

Vapour-Phase Reaction of Acetophenone with Methanol or Dimethyl Carbonate on Magnesium Oxide and Magnesium Phosphates

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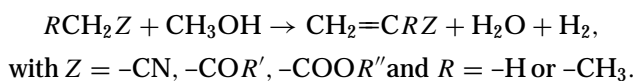
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The vapour-phase reaction of acetophenone with methanol on magnesium oxide, various magnesium phosphates, and combinations of the two types of catalysts was studied. The process was found to involve the Meerwein–Ponndorf–Verley reaction, aldol condensations, dehydrations, and hydrogenations. The presence of basic sites is indispensable for the reaction to develop; however, acid sites also play an active role. The selectivity for each reaction product depends on the particular catalyst used. The total conversion is maximal with the catalysts containing the largest populations of acid and basic sites. Also, catalysts with large numbers of acid sites exhibit an increased selectivity towards the corresponding alkenes. The use of dimethyl carbonate instead of methanol alters the reaction selectivity to an extent dependent on the particular catalyst and operating conditions. However, this also results in markedly decreased total conversion in some instances. © 1999 Academic Press

Key Words: acetophenone; methanol; condensation; MPV reaction; magnesium phosphates; magnesium oxide; zinc oxide.

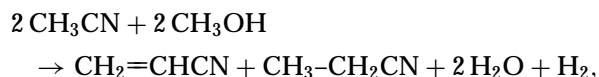
INTRODUCTION

The use of C₁ sources in applied catalysis research has grown enormously in the past few years (1). The fact that methanol can be conveniently obtained from methane or coal has promoted research into the reactions involved [e.g., the methanol to gasoline conversion based on ZSM-5 (2)]. The acid-catalysed coupling of olefins to form ethers is also a major reaction in this context and is used, among others, to synthesize octane-enhancing methyl *tert*-butyl ether (MTBE) from methanol and isobutene (3). Ueda *et al.* (4–8) found methanol to react with activated C–H containing compounds such as nitriles, ketones, and ethers to form α , β -unsaturated compounds. The reaction takes place on catalysts possessing both acid and basic functions and can be formulated as follows,



This process involves dehydrations, dehydrogenations, and cross-coupling reactions.

Active catalysts for this process include MgO doped with 2–15% by weight of a transition metal such as Al, Fe, Cr, Ni, or Cu (4). On these catalysts, acetonitrile reacts with methanol to give acrylonitrile and, by subsequent hydrogenation, propionitrile,



which reacts with methanol to yield methacrylonitrile as a major product and small amounts of isobutyronitrile and crotonitrile (6). Chromium(III)-doped MgO exhibits high activity and selectivity in both reactions.

Acetone reacts with methanol to form methyl vinyl ketone as a major product and methyl ethyl ketone, C₅ ketones, and isopropyl alcohol as minor products (7). MgO doped with Cr(III), Cu(II), or, especially, Fe(III) provides high activity and selectivity.

Propionic ester also reacts with methanol. In addition to methyl methacrylate, the reaction produces methyl 2-methylpropionate and C₅–C₆ ketones. The highest selectivity for the methacrylate, 65%, is provided by Mn(II)-doped MgO.

The reaction of methanol with acetone has also been developed on H-ZSM-5 (9). Based on the results, the reaction yields propene and isobutene as major products, in addition to small amounts of dimethyl ether and various aromatics. Experiments involving Cs-impregnated X zeolites (10) have revealed that most of these products result from aldol condensation of acetone and that small amounts of methyl vinyl ketone are formed in the process.

α , β -Unsaturated compounds are very important for the chemical industry [particularly in the manufacturing of polymers] (11). Thus, vinyl ketones are gaining increasing significance (12) as polymer photosensitizers and electroconducting polymers.

In recent years, various magnesium phosphates have been used as catalysts for organic processes. Thus, Sokolovskii *et al.* (13) have examined the oxidative transformations

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of methane on magnesium–phosphorus catalysts. Based on their results, increasing the catalyst acidity by raising its phosphorus content shifts the direction of the methane transformation from dimerization to selective oxidation. Sugiyama *et al.* (14, 15) used a commercially available magnesium phosphate in the oxidative dehydrogenation of ethane and the oxidative coupling of methane. Our group (16) has studied the influence of the procedure used to synthesize various magnesium phosphates on their structure, composition, and surface properties, as well as its effect on the gas-phase conversion of alcohols.

This paper reports the results obtained in the vapour-phase reaction of acetophenone with methanol or dimethyl carbonate on various magnesium phosphates, magnesium oxide, and combinations of both types of solid. These catalysts possess differential structure, composition, and surface properties that influence the selectivity of the process.

EXPERIMENTAL

Catalyst Synthesis

Catalysts MgP_C (Aldrich, ref. 34, 470-2), MgPP_C (Aldrich, ref. 34, 075-8), MgO_C (Probus, ref. 3225), and ZnO_C (Probus ref. 50286) were commercially available solids of formula $\text{Mg}_3(\text{PO}_4)_2 \cdot x\text{H}_2\text{O}$, $\text{MgHPO}_4 \cdot 3\text{H}_2\text{O}$, $\text{Mg}(\text{OH})_2$, and $\text{Zn}(\text{OH})_2$, respectively. The procedure used to synthesize solid NaMgP has been described elsewhere (16).

Catalyst $\text{MgP}_{(\text{Cl,H,W})}$ was prepared as follows. A solution containing 40 g of $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ and 8.9 ml of 85% H_3PO_4 in 125 ml of distilled water was placed in an ice bath and supplied with 3 N NaOH dropwise up to pH 9 under continuous stirring. The solid thus obtained was filtered, suspended in distilled water (20 ml/g solid), and stirred for 30 min, after which it was allowed to stand for 24 h, filtered, and air-dried.

The procedure used to synthesize catalyst NaMgP-O involved placing 12.3 g of $\text{Mg}(\text{OH})_2$ and 20 g of Na_2HPO_4 in a flask and suspending the mixture in 200 ml of distilled water. Following refluxing for 24 h, the suspended solid was filtered while hot and washed with distilled water and isopropyl alcohol prior to air-drying.

Catalyst NaMgP-P was synthesized by refluxing a mixture of 24.5 g of $\text{MgHPO}_4 \cdot 3\text{H}_2\text{O}$ and 6.27 g of NaOH in 200 ml of distilled water for 5 days. The suspended solid was filtered while hot and air-dried.

All solids were subjected to the following stepwise calcination programme: 1 h at 473 K, 1 h at 573 K, 1 h at 673 K, and 3 h at 773 K. All were sifted through 200–250 mesh.

Catalyst Characterization

The solids were structurally characterized from their X-ray diffraction (XRD) patterns, which were recorded

on a Siemens D 500 diffractometer using $\text{CuK}\alpha$ radiation. Scans were performed over the 2θ range from 2 to 80. The catalysts were also characterized by thermogravimetric analysis (TA) and diffuse reflectance infrared spectroscopy (DRIFT).

The composition of the catalysts was determined by energy dispersive X-ray analysis (EDAX) on a Jeol JSM-5400 instrument equipped with a Link ISI analyser and a Pentafet detector (Oxford), as well as from XPS measurements made on a Leybold–Heraeus LHS-10 spectrometer using a constant pass energy of 50 eV and $\text{MgK}\alpha$ radiation for excitation ($h\nu = 1253.6$ eV).

Chemical and Textural Properties of the Catalysts

The specific surface area of the solids was determined by using the BET method on a Micromeritics ASAP 2000 analyser.

Acid and basic sites were quantified from the retention isotherms for two different titrants (cyclohexylamine and phenol, respectively, dissolved in cyclohexane). The amount of titrant retained by each solid was measured spectrophotometrically (λ_{max} 226 and 271.6 nm for cyclohexylamine and phenol, respectively). By using the Langmuir equation, the amount of titrant adsorbed in monolayer form, X_m , was obtained as a measure of the concentration of acid and basic sites (17).

Reactor

Reactions were carried out in a glass tubular reactor of 6 mm ID that was fed at the top with the reaction mixture by means of a SAGE propulsion pump, the flowrate of which was controlled via a nitrogen flowmeter. The reactor was loaded with 0.175 g of catalyst, over which 5 g of glass beads acting as a vaporizing layer were placed. The temperature was controlled via an externally wrapped heating wire that covered the height of both the catalytic bed and the vaporizer, and was connected to a temperature control. Evolved gases from the reactor were passed through a condenser and onto a collector that allowed fluids to be withdrawn at different times.

No diffusion control mechanism was detected (18), nor were any of the reactor elements found to contribute to the catalytic effect under the reactor's operating conditions (viz. feed rate 1–10 ml h^{-1} , T 575–773 K, N_2 flowrate 30 ml min^{-1} , amount of catalyst 0.1–0.5 g) used in preliminary blank runs.

Collected samples were analysed by gas chromatography using both an SPB-5 60 $\text{m} \times 0.25$ mm ID phenylsilicone capillary column and raising the temperature from 343 to 553 K at 10 K min^{-1} , and a 2 $\text{m} \times 1/8$ in ID column packed with Carbowax over Chromosorb P-10% CW 20 M that was heated linearly from 333 to 423 K at 30 K min^{-1} .

Reaction products were identified by comparison with standards and by gas chromatography–mass spectrometry on a Hewlett–Packard 5971A analyser.

RESULTS AND DISCUSSION

Catalyst Characterization

Based on its XRD patterns, uncalcined solid MgP_C consists of Mg₃(PO₄)₂ · 8H₂O. Its crystallization water can be removed by heating at 442 K. Above 923 K, the solid consists of Mg₃(PO₄)₂ (crystalline farringtonite phase). At the operating temperature, 773 K, this solid consists of amorphous Mg₃(PO₄)₂. Uncalcined MgO_C consists of Mg(OH)₂ that becomes periclase MgO at 773 K. Similarly, solid ZnO_C is Zn(OH)₂ and becomes zincite ZnO upon calcination at 773 K. On the other hand, uncalcined MgPP_C is MgHPO₄ · 3H₂O, loses its crystallization water at ca. 440 K, and becomes α-Mg₂P₂O₇ at 773 K. Its structure and thermal behaviour were examined elsewhere (19).

Solid NaMgP, which was studied in previous work (16, 20), consists largely of NaMgPO₄, accompanied by residual amounts of MgO, NaCl, and Na₂CO₃. Based on its XRD patterns, solid NaMgP–P calcined at 773 K consists of NaMgPO₄ and Mg₂P₂O₇ but is poorly crystalline. Finally, solid NaMgP–O calcined at 773 K consists of NaMgPO₄ and MgO.

Table 1 shows the percentage atomic composition of each catalyst.

Textural and Surface Acid–Base Properties of the Catalysts

Table 2 summarizes the textural and acid–base properties of the catalysts studied. It also shows the above-described crystal phases as identified from the XRD patterns.

As can be seen, the specific surface area varies markedly among the solids. Thus, the areas of the catalysts containing MgO as main phase are much higher than those of the solids consisting largely of a magnesium phosphate. The latter also exhibit some differences among individual solids. Thus, catalysts MgP_(Cl,H,w) and NaMgP–P have areas three times

TABLE 1

Percentage Atomic Composition of the Catalysts as Determined by EDAX and XPS

Catalyst	Mg	P	O	Na	Cl
MgP _C	22.3	13.6	64.1	—	—
MgPP _C	16.4	14.2	69.3	—	—
MgP _(Cl,H,w)	22.6	11.2	65.1	1.0	0.1
NaMgP	14.1	7.4	58.1	8.6	2.3
NaMgP–P	15.0	9.3	63.5	9.3	—
MgO _C	33.2	—	66.8	—	—
NaMgP–O	20.6	6.6	63.5	9.3	—

TABLE 2

Chemical Textural Properties and Crystal Phases Present in the Catalysts Studied

Catalyst	S _{BET} (m ² g ⁻¹)	Acidity (μmol g ⁻¹) ^a	Basicity (μmol g ⁻¹) ^b	Phases
MgP _C	7	24	6	Mg ₃ (PO ₄) ₂ ^c
MgPP _C	11	51	9	α-Mg ₂ P ₂ O ₇
MgP _(Cl,H,w)	31	83	44	Mg ₃ (PO ₄) ₂ ^c
NaMgP	8	12	5	NaMgPO ₄
NaMgP–P	30	52	25	NaMgPO ₄ , Mg ₂ P ₂ O ₇
MgO _C	241	123	254	MgO
NaMgP–O	108	88	77	MgO, NaMgPO ₄
ZnO _C	2	—	4	ZnO

^a Vs cyclohexylamine.

^b Vs phenol.

^c Crystalline only above 923 K.

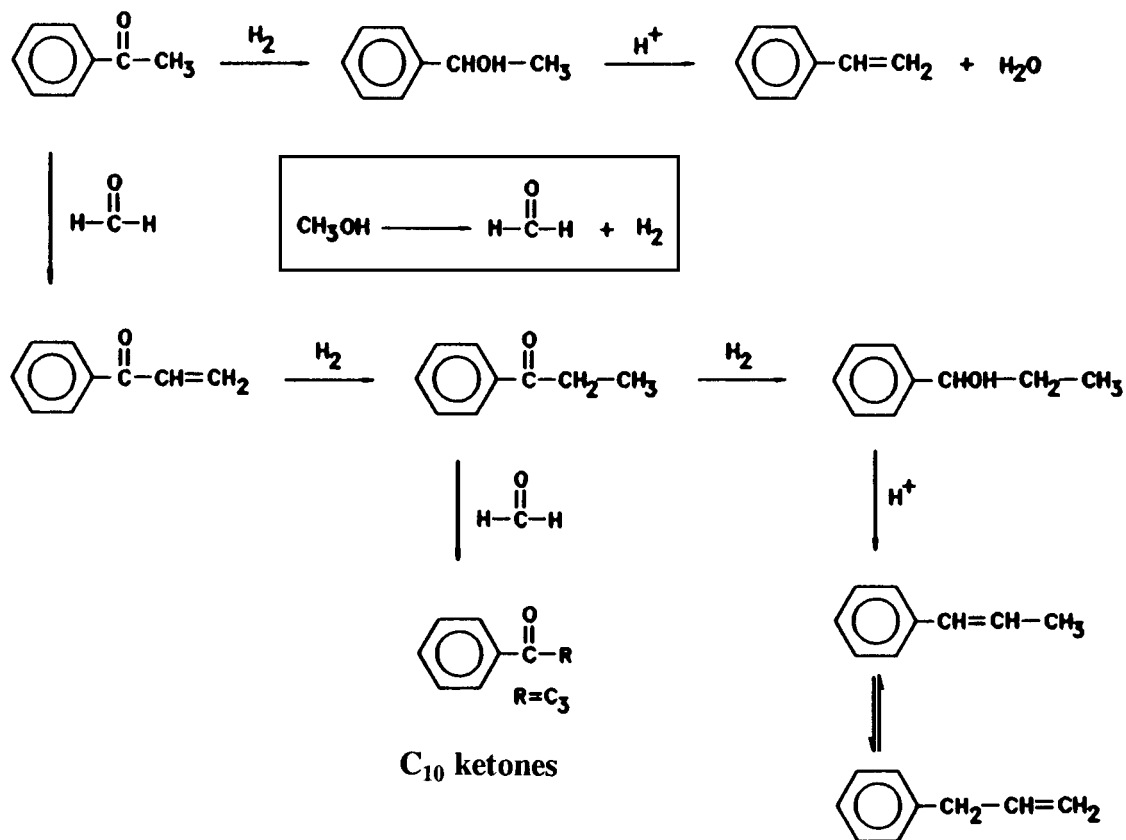
as large as those of MgP_C, MgPP_C, and NaMgP. Solid ZnO_C is the one with the smallest surface area.

The catalysts also differ markedly in acidity and basicity. The two oxides, MgO_C and ZnO_C, are essentially basic but possess a markedly different number of sites. MgO_C is another solid containing a fairly large population of acid sites. Magnesium oxide is considered a strongly basic compound by virtue of the presence of O²⁻ surface sites that can act as proton acceptors; however, Mg²⁺ ions are considered to be weak Lewis acids (21). Catalyst NaMgP–O contains a similar number of acid and basic sites. The other solids possess more acid sites than basic sites (particularly MgPP_C, which is essentially acidic).

Catalytic Activity

Reaction between acetophenone and methanol. This reaction can yield a wide variety of products depending on the particular catalyst used. As a rule, the formation of the main reaction products can be accounted for on the basis of Scheme 1. A series of dehydrogenation, hydrogen-transfer, dehydration, isomerization, and condensation reactions result in a wide range of products, the identification and analysis of which entail the use of gas chromatography in combination with mass spectrometry.

The main products of the reaction include styrene, 1-phenylethanol, phenyl vinyl ketone, and propiophenone. Alkene homologues include C₉ olefins such as 1- and 2-propenylbenzene, and C₁₀ olefins such as 1-methyl-1-propenylbenzene and 2-methyl-1-methylpropenylbenzene, the former product being obtained in a lower proportion. These compounds are grouped together because they can occur in various isomeric forms in addition to those described above. Similarly, C₁₀ ketones are also dealt with as a whole since they occur in various structures of molecular weight 146 and 148.



SCHEME 1. Selected products formed in the reaction between acetophenone and methanol.

Table 3 gives the results obtained in the reaction between acetophenone and methanol on the different catalysts tested, at 773 K, under the conditions stated under Experimental. X_T denotes the percentage overall conversion to acetophenone derivatives and S_i the selectivity towards compound i ($100 \times$ conversion to i/X_T), which includes styrene (styr.), C₉ and C₁₀ olefins (alkenes), 1-phenylethanol (1-ph.e.), phenyl vinyl ketone (ph.v.ket.), propiophenone (propioph.), and C₁₀ ketones (C₁₀ ket.).

TABLE 3

Total Conversion and Selectivity in the Reaction between Acetophenone and Methanol on the Catalysts Studied

Catalyst	X_T	$S_{\text{styr.}}$	S_{alkenes}	$S_{1\text{-ph.e.}}$	$S_{\text{ph.v.ket.}}$	$S_{\text{propioph.}}$	$S_{\text{C}_{10}\text{ ket.}}$
MgP _C	24.3	32.1	7.9	—	28.2	21.0	6.8
MgP _(Cl,H,w)	61.5	18.1	25.6	—	12.6	21.9	19.8
NaMgP	27.7	—	—	34.3	24.0	22.9	5.6
NaMgP-P	32.4	13.3	12.6	9.3	25.3	30.1	7.4
MgO _C	78.2	8.8	14.6	5.5	7.8	22.7	17.1
NaMgP-O	61.7	5.5	4.5	—	20.4	37.6	25.1
ZnO _C	10.7	4.9	4.9	—	63.1	22.0	5.0

Note. Reaction conditions: N₂ flowrate 30 ml min⁻¹, amount of catalyst 0.175 g, acetophenone/methanol molar ratio 1 : 5, feed rate 3.88 ml h⁻¹, T_{reac} 773 K. Data obtained at $t_{\text{reac}} = 80$ min.

As can be seen, all the catalysts except MgPP_C (with $X_T < 2\%$) exhibit acceptable selectivity in the reaction between acetophenone and methanol. This suggests that the reaction requires the presence of basic sites to develop—in fact, solid MgPP_C possesses a large population of acid sites and a very small one of basic sites. Its typically acidic nature was demonstrated elsewhere (19). Also prominent among the catalysts is solid NaMgP, which contains few acid and basic sites. Although its acid sites are in greater numbers, the solid has been found to be predominantly basic, as it only yields the dehydrogenation product in the transformation of cyclohexanol (16). Consistent with this behaviour, the solid exhibits a high selectivity for 1-phenylethanol, which results from a Meerwein-Ponndorf-Verley (MPV) reaction between acetophenone and methanol. The absence of dehydrating activity prevents the subsequent formation of alkenes. Also, the presence of basic sites facilitates the formation of the condensation products (mainly phenyl vinyl ketone and propiophenone). Figure 1 shows the variation of the total conversion and the selectivity towards each product during the reaction. As can be seen, the total conversion decreases slightly as the reaction develops; in contrast, the selectivity for each product remains virtually constant throughout.

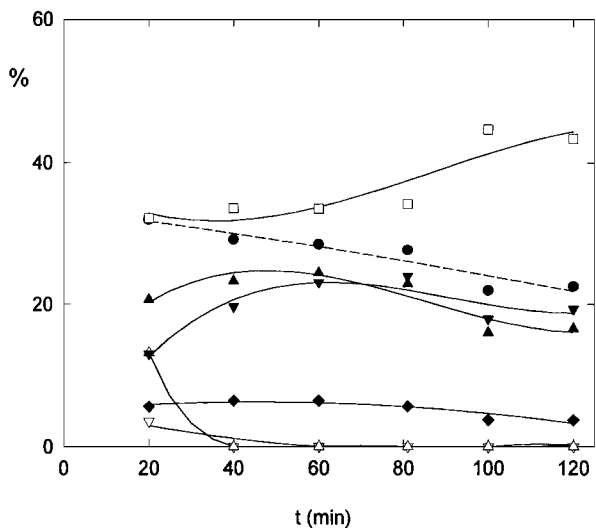


FIG. 1. Total conversion (●) and selectivity towards styrene (▽), C₉-C₁₀ alkenes (△), 1-phenylethanol (□), phenyl vinyl ketone (▼), propiophenone (▲), and C₁₀ ketones (◆) in the reaction between acetophenone and methanol on catalyst NaMgP at 773 K.

Catalyst MgP_C exhibits a differential behaviour. Although it possesses acid and basic sites, it is predominantly acidic. Accordingly, it is the solid exhibiting the highest selectivity for styrene, which is accompanied by phenyl vinyl ketone and propiophenone, in addition to smaller amounts of other alkenes and C₁₀ ketones. The magnesium orthophosphate MgP_(Cl,H,w) possesses higher specific surface area, acidity, and basicity than its commercially available counterpart. It exhibits a high conversion and yields a wide range of products. Figure 2 shows the total conversion

and selectivity towards different products achieved with this catalyst.

Using the same reactor feed rate but an acetophenone/methanol molar ratio of 1 under the operating conditions of Table 3, we obtained the following results: $X_T = 26.5$, $S_{\text{styr.}} = 28.5$, $S_{\text{alkenes}} = 11.7$, $S_{\text{ph.v.ket.}} = 21.9$, $S_{\text{propioph.}} = 25.0$, and $S_{\text{C}_{10}\text{ ket.}} = 7.6$. As expected, the total conversion to acetophenone was lower than in the previous experiments. Also worth noting is the decreased selectivity for C₉-C₁₀ alkenes and C₁₀ ketones, as well as the increased selectivity towards styrene and phenyl vinyl ketone (the first two products obtained according to Scheme 1).

Unlike MgPP_C, catalyst NaMgP-P, which contains Mg₂P₂O₇ and NaMgPO₄ phases, is also active in this reaction. Obviously, the presence of basic sites, provided by the NaMgPO₄ phase, is indispensable for the solid to have catalytic activity. This solid is especially selective towards propiophenone and phenyl vinyl ketone. Its total conversion, however, is similar to those of MgP_C and NaMgP.

Catalyst MgO_C exhibits outstanding activity in this reaction. Figure 3 shows the total conversion and the selectivity towards the different reaction products obtained with it. As can be seen, the solid preserves its activity throughout the reaction. Worth a special note is its low selectivity for phenyl vinyl ketone, a result of its ability to promote further reactions. Although this is an essentially basic solid, the presence of acid sites endows it with dehydrating activity that leads to the production of alkenes (mainly C₉ and C₁₀ olefins). In addition, the catalyst gives a number of condensation products of high molecular weights that are all obtained in low proportions but, as a whole, decrease the selectivity towards the previous ones.

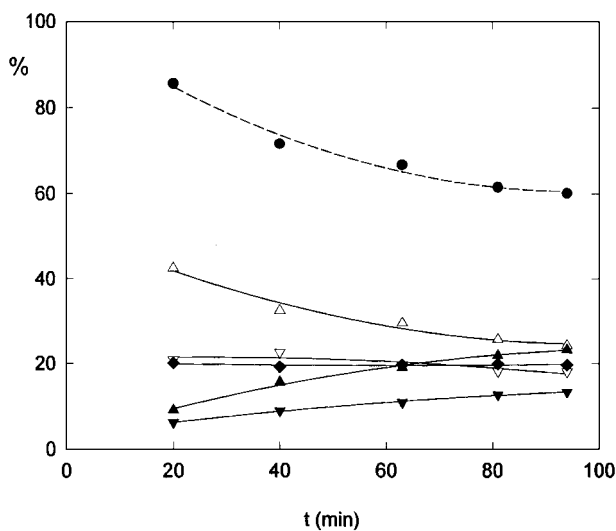


FIG. 2. Total conversion (●) and selectivity towards styrene (▽), C₉-C₁₀ alkenes (△), phenyl vinyl ketone (▼), propiophenone (▲), and C₁₀ ketones (◆) in the reaction between acetophenone and methanol on catalyst MgP_(Cl,H,w) at 773 K.

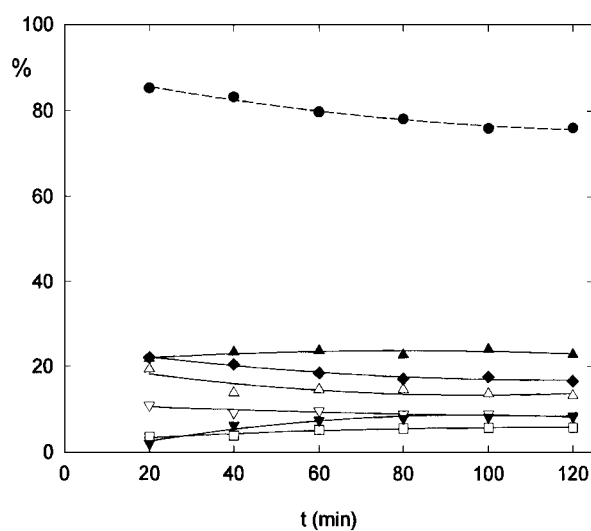
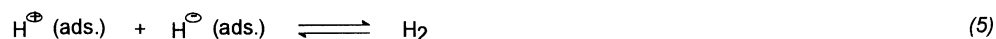
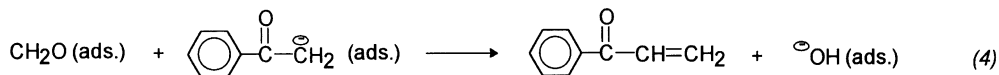
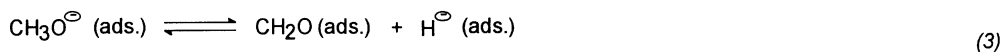
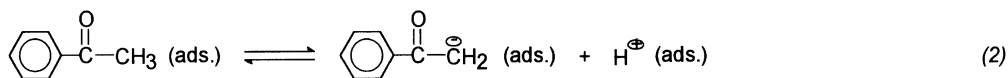


FIG. 3. Total conversion (●) and selectivity towards styrene (▽), C₉-C₁₀ alkenes (△), 1-phenylethanol (□), phenyl vinyl ketone (▼), propiophenone (▲), and C₁₀ ketones (◆) in the reaction between acetophenone and methanol on catalyst MgO_C at 773 K.



SCHEME 2. Mechanism for the reaction between acetophenone and methanol.

Solid NaMgP-O is also highly active (see Table 3). In addition, it exhibits a low selectivity towards alkenes and an acceptable one for C₉ and C₁₀ ketones. It produces virtually no other product, which suggests that its basic sites are weaker than those of MgO_C.

Table 3 also shows the results provided by catalyst ZnO_C. It exhibits a high selectivity for phenyl vinyl ketone but also a low total conversion; accordingly, its main reaction products must be those obtained in the early reaction steps (see Scheme 1). The reaction also produces alkenes as the likely result of the presence of Lewis acid sites. Although this catalyst is considerably less active than MgO_C in this reaction, it clearly surpasses it in the dehydrogenation of alcohols (22); consequently, the reaction between acetophenone and methanol requires the presence of other types of active sites.

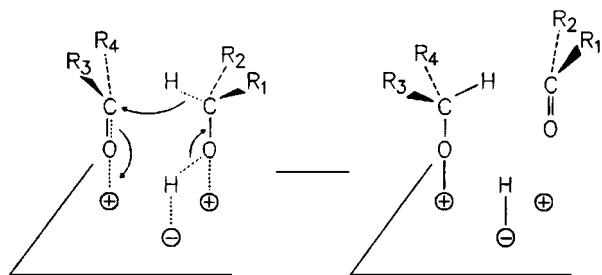
Some of the above-mentioned products can only result from dehydration, dehydrogenation, or cross-coupling reactions. Both acid and basic sites are likely to take part in the process. Basic sites must play a prominent role since the reaction rate is highly correlated to the acidity of the reactants. Thus, Ueda *et al.* (8) determined the reaction rate for reactants of variable p*K_a* for their α proton. The p*K_a* is associated to the dissociation of the H atom that is abstracted in the cross-coupling reaction. As a result, the more readily the H atom can dissociate as H⁺, the higher the reaction rate is. The p*K_a* for the α proton in acetophenone is 19. At a later stage, Ueda *et al.* (23, 24) studied in greater depth the conversion and selectivity of MgO doped with transition metal ions, the influence of their surface basic properties on the reaction, and, especially, the mechanism for the process, which they investigated by using deuterium-labelled methanol-d₁(CH₃OD), methanol-d₄(CD₃OD), and acetonitrile-d₃(CD₃CN).

In the base-catalysed reaction of methanol, the C-H bond in the methyl or methylene group of the other reactant must be activated by an electron-withdrawing group such as carbonyl, cyano, or phenyl. The intermediate carbanion formed after the uptake of the acid hydrogen by a sur-

face basic site reacts with adsorbed methanol to yield the product. Consequently, the activated state of methanol on the oxide must play a central role in the process. By analogy with the aldol condensation and the reported mechanism for the alkylation of toluene on basic solids to form styrene and ethylbenzene (25-27), the reaction probably takes place via a formaldehyde intermediate resulting from the dehydrogenation of methanol, followed by condensation with the carbanion. The mechanism on our catalysts must be similar to that put forward by Ueda and co-workers (23, 24) for the reaction between acetonitrile and methanol. Scheme 2 shows the mechanism for that between acetophenone and methanol. Steps 1 and 2 are in equilibrium. Both involve the dissociation of a proton that is adsorbed at a basic site on the catalyst surface. The methoxide anion or the carbanion formed from acetophenone must be adsorbed on a surface Lewis acid site. Step 3 must be the rate-determining one. This, however, depends strongly on the particular catalyst, substrate, and operating conditions. Thus, if the reactant p*K_a* is very high (e.g., that for toluene is 37), then the second step is the rate-determining one. Step 4 involves the aldol condensation between the acetophenone carbanion and adsorbed acetaldehyde.

Similar steps are also possible. Thus, any ketone possessing strong enough acid α protons could be dissociatively adsorbed on the catalyst and give successive condensation reactions that would yield, for example, C₁₀ ketones as shown in Scheme 1.

Based on the previous results, the dehydrogenation of methanol on the catalyst surface under the operating conditions used in this work must proceed via an MPV reaction between acetophenone and methanol. As a rule, the MPV reaction is concerted and takes place at a lower temperature than the dehydrogenation of the alcohol, which acts as a donor; this suggests that adsorbed ketone in the vicinity of the alcohol favours its dehydrogenation and lowers the temperature at which the hydrogen is lost from it. Based on the mechanism of Kibby and Hall (28), the alcohol and the ketone are both adsorbed at acid sites but require the



SCHEME 3. Mechanism for the Meerwein–Ponndorf–Verley reaction between acetophenone and methanol.

presence of a basic site in their vicinity. The transfer must take place as depicted in Scheme 3.

The adjacent basic site favours ionization of the adsorbed alcohol and facilitates the transfer of a hydride ion to the ketone. In binding to a basic site, the proton weakens the O–H bond and facilitates the formation of the C=O bond and the transfer of the hydride ion. In the last step of the process, the proton adsorbed at the basic site attacks the alkoxide formed from the ketone.

The MPV reaction takes place preferentially on basic catalysts and the activity of MgO–SiO₂ in it has been unequivocally correlated to its basicity (29–31). The production of 1-phenylethanol in our case can be ascribed to this type of reaction. Similarly, the production of styrene and other alkenes of lower molecular weight can be attributed to the dehydration subsequently undergone by the alcohols at the surface acid sites. Thus, a catalyst such as NaMgP, which has no dehydrating ability, is highly selective towards 1-phenylethanol. On the other hand, more acidic catalysts such as MgP_C and MgP_(Cl,H,w) exhibit a high selectivity for alkenes.

The overall reaction scheme also includes hydrogenation reactions that yield products such as propiophenone.

Recently, Huang *et al.* (32) carried out the vapour-phase reaction (623 K) between methanol and acetone on A, X, and Y zeolites exchanged with alkali metals. They identified three types of reaction, namely: (a) the methylation of acetone followed by dehydrogenation to methyl vinyl ketone; (b) the MPV reaction between acetone and methanol, coupled to additional dehydration to propene and formaldehyde; and (c) the condensation of acetone followed by decomposition to isobutene. The latter two types of reaction predominate on LiX and NaX zeolites, which exhibit a relatively strong Lewis acidity. When the Lewis basicity is increased and the Lewis acidity decreased by exchange with K, Rb, and Cs, both reactions develop to a dramatically decreased extent and the selectivity to methyl vinyl ketone rises markedly as a result. The aldol condensation of acetone at 453 K on zeolites exchanged with alkali metals was previously studied (33, 34) and found to be related to Lewis acidity (cations) and basicity (lattice oxygens), the NaX zeolite being the most active in the process. Although, con-

sistent with previous results, as the reaction between acetone and methanol takes place at a higher temperature, it causes the dehydration of the diacetonol and its eventual decomposition to isobutene. This reaction is effectively hindered by a low partial pressure of acetone, an increased basic strength, and a decreased acid strength. The methylation of acetone is also believed to be dependent on Lewis acidity and basicity. The increased basicity and decreased acidity of X zeolites exchanged with alkali ions result in the second and third reaction developing to a dramatically decreased extent and in a consequent increase in selectivity towards methyl vinyl ketone. However, the methylation of methyl vinyl ketone under the operating conditions used in this work prevents its dehydrogenation and leads to the formation of C₅ ketones (mainly 3-pentanone).

Reaction between acetophenone and dimethyl carbonate. Dimethyl carbonate has proven to be an efficient methylating agent in, for instance, the selective *N*-monomethylation of aniline (35, 36). Thus, the reaction between aniline and dimethyl carbonate yields *N*-methylaniline in addition to methanol and carbon dioxide. Accordingly, in the reaction with acetophenone, dimethyl carbonate could be directly involved, leading to methylation of carbanions. In addition, we should expect reactions similar to those described above resulting from the presence of methanol produced in the reaction.

Table 4 shows the results obtained in the reaction between acetophenone and dimethyl carbonate on some of the catalysts studied. Although the total conversion and the selectivity for each product depend on the particular catalyst, the use of dimethyl carbonate instead of methanol as alkylating reagent can be assumed to decrease the selectivity towards all alkenes. For catalyst MgP_C, the total conversion is slightly lower with dimethyl carbonate; also, the selectivity towards propiophenone is very high (71.4%). Catalyst MgP_(Cl,H,w) exhibits very similar selectivity with methanol and dimethyl carbonate. The latter results in increased selectivity towards C₉ and C₁₀ ketones.

Also worth special note among the data of Table 4 is the low conversion obtained with catalyst MgO_C relative to the use of methanol as alkylating agent (Table 3). Figure 4

TABLE 4

Total Conversion and Selectivity in the Reaction between Acetophenone and Dimethyl Carbonate (DMC) on Selected Catalysts

Catalyst	X _T	S _{styr.}	S _{alkenes}	S _{ph.v.ket}	S _{propioph.}	S _{C10.ket}
MgP _C	17.0	3.0	1.1	8.8	71.4	7.2
MgP _(Cl,H,w)	61.0	8.8	17.6	14.0	28.0	26.1
MgO _C	29.6	5.0	11.2	36.3	33.7	8.6

Note. Reaction conditions: N₂ flowrate 30 ml min⁻¹, amount of catalyst 0.175 g, acetophenone/DMC molar ratio 1 : 2.5, feed rate 3.88 ml h⁻¹, T_{reac} 773 K. Data obtained at t_{reac} = 80 min.

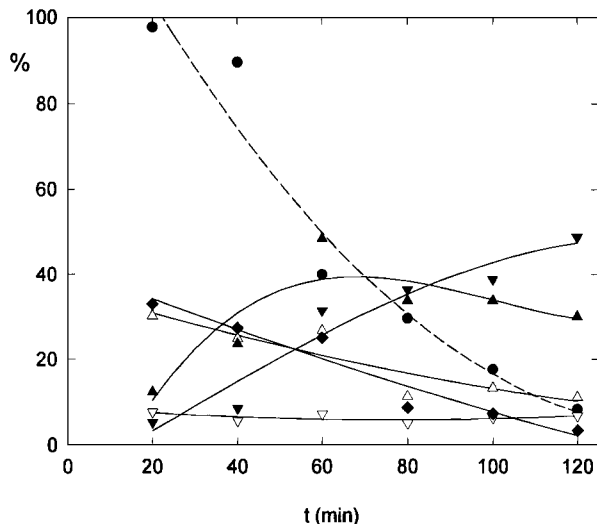


FIG. 4. Total conversion (●) and selectivity towards styrene (▽), C₉-C₁₀ alkenes (△), phenyl vinyl ketone (▼), propiophenone (▲), and C₁₀ ketones (◆) in the reaction between acetophenone and dimethyl carbonate on catalyst MgO_C at 773 K.

shows the total conversion and selectivity for the different products obtained with this catalyst and dimethyl carbonate instead of methanol. As can be seen, the catalyst exhibits a high initial conversion but gradually loses activity. This reveals that the presence of basic sites on the surface of these catalysts is essential for the reaction to develop since, unlike methanol, dimethyl carbonate releases CO₂, which is known to be adsorbed at surface basic sites. In addition, there is decreased selectivity for C₉ and C₁₀ alkenes, and C₁₀ ketones, the formation of which calls for the relative strong basic sites required by typical condensation reactions. Relative to methanol, dimethyl carbonate also decreases the selectivity towards all the alkenes.

Table 5 shows the results obtained in the reaction between acetophenone and methanol or dimethyl carbonate on catalyst MgO_C at 623 K. The conversion is time-independent in both cases and higher with methanol than with dimethyl carbonate. The selectivity towards propiophenone and, especially, phenyl vinyl ketone is very high.

TABLE 5

Total Conversion and Selectivity towards Different Products in the Reaction between Acetophenone (ACP) and Methanol (MeOH) or Dimethyl Carbonate (DMC) on Catalyst MgO_C at 623 K

Reactants	Molar ratio	X _T	S _{styr.}	S _{alkenes}	S _{ph.v.ket.}	S _{propioph.}	S _{C₁₀ ket.}
ACP:MeOH	1:5	15.3	3.0	—	51.8	23.1	3.0
ACP:DMC	1:2.5	9.7	8.3	14.0	30.1	42.9	4.7

Note. Reaction conditions: N₂ flowrate 30 ml min⁻¹, amount of catalyst 0.175 g, feed rate 3.88 ml h⁻¹. Data obtained at t_{reac} = 80 min.

TABLE 6

Total Conversion and Selectivity towards Different Products in the Reaction between Acetophenone and Dimethyl Carbonate (1:2.5) on Catalyst MgP_(Cl,H,w) at Two Different Temperatures

T(K)	X _T	S _{styr.}	S _{alkenes}	S _{ph.v.ket.}	S _{propioph.}	S _{C₁₀ ket.}
623	15.4	7.8	12.6	11.5	57.1	10.8
698	53.3	12.5	10.3	10.3	38.1	21.9

Note. Reaction conditions: N₂ flowrate 30 ml min⁻¹, amount of catalyst 0.175 g, feed rate 3.88 ml h⁻¹. Data obtained at t_{reac} = 80 min.

In addition to the products shown in Table 5, the reaction yields 1-phenylethanol and 1-phenyl-2-propen-1-ol, with selectivities of 10.4 and 8.3%, respectively. Unlike at 773 K, the use of dimethyl carbonate instead of methanol boosts the selectivity for the alkenes. In any case, the selectivity towards phenyl vinyl ketone and propiophenone is very high.

The effect of temperature on the reaction between acetophenone and dimethyl carbonate was studied by using catalyst MgP_(Cl,H,w). Table 6 gives the conversion and selectivity results obtained at 623 and 698 K (see Table 4 for the data at 773 K). Increasing temperatures increase the total conversion; however, the change is especially marked between 623 and 698 K. As regards selectivity, that for propiophenone decreases, whereas those for C₁₀ ketones and C₉-C₁₀ alkenes increase as the temperature is raised.

CONCLUSIONS

The vapour-phase reaction of acetophenone and methanol on various magnesium phosphates [MgP_C, MgP_(Cl,H,w), NaMgP, and NaMgP-P], magnesium oxide [MgO_C], zinc oxide [ZnO_C], and a magnesium oxide-sodium magnesium orthophosphate mixed system [NaMgP-O] was studied and found to yield a wide range of products that are formed via a series of MPV reactions, aldol condensations, dehydrations, and hydrogenations. The result is a series of products including 1-phenylethanol, styrene, phenyl vinyl ketone, propiophenone, C₉-C₁₀ alkenes, and C₁₀ ketones primarily. This reaction requires the presence of acid and basic sites in the catalyst. As a result, magnesium pyrophosphate [MgPP_C] is inactive in the process. Also, the catalysts that exhibit the highest conversions [MgP_(Cl,H,w), MgO_C, and NaMgP-O] are those possessing the largest acid and basic site populations. MgP_(Cl,H,w), where acid sites predominate, exhibits the highest selectivity for alkenes. NaMgP, which consists chiefly of sodium magnesium orthophosphate, gives no alkenes and yields 1-phenylethanol as the main product. ZnO_C is the least active of the catalysts studied. The use of dimethyl carbonate instead of methanol as alkylating agent introduces significant changes in selectivity. Thus, it markedly increases the selectivity of solid MgP_C for propiophenone. In contrast, it decreases

the selectivity towards all alkenes, to an extent dependent on the particular reaction conditions. However, the use of dimethyl carbonate with catalyst MgO_C leads to its rapid deactivation by CO_2 released during the reaction.

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