1008 © 1988 The Chemical Society of Japan NOTES Bull. Chem. Soc. Jpn., 61, 1008—1010 (1988) [Vol. 61, No. 3

Aldol Condensation Reaction between Formaldehyde and Acetone over Heat-Treated Synthetic Hydrotalcite and Hydrotalcite-Like Compounds

Eiichi Suzuki* and Yoshio Ono
Department of Chemical Engineering, Tokyo Institute of Technology, Ookayama, Meguro-ku, Tokyo 152

(Received July 30, 1987)

Synopsis. Synthetic hydrotalcite, $Mg_6Al_2(OH)_{16}CO_3 \cdot 4H_2O$, and its analogues were synthesized, heat-treated at 773 K, and used as catalysts for the title reaction to form methyl vinyl ketone (MVK) at 673 K. MVK was formed over all the catalysts examined, the highest MVK yield (20% on acetone basis) being found over the heat-treated hydrotalcite.

Hydrotalcite is one of the naturally occurring anionic clay minerals and is represented by the formula: $Mg_6Al_2(OH)_{16}CO_3 \cdot 4H_2O$.[1,2] Thus, magnesium–aluminium hydroxide octahedra form positively-charged layers, which are stacked on top of each other. Carbonate ions are located between the layers as interlayer anions. Hydrotalcite-like minerals, i.e. cation-substituted and/or anion-exchanged hydrotalcites, can be obtained by isomorphous substitution of the cations in the layer and/or of the anions in the interlayer of hydrotalcite.[3–7] It has been reported that these minerals can be synthesized[8] and have basicity upon heat treatment.[9] Several base-catalyzed reactions have been demonstrated: polymerizations of β-propiolactone[10] and of propylene oxide,[11] and self-aldol condensation of acetone.[12,13]

The present work was concerned with testing heat-treated hydrotalcite and hydrotalcite-like compounds as catalysts for a cross-aldol condensation reaction which is known to be catalyzed by acids or bases.[14] Here, a reaction between formaldehyde and acetone is examined, where methyl vinyl ketone (MVK) is the condensation product.

Experimental

Synthesis of Hydrotalcite and Hydrotalcite-Like Compounds. Hydrotalcite was synthesized by the procedures described by Reichle,[13] using $Mg(NO_3)_2 \cdot 6H_2O$, $Al(NO_3)_3 \cdot 9H_2O$, NaOH, and Na_2CO_3. According to the method reported by Miyata et al.,[6,8] was prepared isomorphous-substituted hydrotalcite with NO_3^{2-}, SO_4^{2-}, or CrO_4^{2-} anions. Isomorphous-substituted hydrotalcite, containing Co^{2+}–Al^{3+},[13] Ni^{2+}–Al^{3+},[13] Zn^{2+}–Cr^{3+},[13] or Li^+–Al^{3+} [15,16] ions in place of Mg^{2+}–Al^{3+} ions in hydrotalcite, was also prepared. The X-ray diffraction (XRD) patterns of the materials, thus synthesized, were identical to those previously reported.[3,6,16,17]

Cross-Aldol Condensation Reactions. The reactions were performed with a continuous-flow reactor operating at atmospheric pressure. The synthetic minerals were heated under a helium stream at a given temperature for 2 h before starting the reactions. A mixture of acetone and formalin, containing 36.8wt% of HCHO and 6.6wt% of methanol with a given HCHO/acetone molar ratio, was delivered to the reactor. The products from the outlet of the reactor were periodically analyzed by gas chromatograph.

Results and Discussion

Reactions over Anion-Exchanged Hydrotalcites. In Table 1, are summarized the results of reactions at 623 K with W/F of 7.9 g h mol^{-1} over the anion-exchanged hydrotalcites treated at 623 K, where W and F stand for the weight (g) of the catalyst used and the flow rate (mol h^{-1}) of the feed (formaldehyde+acetone+nitrogen+water), respectively. The heating of hydrotalcite samples at 623 K to obtain catalysts gave rise to changes in the XRD patterns of the samples:

Table 1. Reactions between Formaldehyde and Acetone over Anion-Exchanged Hydrotalcites, Containing Mg^{2+}–Al^{3+}–X^{n-} Ions[a)]

Interlayer anion (X^{n-})	Acetone conversion/%	Selectivity to MVK[b)]/%
CO_3^{2-}	20	93
NO_3^-	12	97
SO_4^{2-}	6.0	98
CrO_4^{2-}	3.7	100

a) Reaction conditions: pretreatment temperature=623 K, reaction temperature=623 K, HCHO=10.1 kPa, Acetone=9.1 kPa and W/F=7.9 g h mol^{-1}. b) On acetone basis.

Table 2. Reactions between Formaldehyde and Acetone over Heated Cation-Substituted Hydrotalcites, Containing M_1^{2+}– or M_1^+–M_2^{3+}–CO_3^{2-} Ions[a)]

Cations in layer M_1^{2+}– or M_1^+–M_2^{3+}	Acetone conversion/%	Selectivity to MVK/%	
		(Acetone)[b)]	(HCHO)[c)]
Mg^{2+}–Al^{3+}	21	96	64
Li^+–Al^{3+}	12	100	37
Co^{2+}–Al^{3+}	9.5	98	28
Ni^{2+}–Al^{3+}	11	69	21
Zn^{2+}–Cr^{3+}	2.7	73	5.4

a) Reaction conditions: pretreatment temperature=773 K, reaction temperature=673 K, HCHO=3.0 kPa, acetone=9.1 kPa and W/F=2.7 g h mol^{-1}. b) On acetone basis. c) On formaldehyde basis.

The pattern consisted of diffractions for both hydrotalcite and MgO for CO_3^{2-}- or NO_3^--exchanged hydrotalcite,[18,19] whereas the only pattern observed was that of hydrotalcite for SO_4^{2-}- or CrO_4^{2-}-exchanged one. The formation of MVK was observed for all the catalyst samples examined: Acetone conversion ranged from 3.7 to 20% and the selectivity to MVK on an acetone basis fell within the range 93—100%. The highest yield of MVK (19%) was obtained with heat-treated hydrotalcite containing CO_3^{2-} anions, with which further experiments were conducted.

Reactions over Cation-Substituted Hydrotalcites. In Table 2, are summarized the results of reactions over cation-substituted hydrotalcites. The heat-treated (at 773 K) hydrotalcite containing Li^+-Al^{3+} cations showed a diffuse XRD pattern for hydrotalcite, together with broad and indefinable diffractions. For all the other heated (at 773 K) hydrotalcites examined, no XRD pattern for hydrotalcite could be observed; the MgO phase for a hydrotalcite containing Mg^{2+}-Al^{3+} cations, a Co_3O_4 phase for Co^{2+}-Al^{3+}, a NiO phase for Ni^{2+}-Al^{3+}, and a ZnO phase for Zn^{2+}-Cr^{3+} were observed. Acetone conversion fell within the range 2.7—21%, the selectivity to MVK on an acetone basis being in the range of 69—100%. The selectivity to MVK on a formaldehyde basis decreased to 37% upon substituting Li^+ for Mg^{2+}, the major product being CH_3OH. The substitution of transition metal cations for Mg^{2+} or Al^{3+} also resulted in a decrease in the selectivity to MVK on a formaldehyde basis: Carbon dioxide was detected as the major product, together with CO and CH_3OH. Hydrotalcite, containing Mg^{2+}-Al^{3+}-CO_3^{2-} ions, was found to be the most effective precursor for a catalyst among the hydrotalcites examined.

Effect of Reaction Temperature. With an increasing reaction temperature, acetone conversion increased and reached 21—22% at 673—723 K over heat-treated hydrotalcite containing Mg^{2+}-Al^{3+}-CO_3^{2-} ions (Fig. 1). The selectivity to MVK on an acetone basis was constant (95%) throughout the whole reaction temperature range examined. The selectivity to MVK on a formaldehyde basis slightly depended on the reaction temperature (Fig. 1) and was 25% at 673—723 K.

Effect of Partial Pressure of Formaldehyde. The formation of CH_3OH can be attributed to a bimolecular reaction of formaldehyde, through a Cannizzaro reaction.[14] The Cannizzaro reaction may be suppressed by lowering the partial pressure of formaldehyde. In Fig. 2 the selectivities to MVK are shown both on an acetone and on a formaldehyde basis as a function of the partial pressure of formaldehyde. The selectivity to MVK on an acetone basis is in the range of 94—99%, while that on a formaldehyde basis is 25% at 10 kPa and 87% at 1.2 kPa. The acetone conversion is also given in Fig. 2 and is almost constant (20%) above 3.0 kPa of formaldehyde pressure; it decreases to 5% at 1.2 kPa. Thus, as expected, a higher selectivity to MVK on a formaldehyde basis was obtained at a low formaldehyde pressure, though the acetone conversion decreased drastically.

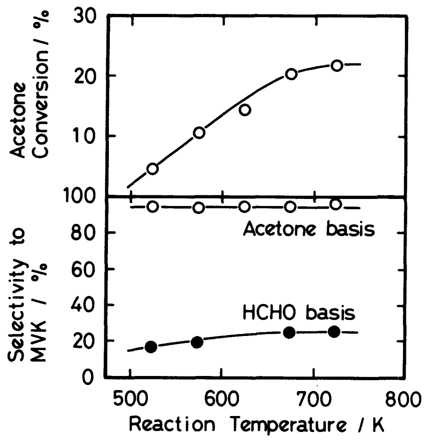

Fig. 1. Temperature dependence of acetone conversion and of selectivity to MVK.
Reaction conditions: pretreatment temperature=773 K, acetone=9.1 kPa, HCHO=10 kPa, and W/F=2.7 g h mol^{-1}.

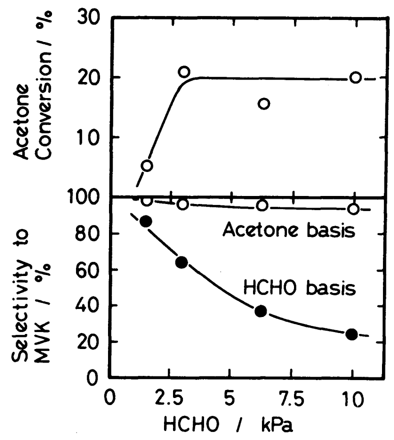

Fig. 2. Dependence of acetone conversion and of selectivity to MVK on partial pressure of formaldehyde.
Reaction conditions: pretreatment temperature=773 K, reaction temperature=673 K, acetone=9.1 kPa, and W/F=2.7 g h mol^{-1}.

Comparison of Results with Literature Data. Several catalytic cross-aldol condensation reactions between formaldehyde and acetone on solid catalysts have been reported. Malinowski et al.[20] obtained a 1% acetone conversion over a Na/SiO_2 catalyst. Tanaka et al.[21] examined the reaction at 573 K, W/F=27 g h mol^{-1} and acetone/HCHO molar ratio=1 over calcium hydroxyapatite ($Ca_5(OH)(PO_4)_3$) calcined at 773 K and obtained a 24% yield of MVK together with mesityl oxide of 2%. Igarashi et al.[22] examined the reaction over a ZrO_2–SiO_2 catalyst at an acetone/HCHO molar ratio ranging from 1 to 4 and obtained an 18—13% MVK yield on an acetone basis and 18—54% on a formaldehyde basis at 573 K and W/F=5 g h mol^{-1}. In the present work, over heat-treated hydrotalcite, a 20% MVK yield on an acetone basis and a 62% on a formaldehyde basis were obtained at $W/F=5$ g h mol^{-1}. It therefore follows that the MVK yield on an acetone basis obtained in this study falls in the range of those reported earlier. The most predominant effect of using heat-treated hydrotalcite as a catalyst can be found in a slightly enhanced MVK yield on a formaldehyde basis.

In conclusion, heat-treated hydrotalcite and hydrotalcite-like minerals can catalyze the cross-aldol condensation reaction between formaldehyde and acetone. Among these, heat-treated hydrotalcite gave the highest MVK yield.

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