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SELECTIVE FORMATION OF METHYL VINYL KETONE FROM ACETONE AND METHANOL WITH SILICA-MAGNESIA BASE CATALYST

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Silica-magnesia was examined as catalyst for the said reaction and was found to give nearly 100% selectivity. Loading of Ag as well as MnO_2 resulted in an increase of the activity of the catalyst but was not detrimental to the selectivity. The course of the reaction was briefly discussed.

Methyl vinyl ketone is extremely useful in organic syntheses, because of its reactivity. An important example is the synthesis of vitamine A.[1)] Methyl vinyl ketone is usually prepared by the reaction of acetone with formaldehyde in the liquid phase in the presence of strong basic catalysts such as sodium hydroxide.[2-5)] Because of difficulty in handling of the aldehyde, a convenient preparation of this ketone is desirable. We have found that the selective formation of this ketone from acetone and methanol in the presence of oxygen could be accomplished with silica-magnesia base catalysts.

The reaction was carried out in a conventional flow type reactor under atmospheric pressure. Silica-magnesia (25% MgO) was prepared by a coprecipitation method. 5% silver and 5% manganese dioxide supported silica-magnesia catalysts were prepared by an impregnation method respectively. These catalysts were activated by calcining at 550°C for 2 hours in air prior to use. The reaction products in the liquid phase were analyzed by gas chromatography.

The catalytic activities and selectivities of the above catalysts for the formation of the ketone in the range 350∼450°C are listed in Table 1. The results show that addition of silver as well as manganese dioxide resulted in an increase of the catalytic activity of silica-magnesia catalyst and that all the catalysts examined had the activity maxima at about 400°C and gave 100% selectivities at temperatures of 350∼450°C.

The liquid products contained very small amount of formaldehyde in addition to methyl vinyl ketone. 2-Hydroxyethyl methyl ketone was easily decomposed to give methyl vinyl ketone and water over silica-magnesia catalyst at about 200°C. From these results it may be considered that methyl vinyl ketone is formed through the reactions as shown below:

$$CH_3OH + \frac{1}{2}O_2 = HCHO + H_2O \qquad (1)$$

$$HCHO + CH_3COCH_3 = CH_3COCH_2CH_2OH \qquad (2)$$

$$CH_3COCH_2CH_2OH = CH_3COCH{=}CH_2 + H_2O \qquad (3)$$

High catalytic activities of the silver and manganese dioxide loaded catalysts compared with silica-magnesia for the overall reaction

$$CH_3COCH_3 + CH_3OH + \frac{1}{2}O_2 = CH_3COCH{=}CH_2 + H_2O \qquad (4)$$

might be explained from a view that the reaction (1) was effectively catalyzed by these promoters. The fact that the formation of methyl vinyl ketone through the reactions (2) and (3) is accomplished with good yield in the presence of silica-magnesia will be published in a subsequent paper.

Table 1 Catalytic activities and selectivities of silica-magnesia base catalysts[a)]

Promoter	Reactor Temp.(°C)	Methyl vinyl ketone[b)] Yield(%)	Selectivity(%)
none	350	4.2	ca. 100
	400	13.5	
	450	12.0	
5% manganese dioxide	350	12.5	
	400	15.5	
	450	13.5	
5% silver	350	17.1	
	400	21.3	
	450	16.5	

a) Total Pressure: 1 atm, W/F ratio: 13.9 g-cat.hr/mole. Partial pressure: 0.07 (acetone), 0.15 (methanol), 0.16 (oxygen), 0.62 atm (nitrogen).

b) In the liquid products.

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