Reactions of Acetophenone with Alcohols over Oxide Catalysts: Alkylation of Ketones by Alcohols

K. GANESAN AND C. N. PILLAI[1]

Department of Chemistry, Indian Institute of Technology, Madras-600 036, India

As part of a study of hydrogen transfer reactions over alumina, the reactions of acetophenone with methanol over η-alumina at 300–500°C were studied. In addition to styrene arising from reductive dehydration, products arising from methylation (propiophenone, β-methylstyrene) were also observed. At higher conversion, secondary reactions like dealkylation of higher ketones and alkylation, dealkylation, and hydrogenation of olefins were also observed. Reactions have also been carried out with modified alumina (fluorided and Na$^+$-doped) catalysts, HY-zeolite, phosphotungstic acid, and silicotungstic acid to study the effect of acidity on the selectivity for these reactions. Reactions of methanol with aralkyl ketones and with olefins were also studied. Acetophenone conversion was found to increase with increasing catalyst basicity while the selectivity for reductive dehydration decreased. Conclusions have also been drawn, on the basis of these studies, regarding the nature of the active catalytic sites responsible for the different reactions and mechanisms have been proposed for the surface reactions. © 1989 Academic Press, Inc.
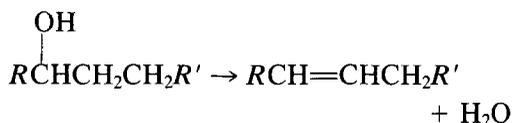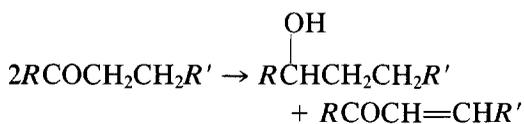
INTRODUCTION

Reactions of ketones over oxide catalysts lead to a variety of products due to aldol condensation, intramolecular dehydration, and intermolecular disproportionation. Most of the systematic studies have been with acetone and its simple homologs (butanone and pentanone). Reactions of acetone over oxide catalysts have been studied by IR spectroscopy (*1*), Raman spectroscopy (*2*), pulse microreactor gas chromatography (*3*), and ^{13}C NMR spectroscopy (*4*). The sequence of reactions of acetone over alumina was shown to be acetone → diacetone alcohol → mesityl oxide → phorone → isophorone (*3, 4*). The last step in this sequence is the irreversible formation of isophorone which appears to be the net driving force for this condensation reaction (*3*). Mesitylene was also detected in these studies. On the basis of studies with butanone, it was suggested that basic sites are responsible for aldol condensation (*5*). The alumina-catalyzed products in the aldol

condensation reactions of butanone were not the α,β-unsaturated ketones expected from the solution studies but β,γ-unsaturated ketone arising from the dehydration of the enolic aldol product (*5*). By comparing aluminas prepared by different methods, Zhang and co-workers concluded that aldol condensation requires an optimum arrangement of acidic and basic sites on the catalyst surface (*6*). Basic alumina has been successfully employed for the laboratory preparation of α,β-unsaturated ketones by the aldol condensation of higher ketones in the liquid phase (*7, 8*). Condensation of acetophenone to dypnone with high selectivity has been achieved in the liquid phase on zeolite catalysts (*9*). Other catalysts employed for aldol condensation are silica with alkaline additives (*10, 11*), lithium phosphate (*12*), thoria (*13*), rutile (*1, 2*), etc. While liquid-phase aldol condensation of aralkyl ketones like acetophenone is known (*7–9*), gas-phase condensation of acetophenone has not been reported.

In the gas phase ketones consisting of α- and β-hydrogen have been reported to undergo ready disproportionation (*14–16*):

[1] To whom correspondence should be addressed.

371

$$2RCOCH_2CH_2R' \rightarrow R\overset{OH}{\underset{|}{C}}HCH_2CH_2R'$$
$$+ RCOCH{=}CHR'$$

$$R\overset{OH}{\underset{|}{C}}HCH_2CH_2R' \rightarrow RCH{=}CHCH_2R'$$
$$+ H_2O$$

Intramolecular dehydration of ketones to allenes, acetylenes, or dienes has also been reported (17–19). Thus, by temperature-programmed desorption of aliphatic ketones from ZSM-5-type zeolites at temperatures up to 450°C, it was shown that in addition to aldol condensation, intramolecular dehydration ($C_nH_{2n}O \rightarrow C_nH_{2n-2} + H_2O$) also took place (18). In another study over ZSM catalysts at 300–350°C, aliphatic ketones gave mainly hydrocarbons including aromatics (19). Isobutene was the major hydrocarbon from acetone. Dehydration of dibenzyl ketone was observed over alumina at 400°C to yield diphenylallene which further cyclized to phenylindene (20, 21).

These reactions are appreciably altered when mixtures of carbonyl compounds and alcohols are made to react over alumina and other oxide catalysts. Transfer hydrogenation of the ketone by the alcohol followed by the dehdyration of the secondary alcohol becomes the major reaction (22, 23). It has been established by stereochemical and substituent effect correlation studies that the reaction involves direct hydride transfer from the alcohol to the carbonyl compound (23, 24). Other catalysts like MgO, CaO, SrO, BaO, SiO$_2$, and hydroxyapatite have also been used for the vapor-phase reduction of carbonyl compounds with alcohols (25–27). Liquid-phase reduction of aldehyde carbonyl α to a benzene ring was achieved by adsorption on an alumina column in benzene followed by elution with methanol (28). Dehydrated alumina has been shown to be a good catalyst for liquid-phase selective reduction of the aldehyde function in presence of the ketone group (29). The reactions of ethanol and 2-propanol with acetophenone over oxide

catalysts like silica and alumina have been known to give reductive dehydration and have been used for the preparation of styrene (17, 30). Alumina has been used as a versatile catalyst for the liquid-phase selective acetalization of aldehydes in the presence of ketones (31).

The present study was originally undertaken to examine the possibility of intramolecular dehydration of acetophenone to phenylacetylene directly or by the route

$$PhCOCH_3 + 2CH_3OH \rightarrow$$
$$PhC(OCH_3)_2CH_3 \rightarrow PhC(OCH_3){=}CH_2 \rightarrow$$
$$PhC{\equiv}CH$$
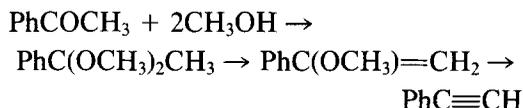
These reactions could not be realized. Instead methylation of acetophenone to propiophenone was observed in addition to the expected transfer hydrogenation products. Aldol condensation products were not observed in these reactions which may be due to the more favorable reverse reaction. Even though there are stray reports on the alkylation of the α-position of acetone by methanol in the presence of alumina (32), these have not been studied in detail. The reaction of acetophenone with methanol was chosen as a model for detailed study. Modified alumina catalysts (fluorided and sodium ion impregnated) which showed different selectivities for these two reactions, namely reductive dehydration and alkylation, were used. To study the secondary reactions at high conversions, the reactions of methanol with propiophenone, styrene, and β-methylstyrene have also been carried out over these catalysts. Acidity of the catalyst has been found to have an important role in the selectivity of these reactions. When the reactions were carried out over other acid catalysts like HY-zeolite, phosphotungstic acid (HPW), and silicotungstic acid (HSiW), selectivity toward the reductive dehydration improved but the overall yield was drastically decreased.

EXPERIMENTAL

Catalyst preparation. The alumina catalyst, **1**, was prepared by the slow hydrolysis

of double-distilled, aluminium isopropoxide (*33*) by atmospheric moisture as reported elsewhere (*34*). Fluorided alumina catalysts (2.11%, **2**, and 4.75%, **3**) were prepared by the reaction of alumina, **1**, with the required amount of aqueous HF solutions as given in the literature (*35*). The fluoride ion content was determined spectrophotometrically (*36*). To prepare sodium-ion-doped catalysts (0.25%, **4**; 0.5%, **5**; 1.0%, **6**; 1.5%, **7**; 2.0%, **8**; and 2.5%, **9**), alumina, **1**, was mixed with the required amount of aqueous sodium carbonate solution as reported elsewhere (*22*). The sodium ion content was estimated by flame photometry (*37*). Alumina and modified alumina catalysts were activated by heating the samples at 100°C for 12 hr in an air oven and further calcining at 600°C for 6 hr in a furnace. High-silica Faujasite zeolite, **10**, was prepared by a seed slurry activated crystallization method (*38, 39*). Sodium ions were exchanged with ammonium ions using 5% NH_4Cl solution and the resulting solid was kept in an air oven at 100°C for 6 hr and calcined at 500°C for 3 hr to get HY-zeolite. Phosphotungstic acid, **11**, was prepared from sodium tungstate and disodium phosphate using the procedure reported elsewhere (*40*). Commercial silicotungstic acid (HSiW) sample,

12 (Loba, India), was used after activation. Both HPW and HSiW were activated at 355°C for 3 hr.

Characterization. X-ray diffraction studies were carried out to characterize alumina (major phase η) and other catalysts. The zeolite catalyst prepared and used in the present study was found to be 95% crystalline when compared to the standard Linde Y-zeolite sample. Both HPW and HSiW exhibited all the required peaks in XRD. Surface area measurement was done for alumina (216 ± 10 m^2/g) and modified alumina catalysts. There was no appreciable change in surface area upon modification.

Acidity measurement. Acidities were determined by the titration of the solid catalyst suspended in dry benzene with *n*-butyl amine solution using Hammett indicators (*41*). Five indicators were used, namely neutral red (pK_a + 6.8), methyl red (pK_a + 4.8), butter yellow (pK_a + 3.3), benzene-azodiphenylamine (pK_a + 1.5), and crystal violet (pK_a + 0.8). The results are given in Table 1.

Reagents. Laboratory-grade acetophenone, benzene, ethylbenzene, and thionyl chloride were used after purification.

Preparation of higher ketones. Propiophenone (30 g) was obtained by the

TABLE 1

Strength and Number of Acid Sites

S. No.	Catalyst No.	Acidity (mmole g^{-1})					
		≤+0.8	+0.8 to +1.5	+1.5 to +3.3	+3.3 to +4.8	+4.8 to +6.8	Total acidity
1	1	0.036	0.111	0.178	0.149	0.117	0.591
2	2	0.051	0.273	0.191	0.110	0.059	0.684
3	3	0.053	0.398	0.198	0.105	0.065	0.819
4	4	0.018	0.108	0.150	0.153	0.160	0.589
5	5	—	0.069	0.115	0.210	0.177	0.571
6	6	—	0.037	0.057	0.234	0.182	0.510
7	7	—	0.018	0.037	0.275	0.180	0.510
8	8	—	0.010	0.040	0.280	0.175	0.505
9	9	—	0.005	0.045	0.280	0.175	0.505
10	10	0.129	0.435	0.220	0.193	0.150	1.127
11	11	1.185	0.282	0.238	0.145	1.355	3.205
12	12	1.105	0.243	0.182	0.228	1.092	2.850

Friedel–Crafts reaction of propionyl chloride (34 g) with benzene using anhydrous AlCl₃ (60 g). The other ketones, namely butyrophenone and isobutyrophenone, were prepared by similar methods from the corresponding acid chlorides and benzene.

Preparation of olefins. Styrene was obtained from acetophenone by reduction with sodium borohydride followed by dehydration with phosphoric acid. The other olefins, β-methylstyrene and β,β-dimethylstyrene, were obtained from the corresponding ketones by the same procedure.

Propylbenzene. Propiophenone (13.4 g) upon Clemensen reduction gave propylbenzene (11.5 g).

Isolation of β-methylstyrene. A mixture of acetophenone (5 ml) and anhydrous methanol (15 ml) was passed over a bed of Al₂O₃, 1, (5 g) at a rate of 22 ml/hr at 400°C. The products were collected in a water-cooled receiver. The organic layer was separated and dried over anhydrous Na₂SO₄. The fraction boiling at 165–175°C was obtained by fractional distillation. This fraction, upon column chromatography (silica gel and hexane), gave β-methylstyrene. It was characterized by a ¹H NMR spectrum. The spectrum showed small amounts of impurities. GLC analysis of the fraction also confirmed small amounts of ethylbenzene and dimethylstyrene.

Apparatus and experimental techniques. The catalytic flow reactor and the general experimental technique had been described previously (20). The reactions were carried out in a flow reactor consisting of a Pyrex tube 2.5 cm in diameter and 40 cm in length kept in a cylindrical ceramic furnace mounted in a sloping manner. The required amount of the catalyst was kept in the middle isothermal region of the reactor. Space above the catalyst was packed with Pyrex glass beads which acted as a preheater zone. Provision was made to read the inside temperature of the catalyst zone using a thermocouple. The catalyst was activated at its activation temperature and the temperature was brought down to the reaction temperature in a stream of pure, dry nitrogen. The liquid mixture was introduced at the top of the reactor by means of an infusion pump. The products were collected in a water-cooled receiver and analyzed by GLC. After each reaction, the catalyst was reactivated by passing CO₂-free air at its activation temperature through the catalyst tube for 3 to 4 hr.

Product analysis. Products were analyzed by gas/liquid chromatography using FFAP (5% on Chromosorb A, 60–80 mesh, acid washed, white, 15.5 ft in length and ⅛ in. in diameter) and Carbowax 7 ft in length and ⅛ in. in diameter) columns and a flame ionization detector.

Reactions of aromatic ketones with alcohols over alumina and modified alumina catalysts. Mixtures of acetophenone and anhydrous methanol in the required mole ratio were passed over 1 g of catalyst at different temperatures (300–500°C) at 22 ml/hr. Styrene, ethylbenzene, propiophenone, β-methylstyrene (*cis* and *trans*), isobutyrophenone, and β,β-dimethylstyrene were formed in major amounts in addition to minor amounts of 1-phenylethanol, 1-phenylpropanol, 1-phenyl-2-methylpropanol, and propylbenzene. Water was also formed and was one of the products for which quantitative determination was not carried out. Gaseous products like methane, formaldehyde, dimethyl ether, and other lower hydrocarbons were also detected. In reactions at low temperatures, trace amounts of unreacted methanol were detected in the product mixture. In reactions at high temperatures, methanol could not be detected. Reactions of acetophenone with ethanol and with 2-propanol and reactions of propiophenone, isobutyrophenone, styrene, methylstyrene, and dimethylstyrene with methanol were carried out in a similar way.

RESULTS AND DISCUSSION

It was found that when a mixture of acetophenone and methanol was passed over alumina at 300–500°C, propiophenone and

its reductive dehydration products, *cis-* and *trans-β*-methylstyrene were formed along with the direct reductive dehydration prod-

uct, styrene, in addition to small amounts of higher ketones, alkenylbenzenes, and ethylbenzene:

$$PhCOCH_3 + CH_3OH \rightarrow Ph\overset{\overset{\displaystyle OH}{|}}{C}HCH_3 + PhCH{=}CH_2 + PhCH_2CH_3$$

$$\downarrow$$

$$PhCOCH_2CH_3 + Ph\overset{\overset{\displaystyle OH}{|}}{C}HCH_2CH_3 + (cis \text{ and } trans) \text{ } PhCH{=}CHCH_3$$

$$+ PhCOCH(CH_3)_2 + Ph\overset{\overset{\displaystyle OH}{|}}{C}HCH(CH_3)_2 + PhCH{=}C(CH_3)_2$$
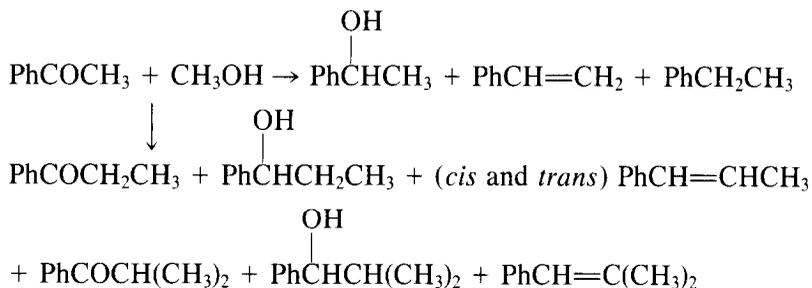
When mixtures of acetophenone and methanol at different mole ratios were passed over 1 g of alumina, **1**, at 350°C, it was found that the selectivity for the two reactions, namely alkylation (formation of propiophenone and methylstyrene) and reductive dehydration (formation of styrene), depended upon the mole fractions of the two reactants.

Styrene formation was maximum at 1 : 1 mole ratio of acetophenone : methanol

whereas there was no detectable formation of products arising from alkylation reaction at and below this mole ratio. Alkylation was observed to take place only above 1 : 1 mole ratio. The combined yield of pro-piophenone, methylstyrene, isobu-tyrophenone, and dimethylstyrene which are formed by the alkylation reaction reached a maximum only at a mole ratio of acetophenone : methanol of 1 : 3 (Fig. 1). In order to observe both types of reaction and
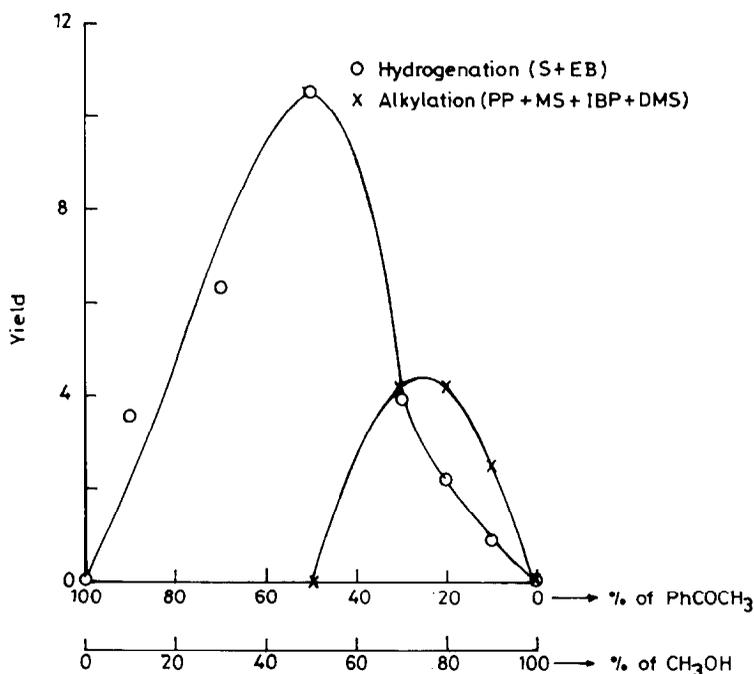
FIG. 1. Effect of concentration of the reactants on hydrogenation and alkylation reactions.
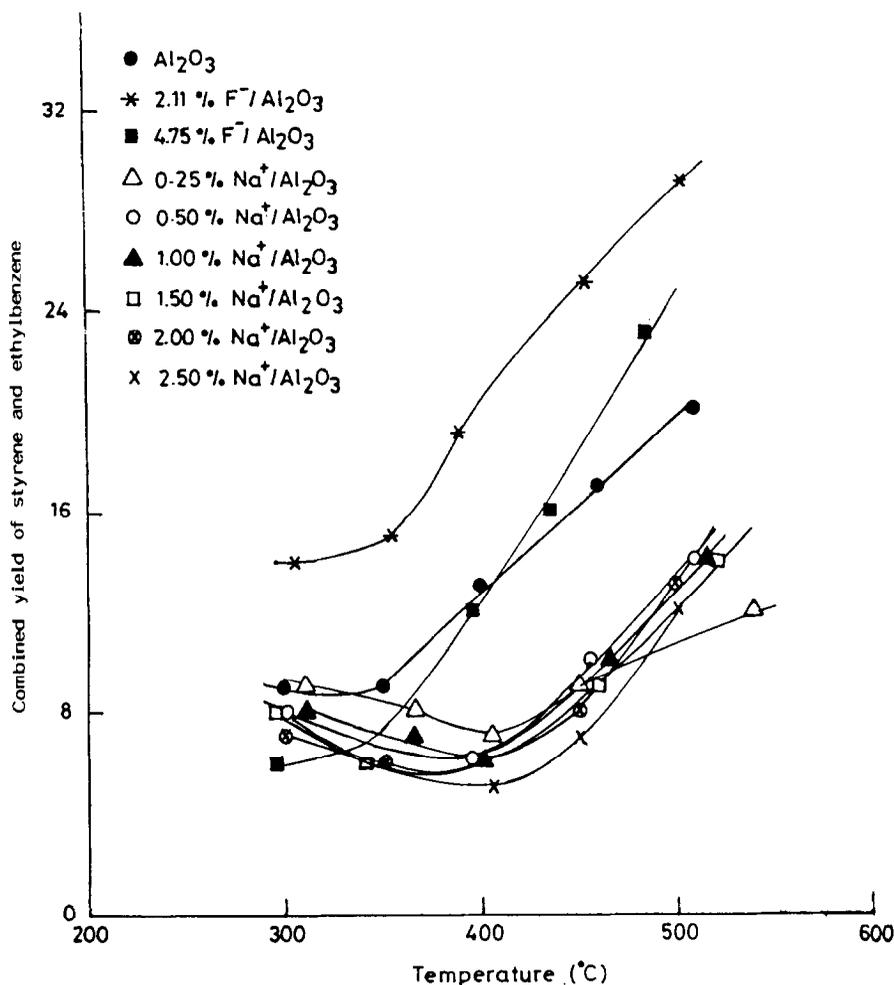
FIG. 2. Effect of temperature and acidity on reductive dehydration.

to keep the overall conversions as well as reductive dehydration low, the subsequent studies were done with a mixture of acetophenone and methanol containing about 10 mole% acetophenone (5 ml acetophenone + 15 ml methanol).

Results of the reactions between acetophenone and methanol over 1 g of alumina at 300°C are given in Table 2. To study the effect of catalyst acidity on the selectivity of these reactions, reactions have also been carried out over fluorided and sodium-ion-impregnated alumina catalysts and the results are also presented in Table 2.

Reductive Dehydration

On all the catalysts studied, selectivity for reductive dehydration increases as the temperature increases (Table 2). The increase is small on sodium-ion-doped alumina, appreciable on pure alumina, and more so on the highly acidic fluorided alumina (Fig. 2). The reaction involves a hydride transfer from a methoxide species to a molecularly adsorbed ketone (22) as given in Scheme I.

The selectivity for styrene formation is very high over the highly acidic fluorided

TABLE 2

Reactions of Acetophenone and Methanol over Different Catalysts at Different Temperatures

| S. No.	Catalyst No.	Temp. (°C)	Product distribution[a] (%)								Hydrogenation[c] / Alkylation
			AP	EB	S	PP	MS	IBP	DMS	Others[b]	
1	1	300	70	—	9	3	15	1	2	—	0.43
2	1	350	64	—	9	5	17	Trace	2	3	0.37
3	1	400	58	1	12	5	19	Trace	3	2	0.48
4	1	460	55	2	15	4	19	—	2	3	0.68
5	1	510	54	3	17	4	16	—	2	4	0.90
6	2	305	84	1	13	1	1	1	—	—	7.33
7	2	355	79	3	12	1	4	—	—	1	2.96
8	2	390	73	4	15	1	5	—	—	2	3.18
9	2	455	68	7	18	1	5	—	—	1	4.11
10	2	505	63	8	21	1	4	—	—	3	5.57
11	3	295	94	1	5	—	—	—	—	—	—
12	3	345	92	1	6	Trace	1	—	—	—	7.33
13	3	395	87	3	9	Trace	1	—	—	—	11.50
14	3	435	82	4	12	Trace	11	—	—	1	14.33
15	3	485	75	7	16	—	—	—	—	2	—
16	4	310	63	—	9	5	18	2	2	1	0.33
17	4	365	57	—	8	6	23	2	2	2	0.25
18	4	405	54	—	7	8	25	2	2	2	0.19
19	4	450	52	1	8	6	27	2	1	3	0.25
20	4	540	50	3	12	5	25	2	1	2	0.45
21	5	300	61	—	8	9	17	3	2	—	0.27
22	5	345	57	—	7	10	20	2	1	3	0.21
23	5	395	52	—	6	11	24	2	2	3	0.16
24	5	445	48	1	9	10	26	3	2	1	0.24
25	5	510	45	2	12	10	25	3	1	2	0.35
26	6	310	54	—	8	10	20	4	1	3	0.22
27	6	365	49	—	7	13	24	4	2	1	0.17
28	6	400	45	—	6	14	24	5	3	3	0.13
29	6	465	42	—	10	15	25	4	1	3	0.22
30	6	515	39	1	13	13	25	3	2	4	0.32
31	7	290	54	—	8	12	18	4	1	3	0.22
32	7	340	50	—	6	13	23	4	2	2	0.14
33	7	395	44	—	6	14	26	4	2	2	0.13
34	7	460	39	—	9	14	30	4	2	2	0.18
35	7	520	37	Trace	14	14	27	4	1	3	0.30
36	8	300	54	—	7	12	19	4	2	2	0.19
37	8	350	50	—	6	12	23	3	2	4	0.15
38	8	395	45	—	6	13	27	3	2	4	0.13
39	8	450	40	—	8	13	30	3	3	3	0.16
40	8	500	40	—	13	11	28	3	1	4	0.31
41	9	300	55	—	7	10	19	4	2	3	0.21
42	9	350	51	—	6	11	23	3	2	4	0.15
43	9	405	45	—	5	13	27	3	3	4	0.11
44	9	450	40	—	7	12	30	3	3	5	0.15
45	9	500	40	—	12	10	28	2	2	6	0.29

Note. Reagents, 5 ml $PhCOCH_3$ + 15 ml CH_3OH; catalyst, 1 g; HLSV, 22 ml · g^{-1} · h^{-1} (HLSV is hourly liquid space velocity and is equal to the volume of liquid injected per gram of catalyst per hour).

[a] AP, acetophenone; EB, ethylbenzene; S, styrene; PP, propiophenone; MS, methylstyrene; IBP, isobutyrophenone; and DMS, dimethylstyrene.

[b] 1-Phenylethanol, 1-phenylpropanol, 1-phenyl-2-methylpropanol, and propylbenzene.

[c] Percentage (EB + S)/percentage (PP + MS + IBP + DMS).
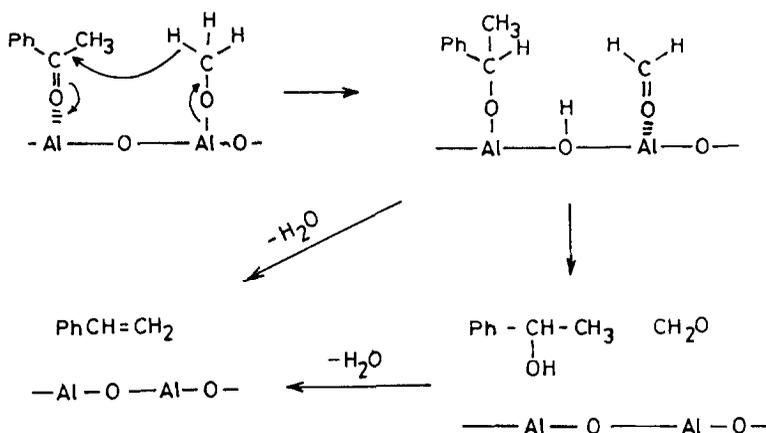
SCHEME I

catalysts and it also depends upon the fluoride ion content of the catalyst. As the fluoride ion content increases, the styrene selectivity also increases (Fig. 3 and Table 2, S. Nos. 6–15). From the results obtained, it is clear that strong acidic sites are responsible for reductive dehydration which is expected from the proposed scheme I which requires the adsorption and activation of the ketone molecule. Over sodium-ion-doped catalysts, this route is not favored as much as over pure alumina (Fig. 3). As the sodium ion content increases from 0.25 to 1.5%, the amount of the products obtained from reductive dehydration decreases (Table 2, S. Nos. 16–35). The reactions with 2.0 and 2.5% Na⁺-doped alumina catalysts showed no significant change in conversion or product distribution (Table 2, S. Nos. 36–45), indicating that further addition of sodium ion does not have any effect on the catalyst. The acidity measurement also showed that there is no change in both total acidity and acidity distribution after impregnating 1.5% sodium ions (Table 1). The reason for the suppression of the reductive dehydration route over sodium-ion-incorporated catalysts may be the poor polarization of the carbonyl group by the weak acid sites.

Alkylation

The methylation of the ketone with methanol over oxide catalysts at the enolate position is a new reaction that was observed during these studies. When the reactions of acetophenone and methanol were carried out over 1 g of alumina, 1, at 300–500°C, propiophenone and isobutyrophenone and their reductive dehydration products (methylstyrene and dimethylstyrene) were also obtained in addition to the direct reductive dehydration product, styrene. The formation of higher ketones can be represented as in Scheme II.

Basic sites are involved in this alkylation reaction. The abstraction of β-hydrogen by a basic site is the first step in this reaction. As the temperature increases from 300°C, the amount of products from the alkylation route also increases (Fig. 4). It reaches a maximum at 400–450°C and then decreases due to the reverse reaction at high temperatures.

Sodium-ion-doped alumina catalysts give better selectivity toward alkylation. Increased strength of basic sites upon sodium ion doping seems to be responsible for the selectivity. The availability of basic sites to abstract the β-H atom to form the enolate
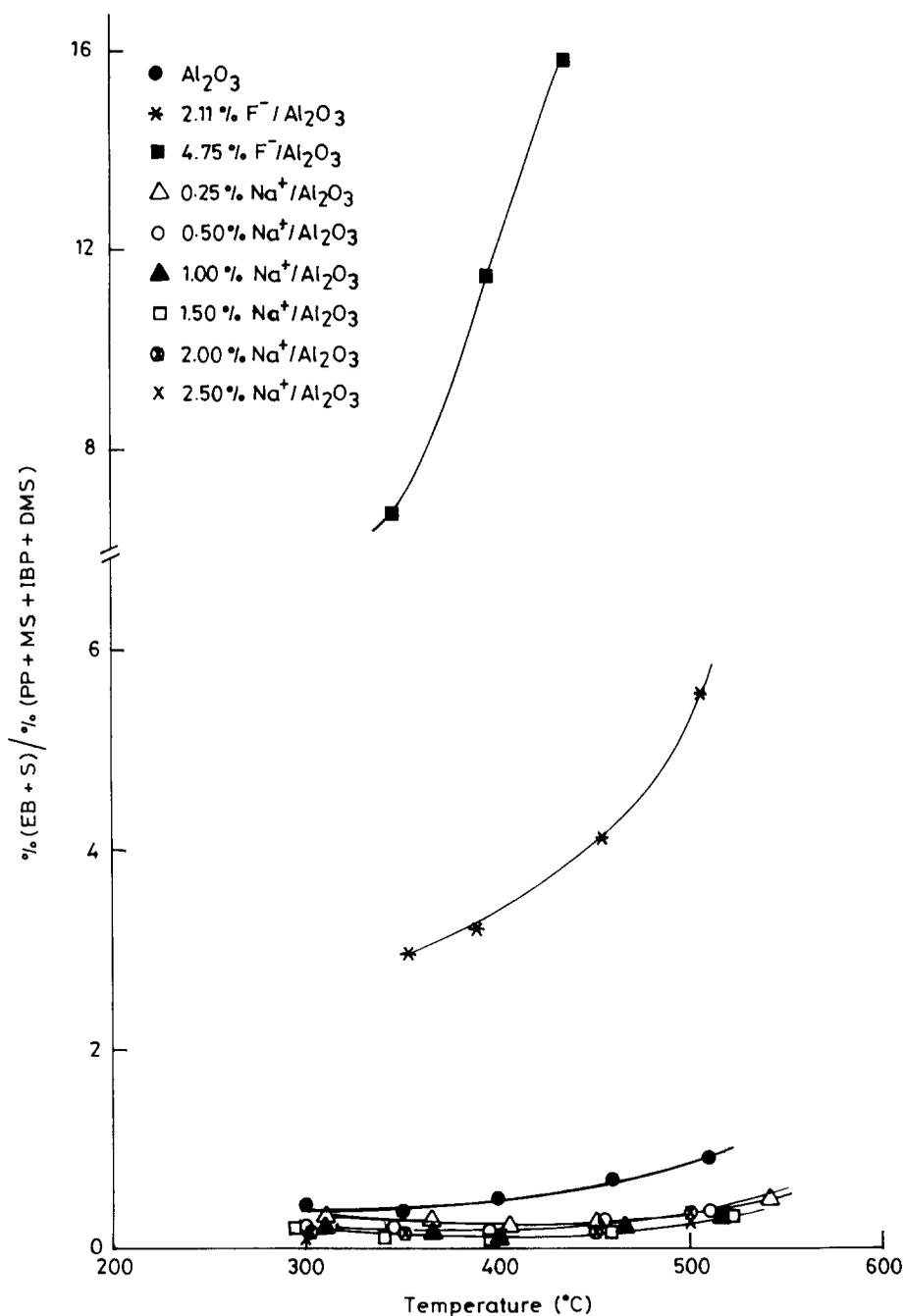
FIG. 3. Effect of temperature and acidity on the selectivity of reductive alkylation and dehydration.

and the presence of methanol as surface methoxide favor the alkylation. Over fluorided alumina catalysts, only small amounts of propiophenone and methylsty-

rene were observed and higher alkylated ketone (isobutyrophenone) and olefin (dimethylstyrene) were not detected at all. These results clearly show that alkylation
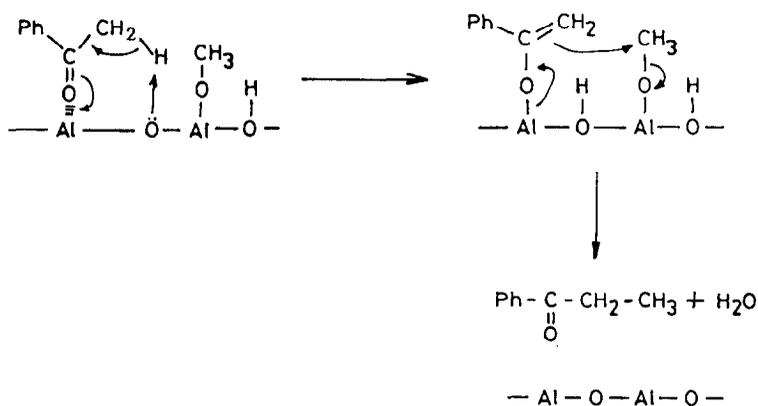
Scheme II

Fig. 4. Effect of temperature and acidity on alkylation.

TABLE 3

Reactions of Acetophenone and Methanol over Different Catalysts

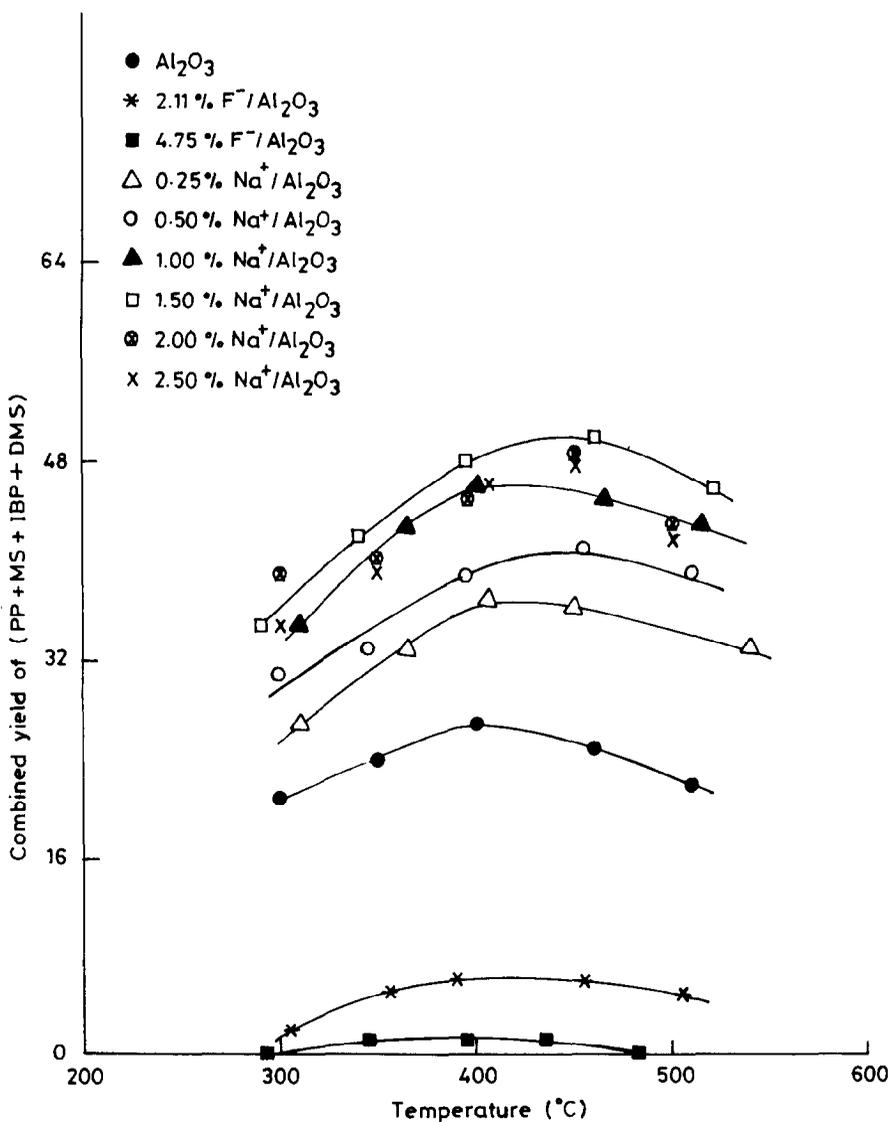| S. No.	Catalyst No.	Temp. (°C)	Product distribution[a] (%)							
			AP	EB	S	PP	MS	IBP	DMS	Others
1	1	265	44	—	16	4	26	5	Trace	5
2	1	310	17	—	15	10	37	14	Trace	8
3	1	350	10	Trace	15	10	42	11	6	6
4	1	370	6	Trace	17	10	46	7	8	6
5	1	400	4	Trace	18	9	53	Trace	9	7
6	1	440	6	8	19	11	38	Trace	9	9
7	1	460	7	9	19	11	37	Trace	8	9
8	1	520	3	13	22	14	36	Trace	3	10
9	10	350	68	2	28	—	Trace	—	—	2
10	11	350	72	2	23	—	—	—	—	3
11	12	350	76	2	20	—	—	—	—	2

Note. Reagents, 5 ml $PhCOCH_3$ + 15 ml CH_3OH; catalyst, 5 g; HLSV, 4.4 ml $\cdot$ g^{-1} h^{-1}.
[a] See footnotes to Table 2.

at the enolate position is a base-catalyzed reaction.

Reactions with Other Acid Catalysts

To confirm our earlier results that reductive dehydration is favored over strongly acidic catalysts and alkylation is facilitated over weakly acidic or basic catalysts, reactions were carried out over highly acidic catalysts like HY-zeolite, 10, phosphotungstic acid, 11, and silicotungstic acid, 12. The results are given in Table 3 (S. Nos. 9–11). As expected, a selectivity of 100% toward reductive dehydration was observed over all three catalysts. However, the overall conversion was very low when compared to alumina.
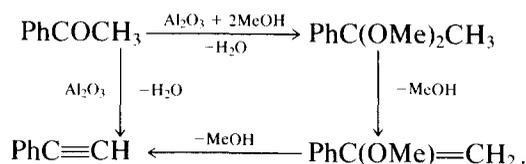
Aldol Condensation

Acetophenone is known to undergo aldol condensation selectively in liquid-phase reaction over zeolite catalysts (9). Other aromatic ketones also give aldol condensation products only in the liquid phase (7, 8). Vapor-phase aldol condensation of aromatic ketones has not been reported in the literature. In the present study also, aldol condensation products of acetophenone were not observed. When acetophenone alone was passed over these catalysts at different temperatures (300–450°C), more than 95% of the reactant was recovered unchanged. The products arising from acetophenone and formaldehyde were also not detected. Formaldehyde gas passed over the catalyst at 300–450°C was essentially recovered unchanged but coke formation was noticed during this experiment. Unlike acetophenone, aliphatic carbonyl compounds undergo mainly aldol condensation reactions to give a variety of products over alumina at 250–350°C. In the case of acetone, the last step in the sequence of reactions is the irreversible formation of isophorone which appears to be the net driving force of this condensation reaction (3).

Involvement of Ketal

The present study was originally undertaken to examine the possibility of formation of phenylacetylene from acetophenone either by direct intramolecular dehydration or via an intermediate ketal formation:

$$PhCOCH_3 \xrightarrow[-H_2O]{Al_2O_3 + 2MeOH} PhC(OMe)_2CH_3$$

$$\begin{array}{cc} Al_2O_3 \downarrow -H_2O & \downarrow -MeOH \end{array}$$

$$PhC\equiv CH \xleftarrow{-MeOH} PhC(OMe)=CH_2.$$

When the reactions of acetophenone and methanol were carried out over alumina at different temperatures (250–500°C), no phenylacetylene could be detected. The anticipated intermediate, dimethyl ketal, of acetophenone was prepared independently and passed over alumina at various temperatures (200–500°C). The expected elimination of methanol leading to phenylacetylene was not observed. Instead, decomposition (hydrolysis) of the ketal to the ketone took place. At high temperatures, the ketone formed underwent reactions with the alcohol formed by the hydrolysis of the ketal to give a spectrum of products similar to that obtained from the reaction of acetophenone and methanol. When acetophenone was passed alone over these catalysts at 250–500°C, the reactant was recovered unchanged and no phenylacetylene was detected though there are a few reports on the intramolecular dehydration of ketones over oxide catalysts to give allenes, acetylenes, or dienes (17–21). When a mixture of phenylacetylene and water was passed over alumina at 300°C, acetophenone was the only product formed.

Effect of Acidity on Acetophenone Conversion

It is seen from Fig. 5 that overall acetophenone conversion decreases as the acidity of the catalyst increases. Among the alumina catalysts, the fluorided alumina catalysts show least activity for acetophenone conversion. The highly acidic HY-zeolite and heteropoly acids also show very low acetophenone conversion. This is because both hydrogenation and alkylation reactions are bimolecular reactions which require both reactants to be present on the surface. Over acidic catalysts, the major reaction is the decomposition of methanol, disproportionation to formaldehyde, methane, and water, and conversion of dimethyl ether to hydrocarbons (42). The required concentration of methanol molecules on the surface may not be available for the above-

mentioned bimolecular reactions (hydrogenation and alkylation) to take place. Reactions of methanol alone over these catalysts at different temperatures revealed that conversion of methanol was 100% and the major products over highly acidic fluorided alumina, HY-zeolite, and heteropoly acids are formaldehyde, methane, and other lower hydrocarbons in addition to traces of dimethyl ether. On the other hand, over sodium-ion-doped alumina catalysts, the major product from methanol alone was dimethyl ether with very small amounts of disproportionation products and hydrocarbons. Unreacted methanol was also detected in the product mixture. Formation of dimethyl ether is reversible and it is capable of reacting with acetophenone in the same way as methanol itself.

Reactions with Ethanol and 2-Propanol

Reactions of acetophenone with ethanol were carried out in a manner similar to those with methanol. The products were styrene, butyrophenone, and cis- and trans-β-ethylstyrene. The yield was low when compared to the reaction of acetophenone with methanol. With 2-propanol, acetophenone gave mainly styrene. No alkylation product was observed. This may be because

(i) secondary alcohols are better hydride donors than primary alcohols and

(ii) isopropylation may be sterically less favorable than methylation and ethylation. Dehydration of ethanol and 2-propanol to give olefins was also observed in the above experiments.

Reactions of Other Aryl Alkyl Ketones with Methanol

The study of reactions of acetophenone with methanol was extended to other aryl alkyl ketones also. Table 4 (S. Nos. 1, 4, 7, 10, 13, 16, 19, 22, and 25) shows the results of the reactions of propiophenone with methanol at 400°C over 1 g of oxide cata-
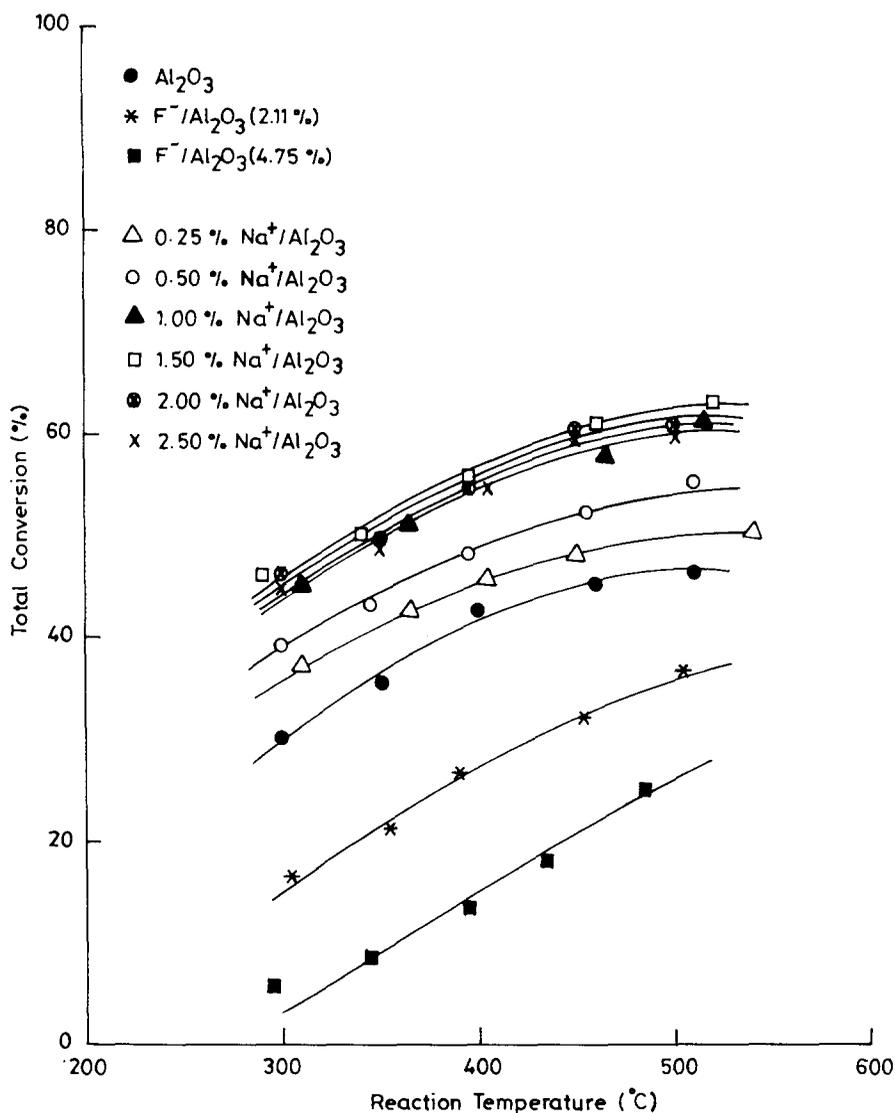
FIG. 5. Effect of temperature and acidity on total conversion.

lyst. As expected, both methylation and reductive dehydration products were obtained. Both the total conversion and the methylation reaction were higher over sodium-ion-doped catalysts than over pure alumina and fluorided alumina catalysts. Acetophenone was detected in the product mixture, indicating the dealkylation of propiophenone.

The reactions of isobutyrophenone and methanol over alumina and modified alumina catalysts gave mainly reductive dehydration products in addition to small amounts of demethylated products (Table 4, S. Nos. 3, 6, 9, 12, 15, 18, 21, 24, and 27). The methylated product, phenyl t-butyl ketone, was not detected which may be due to steric reasons.

Reactions at High Conversions

When the reactions of acetophenone with methanol over alumina were carried out at

TABLE 4

Reactions of Propiophenone and Isobutyrophenone with Methanol over Alumina and Modified Alumina Catalysts at 400°C

S. No.	Catalyst No.	Ketone	HLSV (ml · g⁻¹ · h⁻¹)	Product distribution[a] (%)								Hydrogenation / Alkylation
				AP	EB	S	PP	MS	IBP	DMS	Others	
1	1	PP	22	· 0.2	—	—	58.9	19.8	5.3	13.1	2.7	1.08
2	1	PP	4.4	14.0	0.5	19.2	3.5	17.4	24.6	19.4	1.4	0.76
3	1	IBP	22	—	—	—	1.0	2.4	61.4	33.0	2.2	
4	2	PP	22	—	—	—	75.0	18.8	1.4	3.7	1.1	3.73
5	2	PP	4.4	0.5	1.4	7.1	16.9	67.4	1.0	4.7	1.0	1.58
6	2	IBP	22	—	—	—	—	Trace	78.0	20.2	1.8	
7	3	PP	22	—	—	—	87.1	11.1	0.8	0.5	0.6	8.55
8	3	PP	4.4	0.7	1.2	11.6	48.0	26.2	1.4	10.2	0.7	1.17
9	3	IBP	22	—	—	—	—	Trace	90.3	9.2	0.5	
10	4	PP	22	0.3	—	—	57.3	17.1	9.4	14.1	1.8	0.73
11	4	PP	4.4	18.0	Trace	18.2	4.1	15.4	22.3	21.4	0.6	0.81
12	4	IBP	22	—	—	—	1.1	1.9	60.1	34.8	2.1	
13	5	PP	22	0.3	—	—	54.3	17.5	11.3	14.8	1.8	0.67
14	5	PP	4.4	24.2	Trace	17.1	4.1	14.6	18.9	20.5	0.6	0.83
15	5	IBP	22	—	—	—	1.2	1.5	57.0	38.4	1.9	
16	6	PP	22	0.4	—	—	47.1	19.1	13.6	17.7	2.1	0.61
17	6	PP	4.4	25.6	—	16.5	2.9	14.4	19.9	19.7	1.0	1.05
18	6	IBP	22	—	—	—	1.3	1.0	50.3	45.4	2.0	
19	7	PP	22	0.4	—	—	45.3	18.5	15.2	18.3	2.3	0.55
20	7	PP	4.4	28.8	—	15.3	3.1	13.5	19.4	19.1	0.8	1.06
21	7	IBP	22	—	—	—	1.5	0.6	47.9	48.0	2.0	
22	8	PP	22	0.4	—	—	45.5	18.1	16.1	17.7	2.2	0.54
23	8	PP	4.4	29.4	—	15.1	2.9	13.4	19.3	19.0	0.9	1.15
24	8	IBP	22	—	—	—	1.5	0.5	48.0	48.0	2.0	
25	9	PP	22	0.4	—	—	45.7	18.0	15.8	17.3	2.8	0.54
26	9	PP	4.4	29.2	—	15.0	3.4	13.4	19.4	19.0	0.6	1.16
27	9	IBP	22	—	—	—	1.5	0.5	48.0	47.8	2.2	

Note. Reagents, 5 ml ketone + 15 ml methanol.
[a] See footnotes to Table 2.

high conversions (5 g of catalyst were used; Table 3, S. Nos. 1–8) the product distribution changed compared to the same reactions at low conversions (1 g catalyst; Table 2). It was suspected that other secondary reactions like dealkylation of ketones, alkylation, and dealkylation of olefins might have taken place. Hence it was decided to study the reactions of higher ketones and olefins with methanol at high conversions.

Dealkylation of Higher Ketones

To study the dealkylation reaction, the propiophenone–methanol system was taken as a model since it can lead to three different reactions, namely hydrogenation, alkylation, and dealkylation. Table 4 (S. Nos. 2, 5, 8, 11, 14, 17, 20, 23, and 26) gives the results obtained from the reactions of propiophenone and methanol over 5 g of alumina, and fluorided and sodium-ion-doped aluminas at 400°C:

$$\begin{array}{ccc}
\text{Ph} & \text{CH}_2 & \\
\diagdown\text{C}\diagup\diagdown\text{CH}_3 & & \\
\parallel\diagdown & & \\
\text{O}\equiv & & \\
-\text{Al}-\text{O}-\ \text{Al}-\ddot{\text{O}}- & &
\end{array}
\longrightarrow
\begin{array}{c}
\text{Ph}\diagdown_{\text{C}}\diagup^{\text{CH}_2} \\
\diagdown \\
\text{O}\text{H}\text{CH}_3 \\
-\text{Al}-\text{O}\equiv\ \text{Al}-\text{O}-
\end{array}$$

$$\downarrow$$

$$\begin{array}{c}
\text{Ph}\diagdown\diagup\text{CH}_3 \\
\text{C} \quad + \ \text{CH}_3\text{OH} \\
\parallel \\
\text{O} \\
-\text{Al}-\text{O}-\text{Al}-\text{O}-
\end{array}$$

SCHEME III

$$
\begin{array}{l}
\quad \overset{\text{OH}}{\underset{|}{\text{PhCHCH}_2\text{CH}_3}} + \text{PhCH}{=}\text{CHCH}_3 \\[4pt]
\nearrow \qquad\qquad\qquad \overset{\text{OH}}{} \\
\text{PhCOCH}_2\text{CH}_3 \\
+ \qquad\longrightarrow\ \text{PhCOCHMe}_2 + \overset{\text{OH}}{\underset{|}{\text{PhCHCHMe}_2}} + \text{PhCH}{=}\text{CMe}_2 \\[4pt]
\text{CH}_3\text{OH} \qquad\searrow \qquad\qquad \overset{\text{OH}}{} \\
\quad \text{PhCOCH}_3 + \overset{\text{OH}}{\underset{|}{\text{PhCHCH}_3}} + \text{PhCH}{=}\text{CH}_2 + \text{PhCH}_2\text{CH}_3
\end{array}
$$
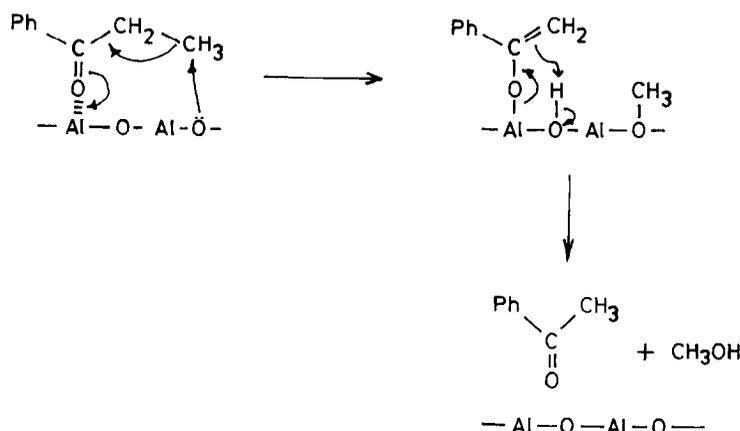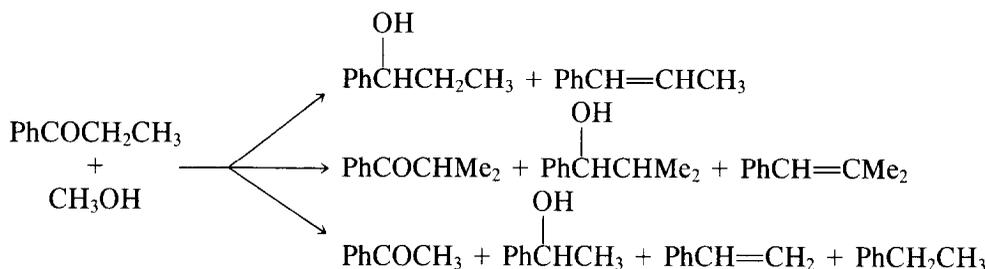
The results clearly show that fluorided catalysts favor the hydrogenation route and sodium-ion-doped catalysts favor both alkylation and dealkylation routes. The ratio of alkylation to dealkylation also seems to be high with high sodium content. Basic sites are involved in the dealkylation reactions and the probable mechanism is given in Scheme III.

When propiophenone alone was passed over alumina (Table 5), the product mixture contained acetophenone and methanol (detectable) as expected from the proposed mechanism (Scheme III).

Formation of Ethylbenzene

One of the products obtained from the reactions of acetophenone with methanol at high temperatures ($\geq 400°$C) over fluorided alumina was ethylbenzene. It is interesting

TABLE 5

Reactions of 1-Phenylethanol, Styrene, and Propiophenone over Alumina at 400°C

S. No.	Reactant	Solvent	Conver-sion (%)	Product distribution[a] (%)								AP/EB
				AP	EB	S	PP	MS	IBP	DMS	Others	
1	1-Phenylethanol	Benzene	100	12	14	70	—	—	—	—	4	0.86
2	1-Phenylethanol	Methanol	100	3	37	32	1	22	Trace	Trace	5	0.08
3	Styrene	Methanol	37	2	16	63	1	16	Trace	1	1	0.13
4	Propiophenone	Benzene	51	Trace	Trace	11	49	28	Trace	—	12	—

Note. Reagents, 5 ml reactant in 15 ml solvent; catalyst, 5 g Al_2O_3, 1; temperature, 400°C; HLSV, 22 ml · g^{-1} · h^{-1}.
[a] See footnotes to Table 2.

to study the mechanism of formation of ethylbenzene. One of the routes for obtaining ethylbenzene is by the disproportionation of 1-phenylethanol, which is formed by hydrogenation, to acetophenone and ethylbenzene.

When a reaction of 1-phenylethanol in benzene was carried out over alumina at 400°C, the products arising from dehydration (styrene) and disproportionation (acetophenone and ethylbenzene) were observed (Table 5). The ratio of acetophenone to ethylbenzene was also around unity as expected from the disproportionation stoichiometry (43). When the reaction of 1-phenylethanol was carried out in methanol, the amount of styrene formed was less than that obtained when no methanol was used (benzene solvent). The ratio also became 0.08 indicating that there was a possibility of obtaining ethylbenzene directly from 1-phenylethanol and methanol by crossed disproportionation or from one of the products by reduction (Scheme IV).

Reactions of Olefins with Methanol

To confirm the possibility of formation of ethylbenzene from styrene by hydrogen transfer, reactions were carried out with styrene and methanol over different catalysts at 400°C. The results are given in Table 6 (S. Nos. 1, 3, 5, 7, and 9). Ethylbenzene was obtained as one of the major products. Fluorided catalysts favor the hydrogen transfer reaction indicating that Brønsted acid sites which can stabilize the intermediate carbocation are required for the reaction

$$PhCH{=}CH_2 \xrightarrow{H^+/Al_2O_3} Ph\overset{+}{C}HCH_3$$

$$\xrightarrow{H^-/CH_3OH} PhCH_2CH_3$$
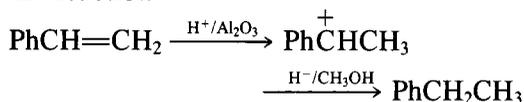
The reactions over sodium-ion-doped catalysts showed very low activity for the reduction and the overall conversion also decreased.

The other major product of the reaction of styrene and methanol is β-methylstyrene, a product formed by methylation. This alkylation is also found to be facilitated by acidic catalysts unlike the alkylation of ketones discussed earlier:

$$PhCH{=}CH_2 + CH_3OH \xrightarrow[+\,H^+,\,-H_2O]{Al_2O_3}$$

$$Ph\overset{+}{C}HCH_2CH_3 \xrightarrow{-H^+} PhCH{=}CHCH_3$$
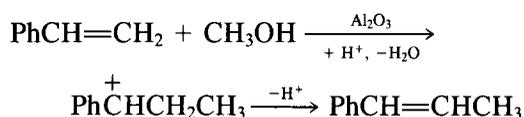
The results of the reactions of β-methylstyrene and methanol over alumina and modified alumina catalysts at 400°C are given in Table 6 (S. Nos. 2, 4, 6, 8, and 10). The hydrogenation product, namely propylbenzene, was detected only in traces. Methylation and demethylation products were the major products. The intermediate carbocation for the formation of propylbenzene readily undergoes demethylation instead of abstracting a hydride ion from methanol:

SCHEME IV

TABLE 6

Reactions of Styrene and Methylstyrene with Methanol over Alumina and Modified Alumina Catalysts at 400°C

S. No.	Catalyst No.	Olefin	Product distribution[a] (%)							
			AP	EB	S	PP	MS	IBP	DMS	Others
1	1	S	1.6	16.1	62.8	0.9	15.5	Trace	1.2	1.9
2	1	MS	1.3	12.4	6.3	1.5	60.4	1.3	14.9	1.9
3	2	S	1.9	23.9	49.5	1.4	18.5	0.6	2.8	1.4
4	2	MS	2.2	16.9	9.2	2.1	47.2	1.4	18.0	3.0
5	3	S	2.1	28.2	42.6	1.5	20.1	0.8	3.4	1.3
6	3	MS	3.8	19.4	11.0	2.4	40.6	1.9	18.6	2.3
7	5	S	Trace	3.6	81.5	Trace	13.3	Trace	0.7	0.9
8	5	MS	Trace	Trace	2.4	0.4	84.2	Trace	12.2	0.8
9	6	S	Trace	0.7	87.7	Trace	10.6	—	0.5	0.5
10	6	MS	—	—	0.5	Trace	88.5	—	10.4	0.6

Note. Reagents, 5 ml olefin + 15 ml methanol; catalyst, 5 g; HLSV, 4.4 ml · g^{-1} · h^{-1}.
[a] See footnotes to Table 2.

$$PhCH\!=\!CHCH_3 \xrightarrow{H^+/Al_2O_3} Ph\overset{+}{C}HCH_2CH_3 \xrightarrow{H^-/CH_3OH} PhCH_2CH_2CH_3$$

(minor)

$$\downarrow \overset{+}{_{-CH_3}}$$

$$PhCH\!=\!CH_2$$

(major)

The possible mechanisms for the demethylation and methylation of olefins may be given as in Schemes V and VI, respectively.

According to Scheme V, the dealkylation involves a Brønsted acidic site in the first step. Fluorided catalysts contain greater numbers of Brønsted acids and therefore

they are found to be more selective for dealkylation than other catalysts according to the results obtained.

Disproportionation of Ketones

Ketones which contain α- and β-hydrogen atoms such as propiophenone undergo disproportionation to give the correspond-

SCHEME V

$$Ph-CH\overset{\curvearrowright}{=}CH-CH_3 \quad \overset{CH_3}{\underset{\underset{H}{|}}{C}}\overset{}{\underset{}{O}} \; H$$

$$-O-Al-O\underline{\qquad} Al-O-$$

$\longrightarrow$

$$Ph-CH\overset{\oplus}{-}\overset{CH_3}{\underset{\underset{H}{|}}{C}}\overset{}{\underset{CH_3}{}} \quad OH$$

$$-O-Al-\overset{\downarrow}{O}\underline{\qquad}\overset{|}{Al}-O-$$

$$\downarrow$$

$$PhCH=C\overset{CH_3}{\underset{CH_3}{}} + H_2O$$

$$-O-Al-O-Al-O-$$

$\longleftarrow$

$$Ph-CH=C\overset{CH_3}{\underset{CH_3}{}}$$

$$\underset{H\ OH}{\underset{|\ \ |}{}}$$

$$-O-Al-O-Al-O-$$

SCHEME VI

ing alcohols and α,β-unsaturated ketones (16). The formation of β-methylstyrene from propiophenone also arises from the dehydration of 1-phenylpropanol formed by this route. While this is the major reaction of such ketones when passed alone over alumina (Table 5), it becomes less important in the presence of methanol.

CONCLUSIONS

The main finding of the present study is the discovery that ketones like acetophenone can be alkylated by methanol at the enolate position over alumina. This has not been reported by previous investigators. Most of the earlier studies (22, 23, 44) have used higher, especially secondary, alcohols which are better hydride donors than alkylating agents, as the present study also verified. This could be the reason why alkylation has not been reported earlier. Excellent correlation has been obtained between the acid–base character of the catalyst and the activity for alkylation and for the competing reductive dehydration. Aldol condensation was not observed. Alumina catalyst has been modified by fluoridation or sodium ion doping to obtain more or less acidic catalyst and has been used for the reactions under identical conditions.

Thus it was possible to understand the role of acidity in the various reactions. The following are the conclusions drawn from the results of the present study.

1. Both reductive dehydration and alkylation reactions depend on the mole ratio of the reactants. The rate of the former reaction reaches a maximum at a mole ratio of acetophenone : methanol of 1 : 1. The latter reaction is observed only after the mole ratio of 1 : 1 and reaches a maximum at 1 : 3.

2. Reductive dehydration of ketones by alcohols requires strong acidic sites and is facilitated by fluorided alumina catalysts and other super acids like HY-zeolite and heteropoly acids.

3. Alkylation of ketones at α-position requires both acidic and basic sites and sodium-ion-impregnated catalysts favor this reaction.

4. The total acetophenone conversion is greater on less acidic catalysts. On highly acidic catalysts, other reactions of methanol such as disproportionation and hydrocarbon formation became important.

5. The effect of sodium ion doping reaches a maximum at 1.5% Na$^+$. Further addition of sodium ions does not have any effect on acidity, activity, and selectivity.

6. Reactions of propiophenone with

methanol bring about dealkylation which is favored over basic Na$^+$-doped alumina catalysts.

7. Reduction of styrene to ethylbenzene with methanol takes place over fluorided alumina with Brønsted acid sites.

8. Styrene undergoes methylation to β-methylstyrene and β-methylstyrene can be methylated to β,β-dimethylstyrene and demethylated to styrene under the reaction conditions. The dealkylation of olefins is favored at high temperatures and on highly acidic catalysts.

ACKNOWLEDGMENTS

REFERENCES

1. Griffiths, D. M., and Rochester, C. H., *J. Chem. Soc. Faraday Trans. 1* **74**, 403 (1978).
2. Winde, H., *Z. Chem.* **10**, 64 (1970).
3. Reichle, W. T., *J. Catal.* **63**, 295 (1980).
4. Bell, V. A., and Gold, H. S., *J. Catal.* **79**, 286 (1983).
5. Bell, V. A., Carver, R. F., Dybowski, C., and Gold, H. S., *J. Chem. Soc. Faraday Trans. 1* **80**, 831 (1984).
6. Zhang, G., Hattori, H., and Tanabe, K., *React. Kinet. Catal. Lett.* **34**, 255 (1987).
7. Barot, B. C., Sullins, D. W., and Eisenbraun, E. J., *Synth. Commun.* **14**, 397 (1984).
8. Muzart, J., *Synth. Commun.* **15**, 285 (1985).
9. Venuto, P. B., and Landis, P. S., *J. Catal.* **6**, 237 (1966).
10. Malinowski, S., Jedrzejewska, H., Basinski, S., and Benbenek, S., *Chim. Ind. (Paris)* **85**, 885 (1961); *Chem. Abstr.* **56**, 2321g.
11. Malinowski, S., Jedrzejewska, H., Basinski, S., and Benbenek, S., *Rev. Chim. Acad. Repub. Pop. Roum.* **6**, 5 (1961); *Chem. Abstr.* **57**, 11003i.
12. Scheidt, F. M., *J. Catal.* **3**, 372 (1964).
13. Winfield, M. E., *Aust. J. Sci. Res. Ser. A* **3**, 290 (1950).
14. Ganguly, P., *Proc. Indian Acad. Sci. A* **86**, 1, 65 (1977).
15. Ganguly, P., *Proc. Indian Acad. Sci. A* **86**, 3, 283 (1977).
16. Jayamani, M., and Pillai, C. N., *Indian J. Chem. Sect. B* **24**, 687 (1985).
17. Quattlebaum, W. M., Toussaint, W. J., and Dunn, J. T., *J. Amer. Chem. Soc.* **69**, 593 (1947).
18. Novakova, J., Kubelkova, L., and Dolejsek, Z., *J. Mol. Catal.* **39**, 195 (1987).
19. Nedomova, K., Beran, S., and Jiru, P., *React. Kinet. Catal. Lett.* **32**, 353 (1986).
20. Jayamani, M., and Pillai, C. N., *Synth. Commun.* **15**, 535 (1985).
21. Jayamani, M., Nalin Pant, Ananthan, S., Narayanan, K., and Pillai, C. N., *Tetrahedron* **42** (1986).
22. Ramana, D. V., and Pillai, C. N., *Canad. J. Chem.* **47**, 3705 (1969).
23. Ramana, D. V., and Pillai, C. N., *Indian J. Chem.* **8**, 1106 (1970).
24. Venkatasubramanian, N., Ramana, D. V., and Pillai, C. N., *J. Catal.* **51**, 40 (1978).
25. Niiyama, H., and Echigoya, E., *Bull. Chem. Soc. Japan* **45**, 938 (1972).
26. Okamoto, Y., Imanaka, T., and Teranishi, S., *Bull. Chem. Soc. Japan* **45**, 3207 (1972).
27. Kibby, C. L., and Hall, W. K., *J. Catal.* **31**, 65 (1973).
28. Hruby, V. J., *Proc. North Dakota Acad. Sci.* **16**, 12 (1962); *Chem. Abstr.* **62**, 1589g.
29. Posner, G. H., and Ranquist, A. W., *Tetrahedron Lett.* **42**, 3601 (1975).
30. *Carbide and Carbide Chemicals Corp. Brit.* **616**, 844 (1949); *Chem. Abstr.* **43**, 6231a.
31. Kamitori, Y., Hojo, M., Masudo, R., and Yoshida, T., *Tetrahedron Lett.* **26**, 4767 (1985).
32. Dolgov, B. N., and Samsonova, I. N., *Zh. O. Khim. (J. Gen. Chem.)* **22**, 632 (1952); *Chem. Abstr.* **47**, 2691c.
33. Vogel, A. I., "A Textbook of Practical Organic Chemistry," 4th ed., p. 280. Longmans, Green, London, 1980.
34. Jayamani, M., Viswanthan, B., and Pillai, C. N., *J. Catal.* **89**, 560 (1984).
35. Scokart, P. O., Selim, S. A., Damon, J. P., and Rouxhet, P. G., *J. Colloid Interface Sci.* **70**, 209 (1979).
36. Boltz, D. F., and Howell, J. A., "Colorimetric Determinations of Non-metals," 2nd ed., p. 118. Wiley, New York, 1978.
37. Vogel, A. I., "A Textbook of Quantitative Inorganic Analysis," 3rd ed., p. 879. Longmans, Green, London, 1969.
38. Kerr, G. T., *Catal. Rev. Sci. Eng.* **23**, 281 (1981).
39. Elliott, C. H., Jr., McDaniel, C. V., U.S. Patent 3,639,099 (1972); *Chem. Abstr.* **76**, 115618u.
40. Bailor, J. C., *in* "Inorganic Synthesis" (H. C. Booth, Ed.), Vol. 1, p. 132. McGraw–Hill, New York, 1939.
41. Benesi, H. A., *J. Amer. Chem. Soc.* **78**, 5490 (1956).
42. Chang, C. D., *Catal. Rev. Sci. Eng.* **25**(1), 1 (1983).
43. Jayamani, M., Pillai, C. N., *J. Catal.* **82**, 485 (1983).
44. *Carbide and Carbide Chemicals Corp., Brit.* **616**, 844 (1949); *Chem. Abstr.* **43**, 6231a.