Vapor phase hydrogen transfer reaction between methacrolein and ethanol over MgO based catalysts

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Magnesium oxide was modified by addition of several metal oxides to prepare effective catalysts for vapor phase hydrogen transfer between methacrolein and ethanol to form methallyl alcohol and acetaldehyde. The catalytic performances vary with the acidic and basic properties of the catalyst. An effective catalyst was prepared by controlling the acidic and basic properties to be moderately weak by addition of SiO_2 and K_2O to magnesium oxide in proper amounts.

Keywords: Hydrogen transfer; methacrolein; methallyl alcohol; MgO; acid and base sites

1. Introduction

Reduction of methacrolein (MAL) to methallyl alcohol (MAA) with molecular hydrogen does not proceed selectively in liquid phase. Besides the C=O bond, the C=C bond in MAL is hydrogenated to a considerable extent, which lowers the selectivity to MAA. For selective reduction of MAL to MAA, the Meerwein–Ponndorf–Verley reduction, which is a hydrogen transfer between carbonyl compounds and alcohols, is well known. Most of Meerwein–Ponndorf–Verley reductions have been studied in liquid phase. Regarding vapor phase reactions, only a few studies have been reported [1–4]. Among them, only one paper has reported the reduction of unsaturated carbonyl compound [1], the other papers have reported on saturated carbonyl compounds [2–4].

Ballard et al. have reported that MgO–ZnO catalyst promoted the hydrogen transfer between acrolein and ethanol to selectively form allyl alcohol [1]. The catalytic activity, however, was not high. In the present study, we report the preparation of highly active and selective catalysts for vapor phase hydrogen transfer between MAL and ethanol (EtOH). We attempted to control the acidic and basic properties of the catalyst by addition of metal oxides to MgO.

2. Experimental

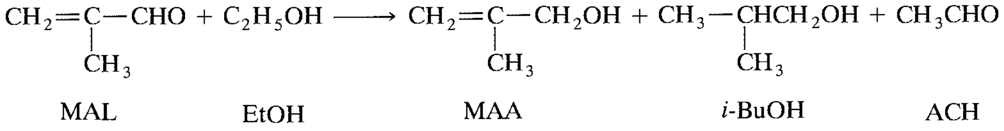
The raw materials used for making catalysts were $Mg(OH)_2$, B_2O_3, TiO_2, ZrO_2, alkali metal hydroxides or nitrates, and SiO_2 (Aerosil OX-50®). A catalyst was prepared as follows. A mixture containing $Mg(OH)_2$ and a metal oxide was suspended in water. The suspension was vigorously stirred and heated at about 90°C to evaporate water until the suspension became a slurry-like mixture. The mixture was evaporated to dryness on a water bath, and then dried at 120°C in air. The dried catalyst was pulverized to 9–16 mesh and calcined at 600°C for 2 h in air.

A flow reactor was employed to carry out the reaction. A catalyst sample of 5 ml was placed in a stainless steel reaction tube of 10 mm inner diameter, and heated at the reaction temperature of 270°C. The reaction gas mixture consisting of MAL, EtOH and N_2 at a mole ratio of 5 : 30 : 65 was passed through the catalyst bed at a space velocity of 1500 h^{-1} (STP). The reaction products were analyzed by gas chromatography. A column packed with Themon-1000 with 10% KOH was operated in the temperature programmed mode from 80 to 180°C at the rate of 5°C/min.

The acid and base strengths of the catalyst were measured by the Hammett indicator method [5]. The amounts of acid sites and base sites of the catalyst were estimated by applying the pulse reaction of tert-butanol dehydration [6] and TPD of acetic acid [7,8], respectively. The surface area was measured by the BET method.

3. Results and discussion

In the vapor phase hydrogen transfer between MAL and EtOH, a high MAA selectivity was observed even for MgO alone. Without additives to MgO, however, the MAL conversion was low. As the reaction temperature was raised, the MAL conversion increased but the MAA selectivity decreased considerably. The decrease in the MAA selectivity was due to the formation of isobutanol (*i*-BuOH) which resulted from hydrogenation of MAA. EtOH acted as hydrogen donor and converted to acetaldehyde (ACH):



$$\underset{\text{MAL}}{CH_2{=}\underset{CH_3}{\underset{|}{C}}{-}CHO} + \underset{\text{EtOH}}{C_2H_5OH} \longrightarrow \underset{\text{MAA}}{CH_2{=}\underset{CH_3}{\underset{|}{C}}{-}CH_2OH} + \underset{i\text{-BuOH}}{CH_3{-}\underset{CH_3}{\underset{|}{C}}HCH_2OH} + \underset{\text{ACH}}{CH_3CHO}$$

The results of catalytic performances of the MgO catalysts containing SiO_2, B_2O_3, TiO_2 or ZrO_2 are summarized in table 1 together with the acidic and basic properties of the catalysts. Since the catalytic performance varied with the composition of the catalyst, the data for optimum composition of each catalyst

Table 1
Effects of addition of acidic oxide to MgO [a]

No.	Catalyst (atomic ratio)	MAL conversion (mol%)	Selectivity (mol%)			MAA OPY [c] (mol%)	SA (m^2/g)	A	B	$[H_0]$
			MAA	i-BuOH	unknown [b]					
1	Mg	56.6	90.5	4.3	5.2	51.2	51.3	1.0	1.0	+4.0–+12.2
2	$Mg_{10}Si_{0.2}$	64.9	90.1	7.4	2.5	58.5	124.1	0.59	0.93	+4.0–+12.2
3	$Mg_{10}B_{0.4}$	65.1	89.0	8.0	3.0	57.9	75.4	0.67	2.69	+4.0– +12.2
4	$Mg_{10}Ti_{0.2}$	60.0	90.2	6.5	3.3	54.1	43.8	1.90	2.88	+4.0– +12.2
5	$Mg_{10}Zr_{0.2}$	65.6	87.5	7.8	4.7	57.4	69.5	1.30	0.79	+4.0–+12.2
	$(Mg_{10}Zr_{0.2})$ [d]	(24.3)	(84.0)	(12.2)	(3.8)	(20.4)				
6	$Mg_{10}Si_{1.0}$	73.3	57.6	20.2	22.2	42.2	150.0	21.0	0.40	+3.3– +15.0

[a] Catalyst 5 ml, reaction gas mixture (vol%) $MAL/EtOH/N_2 = 5/30/65$, $GHSV = 1500\ h^{-1}$, reaction temp. 270°C. A, B; relative ratio in specific surface area of acid and base amount for MgO as a standard ($A = B = 1$).

[b] Unknown compounds are the mixture of unknown carbonyl compounds and polymers.

[c] One pass yield.

[d] Reaction gas mixture (vol%) $MAL/EtOH/N_2 = 5/5/90$.

are presented (catalysts No. 1–5) in table 1. For MgO–SiO_2, the data for the catalyst containing excess amount of SiO_2 (catalysts No. 6, $Mg_{10}Si_{1.0}$) are included. The H_0 values of the catalysts listed in table 1 were in the range from $+4.0$ to $+12.2$ except for the $Mg_{10}Si_{1.0}$ catalyst whose H_0 value ranged from $+3.3$ to $+15.0$.

The MAL conversion increased without decrease in MAA selectivity as SiO_2, B_2O_3, TiO_2 or ZrO_2 were added to MgO in a proper amount. The addition of excess amount of SiO_2 (catalyst No. 6, $Mg_{10}Si_{1.0}$) decreased the MAA selectivity due to the formation of considerable amounts of *i*-BuOH and unknown products. Since both acid and base strengths (H_0 values) of $Mg_{10}Si_{1.0}$ catalyst (catalyst No. 6) are stronger than those of the other catalysts, it is suggested that the ability of a catalyst to hydrogenate the C=C bond in MAA correlates with the acidic and basic properties. It is likely that comparatively weak acid and base sites are important to improve the catalytic activity and selectivity in this reaction.

For all catalysts, the consumption of EtOH was close to the total amounts of MAA and twice *i*-BuOH formed. Although the amount of ACH was not measured, the selectivities to ACH from EtOH were considered to be nearly 100%, because both diethyl ether and ethylene from EtOH were not observed.

For $Mg_{10}Zr_{0.2}$ catalyst, the decrease in EtOH to MAL in the reaction gas mixture (EtOH/MAL = 1/1, No 5 in table 1) resulted in a remarkable decrease in conversion. This suggests that an equilibrium conversion is affected by the partial pressure of EtOH.

For MgO–SiO_2 catalysts with different SiO_2 contents, the conversion and selectivity are plotted against SiO_2 content in fig. 1. The MAL conversion increased markedly with increasing SiO_2 content up to 10%, then slightly up to 50%. The MAA selectivity decreased with SiO_2 content. The decrease in the MAA selectivity is due mainly to the formation of *i*-BuOH. At the SiO_2 content of 50 mol%, the selectivity to *i*-BuOH became as high as 49.4 mol%. The total selectivity of MAA and *i*-BuOH decreased with the SiO_2 content due to the formation of unknown compounds including a small amount of polymers. Therefore, the addition of more than 10 mol% of SiO_2 is not effective for the selective formation of MAA. The addition of excess amount of SiO_2 may enhance the acidic properties, and too strong acid sites may cause the formation of *i*-BuOH and unknown compounds to a considerable extent. Control of acid properties seems important for a high catalytic performance.

In order to control the acidic properties, alkali elements were added to the $Mg_{10}Si_{1.0}$ catalyst. The catalytic results are given in table 2. Addition of any types of alkali elements enhanced the MAA selectivity. The catalytic performance varied with the amount of alkali element added. For MgO–SiO_2–K_2O systems, the catalytic results and the surface properties of the catalysts containing different amounts of K_2O are given in table 3. As the K_2O content increased, the acid amount and strength decreased, whereas the base amount

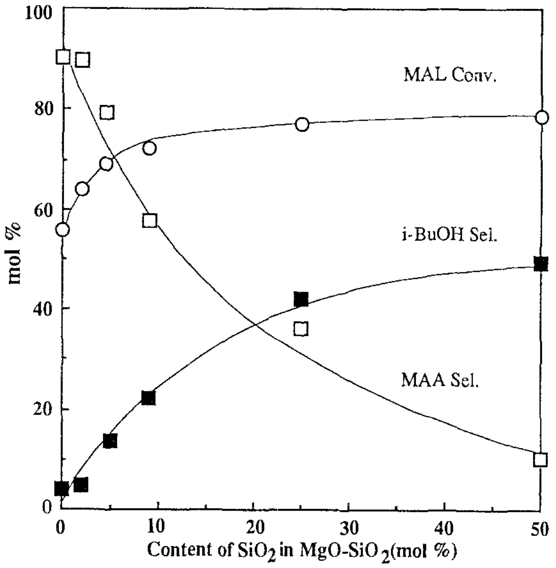


Fig. 1. Effect of SiO_2 content in $MgO-SiO_2$. The reaction conditions are the same as in table 1.

and strength increased slightly. The MAL conversion decreased with the K_2O content. The MAA selectivity rapidly increased and the *i*-BuOH decreased with an increase in the K_2O content up to 0.05 in atomic ratio, and then became nearly constant.

The rate of the MAA formation is plotted against K_2O content (atomic ratio of K, x in $Mg_{10}Si_{1.0}K_x$) in fig. 2 together with the ratios of the amounts of acid and base sites relative to those for MgO. The relative acid amount markedly decreased but the relative base amount did not change much with an increase in K_2O content. The rate of MAA formation showed the maximum at the K content of 0.2 in atomic ratio, where both acid and base amounts were very small.

The results shown in table 3 and fig. 2 suggest that acid and base properties are important factors to determine the catalytic performances in the vapor

Table 2
Addition of alkali metal cation to $MgO-SiO_2$ (10:1) [a]

No.	Alkali metal cation [b]	MAL conversion (mol%)	MAA selectivity (mol%)	MAA OPY (mol%)
1	–	73.3	57.6	42.2
2	Li	71.6	80.3	57.5
3	Na	72.5	85.4	61.9
4	K	69.4	88.6	61.5
5	Rb	71.8	84.5	60.7
6	Cs	64.9	88.8	57.6

[a] The reaction conditions are the same as in table 1.

[b] Mg:Si:alkali = 10:1:0.1 (atomic ratio).

Table 3
Results for $MgO–SiO_2–K_2O$ system catalysts [a]

No.	Atomic ratio			MAL conversion (mol%)	Selectivity (mol%)		SA (m^2/g)	A	B	$[H_0]$ [b]	
	Mg	Si	K		MAA	i-BuOH				+3.3–+15.0	
1	10	1	–	73.3	57.6	20.2	150	21.0	0.4	s	w
2	10	1	0.01	69.1	78.8	13.8	146	9.5	0.4	s	w
3	10	1	0.05	68.5	85.1	5.0	146	3.9	0.6	s	w
4	10	1	0.1	69.4	88.6	4.2	123	1.0	0.8	m	w
5	10	1	0.2	65.0	88.5	4.4	110	0.8	0.9	m	m
6	10	1	0.5	40.4	83.7	4.0	82	0.5	1.0	m	m

[a] The reaction conditions are the same as in table 1. A, B; relative ratio in specific surface area of acid and base amount for MgO as a standard ($A = B = 1$).

[b] Coloring intensity of indicators (acid–base strengths), s: strong; m: medium; w: weak.

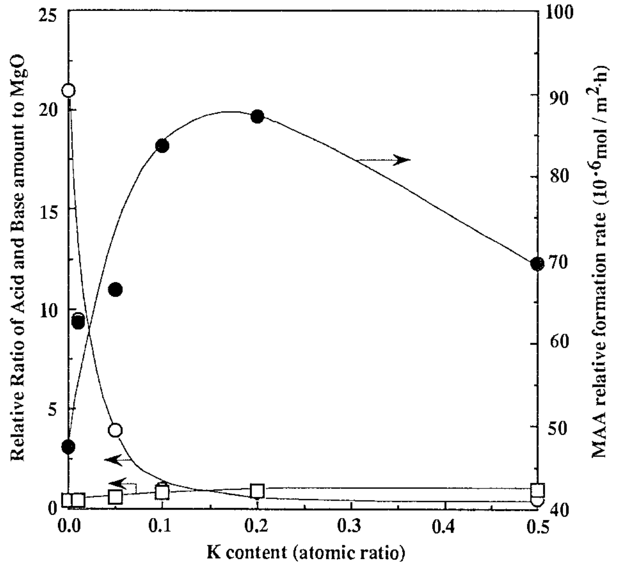


Fig. 2. Correlation between acid–base amounts, catalytic activity and K content in $MgO-SiO_2-K_2O$ (Mg:Si = 10:1, atomic ratio). (○) Relative ratio of acid amount, (□) relative ratio of base amount, (●) MAA relative formation rate.

phase hydrogen transfer between MAL and EtOH. The catalyst with strongly acidic properties gives a high MAL conversion but a low MAA selectivity. To prepare effective catalysts for the reaction, both acid and base properties should be controlled to be moderately weak.

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