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Innovative bifunctional catalytic system for methyl methacrylate synthesis: the peculiar role of gallium

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PURPOSE OF THE ABSTRACT

Methyl methacrylate (MMA) is the monomer for polymethyl methacrylate manufacture. Given its production scale (2.7 ton/y in 2007), different processes have been developed up to commercial level [1]. All processes suffer from two drawbacks: they use dangerous reagents and depend on fossil raw materials. The state of art in MMA production is the Alpha process which employs formaldehyde (FA) for the hydroxy-methylation/dehydration of methyl propionate (MP), the latter produced by ethylene hydroformylation in presence of methanol (MeOH). Even if a commercial process is not yet available, MP may be obtained from bio-based 1,2-propanediol [2] and therefore it remains the most promising starting material for a sustainable MMA manufacture. Finally, FA (known carcinogen) should be avoided in favor of a one-pot approach which consists in its in-situ production by MeOH dehydrogenation. Few autors investigated the heterogeneously catalyzed reaction between MeOH and MP in the gas-phase, but most of them recognized the importance of catalysts possessing both basic and redox properties: the former is required to activate MP to nucleophilic attack on FA by abstraction of an acidic alpha-proton, the latter is needed to enhance the dehydrogenation activity of basic catalysts. For example, Ai [3] investigated a catalyst consisting in Ag, Zr and Cs supported on SiO_2, with atomic ratio between the elements (Ag/Zr/Cs/Si) equal to 4/10/22/1000 and Weda [4] studied a MgO impregnated with 16.7 wt/wt% Mn(II). Since basic catalysts are known to catalyze MeOH dehydration at high temperatures [5], preliminary studies have been conducted with pure MgO at different reaction temperatures, time factor = 0.7 s*g/mL and feed molar ratio MP/MeOH/N_2=0.06/0.12/0.82. Our results showed that in the temperature range 350-450°C the main reaction is the ketonization (Fig.1, step i) of two molecule of MP which produce CO_2, MeOH and 3-pentanone (3-P). Alpha-protons in 3-P are more acidic and in higher number in respect to MP and therefore it reacts faster with FA, producing mono- and di-methyl-pentenones (j,l). At 500°C MgO become much more active for MeOH dehydrogenation (step a) and the higher excess of FA makes ketonization less favorite. Even if the desired reaction (b) become faster, the desired product is never obtained with satisfying yield due to consecutive H-transfer reactions which transform MMA into methyl isobutyrate (MIB,c), methacrolein (MA,d), isobutyraldehyde (IBA,e,f), 2-methylpropanol (2-MP,g) and isobutylene (the latter is formed from 2-MP dehydration, h). The poor catalytic result obtained over MgO (maximum MMA selectivity=3.3%, X=60%, T=450°C) suggest that an effective catalyst should possess a strong dehydrogenating activity at low temperatures in order to produce a large excess of FA to unfavor ketonization; lower reaction temperatures also make H-transfer reactions slower. Starting from this hypothesis we developed some bifunctional catalysts introducing Ga(III) into MgO; on the basis of our results so far, the best one is the Mg/Ga/O mixed oxide with Mg-to-Ga=10. Reagents were also fed to the reactor with molar ratio between MeOH/MP/N_2=0.1/0.01/0.89 to minimize the degree of ketonization. The presence of Ga not only enhances the catalyst dehydrogenating properties at low temperatures leading to higher yields in FA and H_2 but also reduce ketonization to an extent that makes it almost negligible; reaction by-products (MIB, IBA, MA, 2-MP and isobutylene) in this case are those deriving from H-transfer reaction and this way much higher MMA

selectivity and productivity (expressed as Kg/h of MMA divided by Kg of catalyst) were achieved as shown in Table 1. Finally, combining characterization technics and catalytic tests varying reaction temperature, time factor and reagents molar ratio we were able to determine the reaction scheme, minor/major reaction pathways and assess structure-activity relationships.

FIGURES

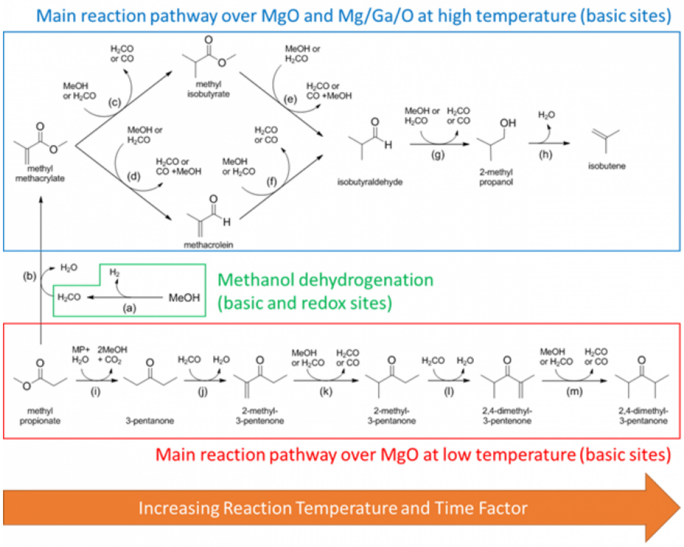
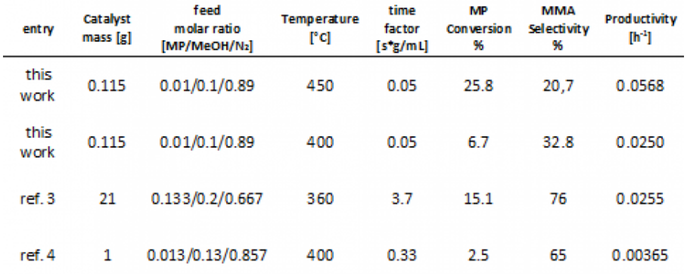


FIGURE 1

Fig. 1

Reaction scheme



entry	Catalyst mass [g]	feed molar ratio [MP/MeOH/N$_2$]	Temperature [°C]	time factor [s*g/mL]	MP Conversion %	MMA Selectivity %	Productivity [h^{-1}]
this work	0.115	0.01/0.1/0.89	450	0.05	25.8	20,7	0.0568
this work	0.115	0.01/0.1/0.89	400	0.05	6.7	32.8	0.0250
ref. 3	21	0.133/0.2/0.667	360	3.7	15.1	76	0.0255
ref. 4	1	0.013/0.13/0.857	400	0.33	2.5	65	0.00365

FIGURE 2

Table 1

comparison between literature and present work

KEYWORDS

methyl methacrylate | methanol | methyl propionate | gallium

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