CHEMISTRY LETTERS, pp. 1843-1846, 1987.

Methylvinyl Ketone Formation over Synthetic Chrysotile

Eiichi SUZUKI,* Satoshi IDEMURA, and Yoshio ONO
Department of Chemical Engineering, Tokyo Institute of Technology,
Ookayama, Meguro-ku, Tokyo 152

Selective formation of methylvinyl ketone (MVK) was attained over chrysotile, $Mg_3(OH)_4Si_2O_5$, through aldol condensation reaction between acetone and formaldehyde, the selectivity being 98% on both acetone and formaldehyde bases. Synthetic Co^{2+}-substituted chrysotile, $Co_xMg_{3-x}(OH)_4Si_2O_5$ (x= 0.15 or 0.9), catalyzed the reaction between acetone and methanol to give MVK and methylethyl ketone (MEK) with 75% selectivity on acetone basis.

Chrysotile, $Mg_3(OH)_4Si_4O_5$, is a layered magnesium silicate and can be synthesized under hydrothermal conditions.1) The synthetic chrysotile has been found to be a catalytically active material in acid- or base-catalyzed reactions.2) It has also been reported that metal cations other than Mg^{2+} can be incorporated in the structure of chrysotile to give a cation-substituted chrysotile such as Co_x-$Mg_{3-x}(OH)_4Si_2O_5$.3)

The aldol condensation reaction is known to be catalyzed by acid or base.4) In this study, a reaction between formaldehyde and acetone over the synthetic chrysotile is examined, the condensation product being methylvinyl ketone (MVK). Condensation reactions between formaldehyde and propionaldehyde,5) or phenol6) over solid catalysts have been reported, in which trioxane is used as a potential precursor for formaldehyde. In the present study, trioxane as well as formalin was used as a formaldehyde source.

The transition metal cation-substituted chrysotile may possibly have a dehydrogenation property together with acid- or base-properties. If methanol underwent dehydrogenation, formaldehyde would be formed. Then it may follow that MVK can be directly formed from a mixture of methanol and acetone through the aldol condensation reaction of formaldehyde and acetone. Ueda et al.7) have reported that MVK was synthesized from methanol and acetone over MgO containing Fe(III) ion catalyst at 350 °C with a 55% selectivity for MVK on acetone basis. Here, the Co^{2+}-substituted chrysotile, $Co_xMg_{3-x}(OH)_4Si_2O_5$, was tested for the reaction.

Chrysotile and Co^{2+}-substituted chrysotile were synthesized hydrothermally accoring to the method reported,1,3) using sodium metasilicate, magnesium chloride and cobalt(II) chloride. The reactions were performed with a continuous flow reactor operating at atmospheric pressure. The minerals thus prepared were pretreated under a helium stream at 500 °C for 2 h before starting reactions. Trioxane or methanol was dissolved in acetone at a given HCHO/acetone molar ratio to be delivered to the reactor. The products from the outlet of the reactor were periodically analyzed by gas chromatography.

In Table 1, are shown the results of aldol condensation of formaldehyde and acetone over chrysotile. When formalin was used as a formaldehyde source, the conversion of formaldehyde was 61.8%, and CH_3OH and C_5-ketones were formed together with MVK. The formation of methanol was observed also in the aldol condensation reaction over hydrotalcite-based catalysts using formalin as a formaldehyde source and was attributed to Cannizzaro reaction of formaldehyde due to the presence of water in formalin.[8)]

On using trioxane in place of formalin, the yields of both CH_3OH and C_5-ketones are remarkably depressed, while the yield of MVK remained essentially unchanged (45.8%). It may follow that elimination of water from formaldehyde source is remarkably effective to increase the selectivity to MVK. As is shown in Table 1, the selectivity for MVK on acetone basis were also very high, C_5-ketones being by-products. Further experiments were conducted using trioxane as a formaldehyde source.

With increasing reaction temperature, formaldehyde conversion monotonously increased from 18.1% to 56.5% under the same reaction conditions as those in Table 1, except reaction temperature ranging from 350 °C to 500 °C. Selectivity for MVK based on formaldehyde was about 98% at 350 and 400 °C, and decreased to 79.5% at 500 °C. At 450 and 500 °C, CO was detected in the products. The maximum yield of MVK (46%) on formaldehyde basis appeared at 400 °C.

Reactions were performed at various acetone pressures (6.0-24.0 kPa) with formaldehyde pressure being kept at 3.0 kPa. The results are shown in Fig. 1 on formaldehyde basis. At 6.0 kPa of acetone pressure, CH_3OH, CO_2, and CO together with MVK were observed in the product. Above 9.1 kPa (acetone/HCHO molar ratio

Table 1. Aldol condensation reaction between formaldehyde and acetone over chrysotile[a)]

HCHO source	Formalin	Trioxane
HCHO conversion / %	61.8	46.9
Selectivity / %		
MVK	80.8	97.6
CH_3OH	11.9	0
C_5-Ketones[b)]	7.3	2.4
Acetone conversion / %	18.7	14.3
Selectivity / %		
MVK	95.7	98.8
C_5-Ketones[b)]	4.3	1.2

a) Reaction conditions: reaction temperature= 400 °C, W/F= 2.7 g h mol^{-1}, HCHO= 3.0 kPa and acetone= 9.1 kPa.

b) Methylisopropyl ketone and ethylvinyl ketone.

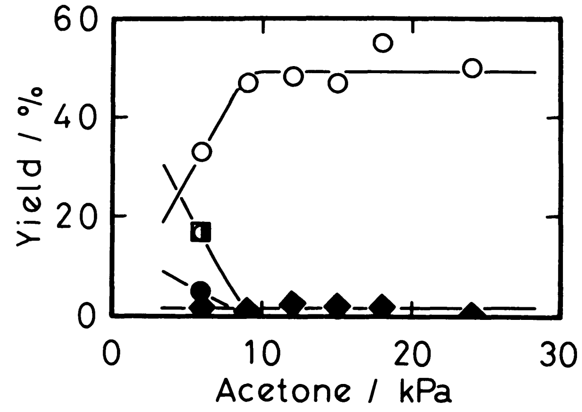

Fig. 1. Changes in yield of products with acetone partial pressure on formaldehyde basis. (○) MVK, (□) CH_3OH, (◑) CO_2, (●) CO and (◆) C_5-ketones. Reaction conditions: reaction temperature= 400 °C, W/F= 2.7 g h mol^{-1} and HCHO= 3.0 kPa.

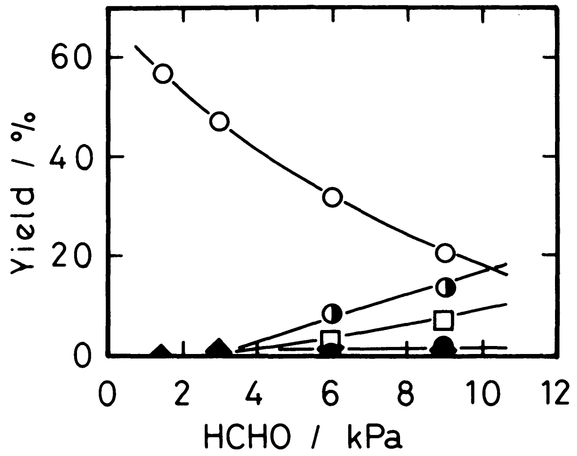

Fig. 2. Changes in yield of products with formaldehyde partial pressure on formaldehyde basis. Symbols are the same as those in Fig. 1. Reaction conditions: reaction temperature= 400 °C, W/F= 2.7 g h mol^{-1} and acetone= 9.1 kPa.

Table 2. Aldol condensation reaction between methanol and acetone over Co^{2+}-substituted chrysotile[a)]

Catalyst	$Co_xMg_{3-x}(OH)_4Si_2O_5$ x= 0.15	x= 0.9
CH_3OH conversion / %	2.5	1.2
Selectivity / %		
MVK	31.1	50.4
MEK[b)]	25.2	31.3
CO_2	32.7	15.7
C_5-Ketones[b)]	11.0	2.6
Acetone conversion / %	19.2	15.6
Selectivity / %		
MVK	41.2	45.1
MEK[b)]	33.3	27.9
IPA[b)]	18.2	24.6
C_5-Ketones[b)]	7.3	2.4

a) Reaction conditions: reaction temperature= 350 °C, W/F= 2.2 g h mol^{-1}, CH_3OH =16 kPa and acetone= 1.6 kPa.

b) MEK: methylethyl ketone; IPA: isopropyl alcohol; C_5-ketones: methylisopropyl ketone and ethylvinyl ketone.

$\geq$3), the yield of MVK was constant (49%). This phenomenon suggests that acetone is so strongly adsorbed on the catalyst surface that the Cannizzaro reaction, a bimolecular reaction of formaldehyde, is suppressed completely. The MVK yield on acetone basis decreased monotonously from 16.4% to 6.3% with the increase in acetone pressure, selectivity to MVK on acetone basis being 97.2-99.4%.

In Fig. 2, is shown the effect of formaldehyde pressure on the yield of products on formaldehyde basis, with acetone pressure being kept at 9.1 kPa. At a formaldehyde pressure lower than 3.0 kPa (acetone/HCHO $\geq$3), MVK is formed selectively. Above 6.0 kPa, the formation of CH_3OH, CO_2, and CO becomes appreciable. With increasing formaldehyde pressure, MVK yield on acetone basis increased and became constant (21.1%) at higher than 6.0 kPa.

Several studies have been reported on the MVK formation from formaldehyde and acetone, using formalin as a formaldehyde source, over solid catalysts such as Na/SiO_2,[9)] calcium hydroxyapatite ($Ca_5(OH)(PO_4)_3$),[10)] ZrO_2/SiO_2[11)] and a hydrotalcite ($Mg_6Al_2(OH)_{16}CO_3 \cdot 4H_2O$)-based catalyst.[8)] Malinowski et al.[9)] reported the conversion of acetone to be 1%, while Tanaka et al.[10)] obtained the yields of MVK and of mesityloxide to be 24% and 2% on acetone basis, respectively. The material balance based on formaldehyde is not found in their reports. Igarashi et al.[11)] and Suzuki et al.[8)] obtained the yield of MVK to be 13% and 15% on acetone basis at W/F= 5 g h mol^{-1}, respectively. In the present study, using trioxane as a formaldehyde source, MVK yield on acetone basis was found to be 14-20% which is in the range of MVK yields ever reported. The selectivity for MVK on formaldehyde basis has been reported to be 65%[11) and 64%.[8) In the present work, the most predominant effect of using trioxane in place of formalin in combination with chrysotile can be found in an enhanced selectivity to MVK (98%) on formaldehyde basis.

The results of reactions of methanol and acetone over the two kinds of Co^{2+}-substituted chrysotile are given in Table 2. The catalysts contain Co^{2+} cations, in place of the part of Mg^{2+} cations in chrysotile with different degree of substitution (x= 0.15 or 0.9). Over the both catalysts, MVK and methylethyl ketone (MEK) were formed as the major aldol condensation products, by-products being CO_2, C_5-ketones and isopropyl alcohol. The selectivities for MVK and MEK were found to be 56-82% and 73-75% on methanol and acetone basis, respectively. The MVK yield was found to be 7-8% on acetone basis. The reaction may proceed via aldol condensation between acetone and formaldehyde which might be formed as a result of dehydrogenation of methanol. Thus, Co^{2+}-substituted chrysotile can behave as a bifunctional catalyst for dehydrogenation reaction and acid/base reaction.

In conclusion, the aldol condensation between acetone and formaldehyde to yield MVK proceeds with a high selectivity over synthetic chrysotile by using trioxane as a formaldehyde source, the selectivity for MVK being 98% on both acetone and formaldehyde bases. Synthetic Co^{2+}-substituted chrysotile was also effective for aldol condensation reaction between acetone and methanol yielding MVK and MEK with a selectivity of 75% on acetone basis.

References

1) W. Noll, H. Kircher, and W. Sybertz, Kolloid-Z., 157, 1 (1958).
2) S. Suzuki and Y. Ono, Appl. Catal., 10, 361 (1984).
3) United States Patent 3848018 (1974).
4) T. A. Geissman, "Organic Reactions," ed by W. E. Bachman, J. R. Johnson, L. F. Fieser, and H. R. Snyder, Robert E. Krieger Publishing Company, Florida (1981), Vol. 2.
5) United States Patent 4433174 (1984).
6) P. B. Venuto and P. S. Landis, J. Catal., 6, 237 (1966).
7) W. Ueda, T. Yokoyama, Y. Moro-oka, and T. Ikawa, J. Chem. Soc., Chem. Commun., 1984, 39.
8) E. Suzuki and Y. Ono, submitted to Bull. Chem. Soc. Jpn.
9) S. Malinowski, S. Basinski, S. Szczepanska, and W. Kiewlicz, Proc. Third Intern. Congr. Catal., p.441, North-Holland Publishing Co., 1965, Amsterdam.
10) Y. Tanaka, K. Urabe, and Y. Izumi, 41st National Meeting of the Chemical Society of Japan, Osaka, April 1980, Abstr., No. 3T29.
11) T. Igarashi and M. Suzuki, Kanagawa Daigaku Kougakubu Kenkyu Hokoku, 19, 64 (1981).

(Received July 16, 1987)