Catalytic Synthesis of Vinyl Ketones over Metal Oxide Catalysts using Methanol as the Vinylating Agent

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Basic binary iron–magnesium oxide has a marked catalytic activity on the vinylation of acetone with methanol to give methyl vinyl ketone.

Polymers of vinyl ketones are becoming increasingly important as polymeric photosensitizers and electroconducting polymers.[1,2] The synthesis of vinyl ketones has been achieved by several methods such as condensation of formaldehyde with ketones, hydration of vinylacetylene, and the Mannich reaction.[3,4] However, these methods have little general applicability. We have developed a conventional and widely applicable method for synthesising vinyl ketones, where basic metal oxides are effective catalysts for the vinylation of ketones using methanol as the vinylating agent. We report here the catalytic vinylation of acetone to give methyl vinyl ketone (MVK).

The reaction was carried out in a conventional flow reactor at atmospheric pressure. The mixture of acetone and methanol was introduced by a syringe pump and evaporated in a preheater tube. Nitrogen was used as the diluent and the flow rate was controlled at 70 ml/min. The Fe/MgO catalyst was prepared by impregnating magnesium oxide with iron(III) nitrate solution. All the catalysts were heated in nitrogen for 2 h at 600 °C before the reaction.

An initial decrease in the conversion of acetone was observed for all the catalysts used but stable activities were obtained within a few hours. Results at the steady state are summarized in Table 1.

Table 1. Conversion and selectivity data for acetone vinylation with methanol.[a]

Wt % Fe/MgO	Catalyst weight/g	Temp. /°C	Conversion[b] (%)	Selectivity (%)[c]			
				MVK	MEK	C_5-Ketones[d]	IPA
0	1	350	12.1	18.7	3.3	trace	33.8
0.48	1	350	24.3	14.8	11.2	2.3	27.2
0.96	1	350	19.0	21.8	11.2	6.4	14.4
3.1	0.25	350	7.2	54.2	21.4	10.3	12.8
,,	0.5	350	12.1	54.5	14.9	13.2	10.7
,,	1	300	10.8	29.6	17.6	trace	23.2
,,	1	350	20.1	34.8	13.9	9.5	13.9
,,	1	400	37.2	36.3	19.9	20.2	4.0
9.1	1	350	19.9	30.2	21.8	22.4	5.0

[a] Reactant mixture: methanol 16%, acetone 1.6%, remainder nitrogen; the catalyst was in the form of pellets. [b] Conversion was calculated at the steady state and was based on the amount of acetone which had reacted. [c] Almost all the methanol was recovered after the reaction but small amounts of CH_4 and CO were found when the catalyst was highly loaded with iron. [d] The C_5-ketones were both saturated and unsaturated.

Solid bases, such as MgO, CaO, SrO, and La_2O_3 were found to be effective to some extent for the vinylation of acetone to MVK. However, the selectivity for MVK formation was fairly low owing to the production of methyl ethyl ketone (MEK) and isopropyl alcohol (IPA), and also probably to the condensation and polymerization of the MVK produced. IPA seems to be formed by hydrogen transfer to acetone from methanol.[5] By analogy with the alkylation of toluene to give styrene and/or ethylbenzene over the same solid bases,[6] this reaction may proceed *via* a formaldehyde intermediate formed from methanol by dehydrogenation.

We obtained improved results both in conversion and selectivity by using an Fe/MgO catalyst. This catalyst, as shown in Table 1, suppresses IPA formation and consecutive C–C bond formation to give C_5-ketones, and shows high activity and selectivity for MVK formation. These characteristics were apparent on the catalysts with high iron content, indicating that the dehydrogenating activity of magnesium oxide was enhanced by combining with iron.

By using high space velocity to avoid condensation and polymerization of MVK produced, 55% selectivity for MVK formation (70% selectivity for combined MVK and MEK formation) at 12% conversion of acetone was attained over 3.1 wt% Fe/MgO catalyst at 350 °C. Further optimization should result in a high yield of MVK from the vinylation of acetone by methanol. Catalytic vinylation using methanol as the vinylating agent over metal oxide catalysts may be applicable to other ketones and esters which have an α-hydrogen atom.

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