at 350°C, where extents of conversion were controlled by adjusting the contact time. The yield of PA increased with the conversion of acetaldehyde, passed through a maximum, and then decreased. The maximum yield of PA is obtained at a conversion of 60% and the yield of IBA increased markedly from this point, while the yields of EE, HC, CA, and OG changed slightly by varying the contact time. This suggests that the IBA is formed by a subsequent reaction of acetaldehyde.

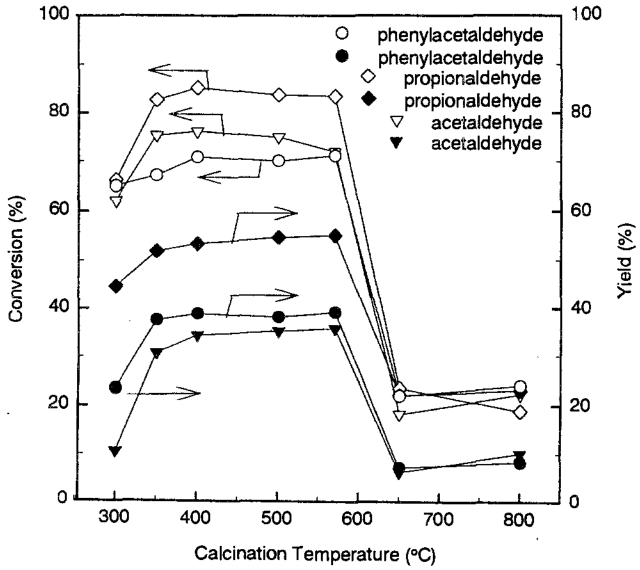

Fig. 4. Effect of calcination temperature on the catalytic activity of V(2.5 wt%)/TiO$_2$ in the reactions of various aldehydes with methanol (1 : 10).

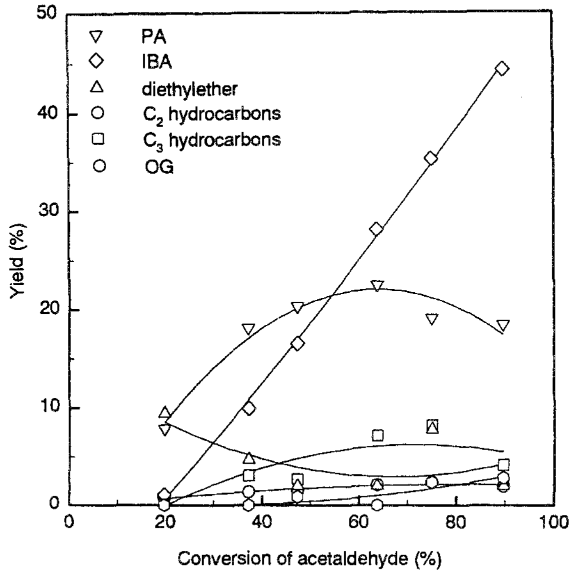

Fig. 5. Variation of the yields of the products with the conversion of acetaldehyde in the reaction of acetaldehyde with methanol (1 : 10) over V(2.5 wt%)/TiO$_2$ by changing contact time.

The effect of the acetaldehyde concentration in the feed on the formation rate of products is illustrated in fig. 6. The reaction was conducted at 350°C by using a 1 g portion of V(2.5 wt%)/TiO$_2$ as a catalyst. The flow rate of the feed was 45 ml/min, as described previously, but the mole ratio of acetaldehyde to methanol was changed. As seen in fig. 6, the formation rate of IBA increased with acetaldehyde concentration, passed through a maximum, and then decreased. It is noteworthy that, when the rate of PA formation is increased, the formation rate of oligomers of acetaldehyde (OG) also increases significantly with the concentration of acetaldehyde. The results imply that formation of alkylated products (PA and IBA) from acetaldehyde and methanol need the activation of methanol as well as acetaldehyde. The increase of the OG formation may be caused by the increase of coverage of acetaldehyde on the catalyst surface at higher acetaldehyde concentration. This implies that self-condensation of acetaldehyde which forms the oligomers is in competition with the cross coupling reaction of acetaldehyde with methanol in forming PA and/or IBA. By using high space velocity to avoid the oligomeri-

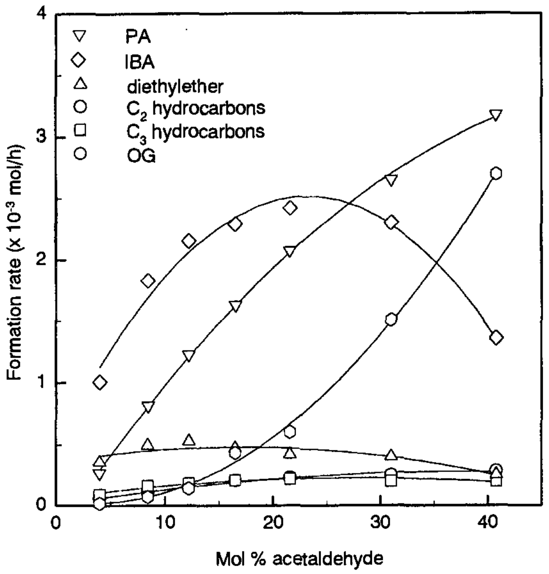

Fig. 6. Effect of the acetaldehyde concentration in the feed on the formation rates of the products in the reaction of acetaldehyde with methanol (1 : 10) over V(2.5 wt%)/TiO_2 at 350°C.

zation of acetaldehyde, PA is expected to be produced more efficiently.

3.2.2. Reaction of propionaldehyde and methanol

The synthesis of PA was adapted for the synthesis of isobutylraldehyde from methanol and propionaldehyde. Fig. 7 shows the dependencies of propionaldehyde conversion and the selectivity of IBA on contact time at various reaction temperatures over a V(2.5 wt%)/TiO_2 catalyst. The reaction of propionaldehyde and methanol yields isobutyraldehyde (IBA) selectively, with minor amounts of by-products, such as C_3 and C_4 hydrocarbons (HC), dimethoxy propane and isobutyl alcohol. It is interesting that although the conversion of propionaldehyde increased with the contact time, the selectivity to the formation of IBA did not change significantly. It still kept a value of about 60%.

The effect of the propionaldehyde concentration in the feed on the formation rate of products is illustrated in fig. 8. The reaction condition was the same as in the reaction of acetaldehyde and methanol as described previously, but propionaldehyde was used instead of acetaldehyde in the reaction of methanol. The formation rate of IBA increased greatly with propionaldehyde concentration up to 30 mol%, but a further increase in its concentration did not change the rate of IBA formation. In addition, the optimum formation rate of IBA in the reaction of propionaldehyde and methanol is less than that of the total alkylated compounds (PA and IBA) in the reaction of acetaldehyde and methanol; however, with regard to selectivity, the situation is reversed. Propionaldehyde appears to be a compound that replaces an α-hydrogen (α-H) of acetaldehyde with a methyl group. According to the results for the vinylation of ketones, esters, and nitriles with methanol to give the corresponding α,β-unsaturated compounds, which indicates that the rate of α-H abstraction of these compounds is the rate-determining step and corresponds to the acidity of the α-H [9,10]. Consequently, the α-H of propionaldehyde might be less acidic than that of acetaldehyde. By analogy, substitution of α-H by an electron-releasing methyl group may decrease the acidity of the α-H of aldehyde, and that will be the reason propionaldehyde is less reactive than acetaldehyde. In addition, the formation of oligomers of propionaldehyde, as compared with the formation of IBA, is rare and is not chan-

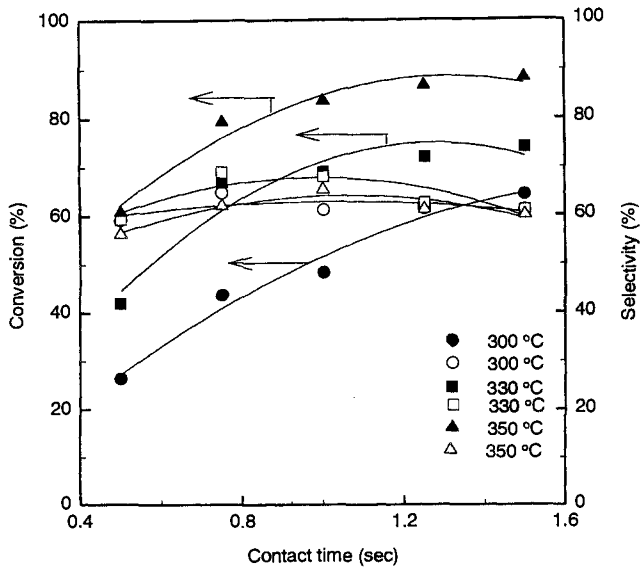

Fig. 7. Effect of contact time on the reaction of propionaldehyde and methanol (1 : 10) over V(2.5)/TiO_2 at 350°C.

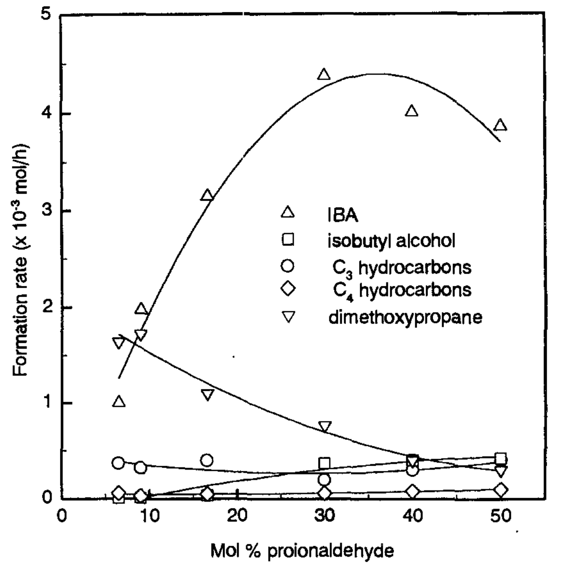

Fig. 8. Effect of the propionaldehyde concentration in the feed on the formation rate of products in the reaction of propionaldehyde and methanol (1 : 10) over V(2.5 wt%)/TiO_2 at 350°C.

ged significantly. This differs from the result of the reaction of acetaldehyde and methanol to give PA, in which the formation of acetaldehyde oligomers increased with the concentration of acetaldehyde. This implies that although the methyl group reduces the acidity of α-H of propionaldehyde, this steric effect may also prevent the self-condensation of propionaldehyde to form oligomers.

3.2.3. Reaction of phenylacetaldehyde and methanol

In order to examine the steric effect of substitute groups in aldehydes, phenylacetaldehyde was used instead of propionaldehyde in this reaction with methanol. Thus, this reaction yielded methylphenyl acetaldehyde (MPA) selectively, with minor amounts of by-products, such as styrene, dimethoxy ethylbenzene and phenylethanol. Fig. 9 shows the dependencies of phenylacetaldehyde conversion and the selectivity of methylphenylacetaldehyde on contact time over a V(2.5 wt%)/TiO_2 catalyst at 350°C. As seen in the figure, the conversion of phenylacetaldehyde and the selectivity to the formation of methylphenylacetaldehyde increased with the contact time, but at a longer contact time, the formation of methylphenylacetaldehyde increased only insignificantly, and then kept a value of about 60%. The reaction pattern is similar to that of the reaction of propionaldehyde and methanol.

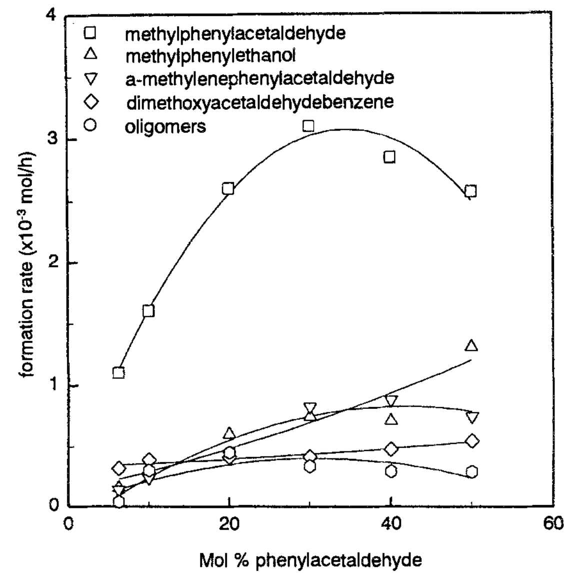

Fig. 10. Effect of the phenylacetaldehyde concentration in the feed on the formation rate of products in the reaction of phenylacetaldehyde and methanol (1 : 10) over V(2.5 wt%)/TiO_2 at 350°C.

The effect of the phenylacetaldehyde concentration in the feed on the formation rate of products is illustrated in fig. 10. The reaction condition was the same as for the reaction of acetaldehyde and methanol, as described previously, but the mole ratio of phenylacetaldehyde to methanol was changed. The formation rate of methylphenylacetaldehyde increased with phenylacetaldehyde concentration, passed through a maximum, and then decreased. Moreover, values of the formation rates of products and the behavior of the dependency of the substrate concentration are similar to those of the reaction of propionaldehyde and methanol (fig. 8). Phenylacetaldehyde is a compound that replaces one of the α-hydrogen of acetaldehyde with a phenyl group, which is bulkier than the methyl group of propionaldehyde, but shows the similar reactivity in the reaction with methanol. It is hard to explain whether this is caused by the steric or electron-withdrawing effect of the substituted phenyl group. To decide whether the steric effect of the electron-withdrawing effect of the substituted phenyl

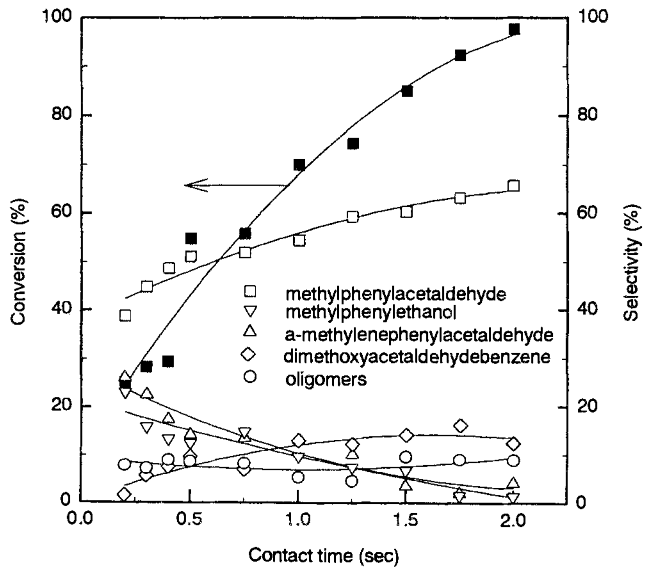

Fig. 9. Effect of contact time on the reaction of phenylacetaldehyde and methanol (1 : 10) over V(2.5 wt%)/TiO_2 at 350°C.

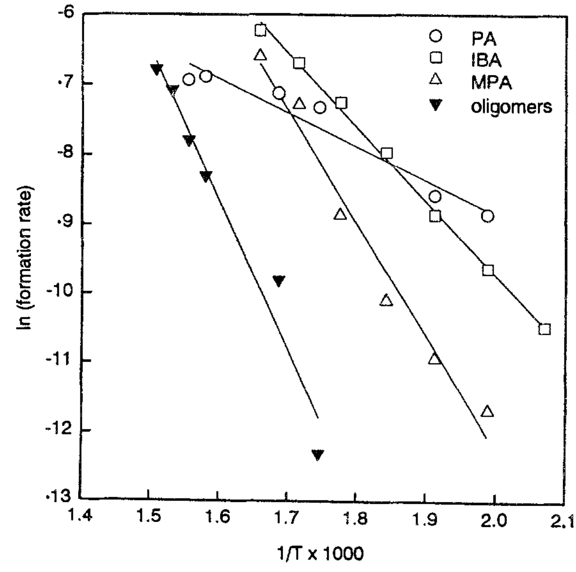

Fig. 11. The formation rates of the products as a function of reaction temperature in the reactions of various aldehydes with methanol (1 : 10) over V(2.5 wt%)/TiO_2.

Table 1
Reaction of various ring substituted phenylethyl alcohols

Runs	Reactant	Conversion (%)	Selectivity (%)			
			α-methylaldehyde	α-methyl alcohol	hydrocarbon	alkylated hydrocarbon
1	Et-OH	85.02	59.4	2.11	16	13.3
2	Ph-OH	76.11	41.07	18.36	26.61	2.15
3	F-Ph-OH	92.9	47.8	10.96	24.39	1.74
4	MeO-Ph-OH	61.78	25.97	4.4	46.93	5.78

group caused this result in this reaction, we further examined the reaction over V(2.5 wt%)/TiO_2, for four compounds: ethanol (Et-OH), phenylethanol (Ph-OH), 4-fluorophenethyl alcohol (F-Ph-OH) and 2-(4-methoxyphenyl)ethanol (MeO-Ph-OH), which are easily dehydrogenated to form the corresponding aldehydes[#1]. Results are given in table 1. There is a clear correlation between the reactivity and character of the substituted group. When phenylethanol is substituted by an electron-withdrawing element, a fluoro ion, to the phenyl group, the formed compound shows a higher reactivity (run 3). By contrast, when an electron-releasing group, for example, a methoxy ion, is used, there is poor methylating activity (run 4). In addition, neither phenylethanol nor substituted phenylethanol forms self-condensation products. For comparison, we also list the reactivity of ethanol (Et-OH). The reactivity of ethanol (Et-OH) is higher than that of phenylethanol (Ph-OH). The relation coincides well with the relation of reactivities of acetaldehyde and phenylethanol (runs 1 and 2, and figs. 4 and 6). By analysis of these results, we can conclude that the substituted phenyl group of acetaldehyde shows both the steric and electron-withdrawing effect. In addition, the steric effect of the phenyl group may also prevent the self-condensation of phenyl acetaldehyde to form oligomers.

3.3. *Effect of reaction temperature*

Temperature dependencies of the formation rates of products in the reactions of methanol and various aldehydes, i.e. acetaldehyde, propionaldehyde, and phenylacetaldehyde, are shown in fig. 11. The line presenting the formation rate of PA has a smaller slope than those of IBA and MPA. However, the slopes of the lines presenting the formation rates of IBA and MPA show no significant difference. This suggests that the formation of PA from methanol and acetaldehyde has a lower activation energy and is faster than the other two reactions. This phenomenon agrees with the postulation described previously. The activation energy for the formation of oligomers from acetaldehyde is similar to that of IBA and MPA, and therefore cannot be neglected in the reaction of methanol and acetaldehyde.

4. Conclusions

The catalyst properties of titanium oxide can be enhanced only by addition of a fairly small amount of vanadium. High-temperature treatment transforms titanium oxide from anatase to rutile, which causes the catalysts to lose their catalytic properties. The reactivity of various aldehydes can be ranked in the following order: acetaldehyde > propionaldehyde > phenylacetaldehyde. The steric effect of the substituted groups in propionaldehyde or phenylacetaldehyde may prevent self-condensation to form oligomers and to give a high selectivity of alkylated products as compared to that of acetaldehyde.

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[#1] Because the phenyl group substituted phenylacetaldehydes are very unstable and are not sold anywhere.