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Alkylation of Acetaldehyde with Methanol over Titanium Oxide-supported Vanadium Oxide

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Among various titanium oxide-supported vanadium oxides (V/TiO_2), V(2.5 wt%)/TiO_2 showed the highest catalytic activity at 350 °C in the reaction of methanol and acetaldehyde, selectively yielding propionaldehyde and isobutyraldehyde. Total alkylated products selectivity attained 83% at 76% acetaldehyde conversion.

The lengthening of carbon chains in compounds, such as nitriles, ketones, and esters of carboxylic acids, by the addition of methanol as a carbon source have been achieved.[1-3] Recently, we have reported that methanol may add to ethanol skeleton for the formation of isobutyraldehyde in one step over titanium oxide-supported vanadium oxide (V/TiO_2).[4] In an extention of the studies, we have found that V/TiO_2 is an effective catalyst for the alkylation of acetaldehyde with methanol.

V/TiO_2 catalysts were prepared by the simple impregnation method described elsewhere.[4] The metal content (wt%) of vanadium on TiO_2 was based on the concentration of metal ion in the preparation solution. The reactions were performed at atomospheric pressure using a continuous flow reaction system with a quartz fixed-bed reactor. An amount of 1.0 g of catalyst was loaded in the reactor and pretreated at 500 °C for 2 h in air. A mixture of acetaldehyde and methanol vapor was fed at constant rate of 15 ml/min together with nitrogen (30 ml/min).

Table 1. Reaction of Methanol and Acetaldehyde over Various V(wt%)/TiO_2

wt	Conv. of	Selectivity					
%	acetaldehyde	PA	IBA	EE	HC	CA	Others
0.1	54.8	22.5	9.9	12.3	1.6	35.3	17.7
1.0	70.6	32.2	28.8	7.5	3.5	14.7	11.4
2.5	75.8	33.4	49.2	10.2	4.0	1.1	2.1
5.0	86.1	19.7	42.3	5.8	3.2	7.9	19.2
10.0	86.5	18.7	40.1	5.4	4.1	4.9	22.6

The results of the reaction of acetaldehyde and methanol (mole ratio; 1:7) at 350 °C are summarized in Table 1, where values of conversion and selectivity are caculated on the acetaldehyde basis. Titanium oxide (TiO_2) shows lower activity for alkylation of acetaldehyde with methanol, but yields crotonaldehyde (45%) as a main product. When vanadium oxide is loaded, it shows a resonable activity for the alkylation of acetaldehyde, selectively yielding propionaldehyde (PA) and isobutyraldehyde (IBA). The activity of catalysts strongly depends on the concentration of vanadium. The optimum results for conversion and selectivity were obtained for V(2.5 wt%)/TiO_2, in which total alkylated products (PA and IBA) selectivity was about 80% with minor by-products, such as ethyl ether (EE), hydrocarbons (HC), crotonaldehyde (CA) and some compounds abbreviated to "others" including oligomers of acetaldehyde. According to the results of the partial oxidation of toluene over V/TiO_2,5) V(2.5 wt%)/TiO_2 seems to be a V-containing monolayer catalyst. On the other hand, vanadium oxide mainly catalyzed the oligomerization of acetaldehyde. Thus the results suggest that vanadium oxide is an essential constituent for the reaction, but some special situations are required.

We have also found that IBA is selectively formed in high yield (60%) from methanol and PA, which indicates that IBA is formed *via* PA as an intermediate. In order to confirm the role of methanol in this reaction, formaldehyde instead of methanol was used in the reaction with acetaldehyde. It was found that the main product was acrolein with little PA and IBA. This differs from the results for the vinylation of ketones, esters, and nitriles with methanol to give the corresponding α,β-unsaturated compounds;1-3) in this case the reaction takes place *via* a formaldehyde intermediate formed from methanol.

The main effect of the feed gas composition on the reaction is summarized in Table 2. At higher substrate ratio, the IBA formation is suppressed, while the rate of PA formation is significantly increased. However, the rate of formation of "others", i.e. the oligomers of acetaldehyde, is also increased. By using high space velocity to avoid the oligomerization of acetaldehyde, PA is expected to be produced more efficiently.

Table 2. Formation Rates of Products at Various Acetaldehyde/Methanol Ratios

Acetaldehyde /Methanol	Rate/10^{-4}·mol·h^{-1}·g-cat^{-1} PA	IBA	Others
1/15	5.7	12.2	1.2
1/7	10.2	14.9	0.9
2/7	14.4	12.3	8.2
2/3	22.2	0.9	18.8

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