Friedel–Crafts catalysis using sol–gel derived supported reagents Metal diketonate modified mesoporous aluminosilicates

Jack M. Miller,*† David Wails, J. Stephen Hartman and Jennifer L. Belelie Department of Chemistry, Brock University, St. Catharines, Ontario, Canada L2S 3A1



Aluminosilicates have been prepared from aluminium tri-*sec*-butoxide and tetraethyl orthosilicate in butanol incorporating transition metal pentane-2,4-dionate complexes, which on calcination give active Friedel–Crafts alkylation catalysts having textural mesoporosity. Addition of β -diketonates to the aluminosilicate sol–gel results in complexation to aluminium which, on calcination, generates a mesoporous aluminosilicate with increased surface area and pore volume. This provides a suitable framework upon which zinc chloride may be supported at higher loadings than for either the unmodified material or K10, the support for the commercial catalyst Clayzic, to give materials with significantly higher catalytic activity in a Friedel–Crafts alkylation reaction.

Friedel-Crafts catalysis traditionally uses Lewis acid catalysts such as aluminium trichloride or Brönsted acids such as hydrofluoric acid, which have environmental drawbacks in addition to often poor selectivity and lack of reusability.¹ In recent years, alternative catalysts such as Clayzic² (zinc chloride supported on montmorillonite K10) have been introduced as useful alternatives. Since Clayzic was first reported in 1989,³ it has been extensively studied.⁴⁻¹¹ The activity of the catalyst can be further enhanced by acid treatment of the support, which destroys much of the original framework structure generating mesoporous materials. The pore size of the mesopores is critical, with the optimum diameter being 8-12 nm for maximum catalytic activity of the resulting supported reagent.^{10,11} Other supports such as mesoporous silica are also more effective than K10, and the pore size characteristics appear to be the most significant factor, rather than the actual chemical nature of the support.^{10,11} These studies however have been limited to commercially, available materials of limited pore size distributions. AlCl₃ supported on 7 nm diameter mesoporous silica has recently been shown to be highly effective as a Friedel-Crafts alkylation catalyst.¹² We have taken the approach of sol-gel synthesis of the support and have recently described the synthesis of Friedel-Crafts catalysts based on a sol-gel derived aluminosilicate.¹³

Sol-gel methodologies offer an attractive approach to the synthesis of materials for a number of applications including ceramics, catalysts and optical devices.¹⁴ The low temperature sol-gel route offers a number of advantages over the traditional high temperature melt processes. Both the chemical composition of the materials and physical properties such as surface area and pore size distributions can often be precisely controlled. The sol-gel process involves the controlled hydrolysis of suitable precursor molecules, often metal alkoxides in a (typically alcoholic) solvent, often with acid or base catalysis. During hydrolysis, partially hydrolyzed metal alkoxides polymerize to give a sol (a colloidal suspension of solid particles in the liquid phase). Further polycondensation results in gelation. The final stages in the process involve ageing the gel, during which further condensation reactions may occur, and drying of the gel to give the final product. Pentane-2,4-dione (Hacac) has been used previously to alter the properties of sol-gel derived materials. Addition of Hacac to a tetramethylorthosilicate based system prevented formation of crystalline precipitates, leading to increased transparency of the resulting gels.¹⁵ Complexation of Hacac to metal alkoxides slows hydrolysis rates, and in a zirconium alkoxide system prevents aggregation of nanosized particles.¹⁶ We here describe the modification of our previously reported aluminosilicate system¹³ with β -diketones and metal β -diketonates to generate improved mesoporous aluminosilicate based Friedel–Crafts alkylation catalysts.

Experimental

Instrumentation

NMR experiments were carried out on a Bruker DPX-300 instrument using a standard bore magic angle spinning (MAS) probe with 4 mm zirconia rotors. ²⁹Si cross-polarization magic-angle spinning (CP MAS) and ²⁷Al MAS spectra were obtained under the conditions reported in our earlier study.¹³ ¹³C CP MAS spectra were obtained at 75.48 MHz using cross-polarization with proton decoupling during acquisition and referenced to external tetramethylsilane (TMS). Samples were spun at 4 kHz in air. A 10 ms cross-polarization time was used with a 4 s delay between pulses, and up to 2048 free-induction decays (FIDs) were typically accumulated over a spectral window of 28 000 Hz.

Surface area and pore volume determinations were carried out at 77 K using a Coulter SA3100 instrument with an automated gas volumetric method employing nitrogen as the adsorbate. Surface areas were determined using the BET adsorption method¹⁷ and pore size distributions using the Barrett, Joyner and Halenda (BJH) method on the desorption branch of the isotherm.¹⁸ For materials having type II hysterisis loops, BJH calculations were made on the adsorption branch of the isotherm which is generally believed to give a more accurate representation of the catalyst pore distribution in this system. Samples were outgassed under high vacuum at 200 °C for 1 h immediately prior to analysis.

Scanning electron microscopy (SEM) analysis was carried out on gold coated samples with a Hitachi SEM S2400 with an electron gun energy of 8 keV.

Simultaneous differential scanning calorimetry (DSC) and thermogravimetry (TG) was carried out using a Thermal Sciences STA625. Approximately 10–20 mg of sample were heated from room temperature to $600 \,^{\circ}$ C at $10 \,^{\circ}$ C min⁻¹ under flowing nitrogen.

Mass spectrometry (MS) was carried out on a Kratos Concept IS mass spectrometer. Samples were heated in silica tubes to approximately 650 °C at a heating rate of $2 \degree C s^{-1}$. Evolved materials were analyzed under electron impact conditions.

[†] E-mail:jmiller@sandcastle.cosc.brocku.ca.

 Table 1
 Comparison of physical properties and catalytic activity of various materials

catalyst ^a	surface area $/m^2 g^{-1}$	pore volume $/cm^3 g^{-1}$	optimum loading /mmol g ⁻¹	conversion(%) ^b
Zn(acac), treated	392.89	1.00	_	28
pentanedione treated	462.42	1.45	7.5	68
untreated	425.16	1.19	5.0	54
K10	226.29	0.30	1.0	7

^a Materials are mesoporous aluminosilicates: optimal loadings are shown in Table 2. ^b Conversion(%) is defined in the Experimental section.

Reagents

Benzene and ethanol were obtained from Caledon Laboratories. Metal acetylacetonate complexes excluding $Zn(acac)_2$ (Aldrich) were obtained from Gelest Inc., Tullytown, PA. All other chemicals were obtained from Aldrich and used as received.

Catalyst preparation

Aluminum tri-sec-butoxide (ATSB) (20.0 g, 0.08 mol) was mixed with butanol (200 ml) with stirring. Tetraethyl orthosilicate (TEOS) (17.4 ml, 0.08 mol) was then added. The mixture was stirred vigorously and heated to 70 °C for approximately 5 min until a clear solution was obtained. For studies in which an experimental variable was to be altered [e.g. amount of Zn(acac)₂], this solution was divided to give five identical samples. For materials modified with metal complexes [typically 1.5 g $Zn(acac)_2$, 5.6 mmol or molar equivalent], the complex was added to the hot solution and stirred to dissolve. For ketone and diketone additives, (typically 1.0 ml Hacac, 9.8 mmol or molar equivalent) the solution was allowed to cool to room temperature before addition. The solution was stirred for 15 min, water added (11 ml), stirred for an additional 15 min and allowed to stand overnight. Solvent was then removed by heating in an oven at 150 °C. Materials were then activated at 500 °C in air to remove residual organics and decompose metal complexes. Elemental analysis of the Zn(acac)₂ modified material gave 20.89% Al, 22.79% Si, corresponding to an Al: Si ratio of 0.98:1, compared with the 0.93 : 1.00 ratio obtained for the unmodified material.¹³

For supports which were loaded after preparation, loading was carried out as previously described from a methanolic solution of zinc chloride.¹³ Catalyst testing was carried out using our previously reported method, using between 0.25 and 0.75 g of catalyst, depending on the series of materials under investigation.¹³ (*i.e.* the alkylation of benzene with benzyl chloride at room temperature for 15 min. The percentage conversion is defined as the total conversion of benzyl chloride to diphenylmethane and the isomers of dibenzylbenzene).

Results and Discussion

Aluminosilicates have been prepared by a number of sol-gel based routes.^{13,19–21} ATSB and TEOS were heated in a 1:1 molar ratio in butanol to give a clear solution, as previously described.¹³ The system was modified by the addition of either a metal diketonate, ketone or diketone before addition of water for hydrolysis. Drying and activation at 500 °C resulted in complete removal of residual organics as evidenced by ¹³C CP MAS NMR and diffuse reflectance IR (DRIFT) spectroscopy. The materials, like the unmodified analogues were amorphous by powder X-ray crystallography. Table 1 details the effect of incorporation of Hacac or $Zn(acac)_2$ on the aluminosilicate support, and Clayzic. Incorporation of Hacac

increases the surface area and pore volume of the support compared to the untreated material, resulting in an increase in the optimum zinc chloride loading from 5.0 to 7.5 mmol g⁻¹ with a corresponding increase in catalytic activity. The optimum loading of zinc chloride is typically that which results in a monolayer surface coverage and filled mesopores.^{10,11} Further addition of zinc chloride results in a system in which the zinc chloride behaves as the crystalline material, which has an inherently low activity in Friedel– Crafts catalysis.^{10,11} Increasing the surface area and pore volume therefore increases the maximum loading achievable. Incorporation of Zn(acac)₂ reduces the surface area and pore volume slightly, however it is likely that some pores are filled



Fig. 1 27 Al MAS NMR spectra of catalysts. a: Untreated; b: Zn(acac)₂ treated; c: Hacac treated. An asterisk denotes a spinning side band.



Fig. 2 ²⁹Si CP MAS NMR spectra of catalysts. a: Untreated; b: Zn(acac)₂ treated; c: Hacac treated.

with zinc oxide upon activation at 500 °C. This supported zinc oxide also shows high catalytic activity in the model Friedel–Crafts reaction. A number of zinc salts including halides, nitrates, phosphates and acetates have been supported on K10 and studied as potential Friedel–Crafts alkylation catalysts, although supported zinc oxide has not previously been investigated.³ Thermal decomposition of soluble metal complexes giving the metal oxide provides a viable route to the synthesis of supported metal oxides.²²

NMR studies

²⁷Al MAS NMR spectra and ²⁹Si CP MAS NMR spectra of the materials are shown in Fig. 1 and 2. The ²⁷Al spectra show three environments,²³ corresponding to tetrahedral framework (*ca.* 55 ppm), octahedral (*ca.* 6 ppm) and a third intermediate site (*ca.* 25 ppm) which is usually interpreted as a five-coordinate site, although recent studies suggest that this site may be better attributed to a distorted tetrahedral site.²⁴ The unmodified material shows the greatest level of octahedral, non-framework sites. Hacac is known to complex to a number of metal alkoxides and substitution reactions, *i.e.*,

$$M(OR)_3 + xHacac \rightarrow M(OR)_{3-x}(acac)_x + xROH$$

are well documented. Complexation reduces hydrolysis rates and has been used to prevent premature precipitation of one component in a multicomponent sol-gel system.²⁵

Since metal alkoxides hydrolyze more rapidly than silicon alkoxides, acac complexation to aluminium reduces the hydrolysis rate increasing the number of Al–O–Si species and therefore increasing the framework aluminium content. The Zn(acac)₂ modified material shows a larger four-coordinate Al peak than the other materials, consistent with the spectra obtained for ZnCl₂ modified materials.¹³ This suggests a possible role for Zn in the formation of four- over five-coordinate environments. It is also possible that the anion has some role since chloride is known to catalyze alkyl silicate polymerization²⁶ and Hacac is known to complex to and alter silicate based polymerization species.¹⁴

The ²⁹Si spectra show broad, unresolved peaks consistent with a range of $Si(OSi)_n(OH)_{4-n}$ and $Si(OAI)_n(OSi)_{4-n}$ sites.²³ The untreated material has the centre of the band at -95 ppm, compared to -91 ppm for the Zn(acac)₂ modified and -93 ppm for the Hacac modified materials. A shift to higher field is consistent with a decrease in the number of framework Al sites, and supports the interpretation of the ²⁷Al spectra previously described.

The ${}^{13}C$ CP MAS NMR spectra of the Hacac modified material dried at 150 °C shows a number of peaks in addition to residual butanol and Hacac (Fig. 3) which correlate to those from an authentic sample of Al(acac)₃.

Thermal studies

Thermal desorption mass spectrometry shows the presence of two intense ions at m/z = 225 and 324, corresponding to $Al(acac)_2^+$ and $Al(acac)_3^+$ respectively. The decomposition of the complex is also observed by thermal analysis (Fig. 4). The unmodified sample shows a broad endotherm up to 200 °C corresponding to loss of residual solvent. Both the Hacac Zn(acac)_2 modified materials show an additional broad endotherm in the 175–275 °C region which are not present in the blank sample, corresponding to metal acetylacetonate decomposition. The overall weight loss for these two samples is significantly higher than that of the untreated material. Carboxylate alumoxanes, $[Al(O)_x(OH)_y(O_2CR)_z]_n$, have been doped with metal acetylacetonate complexes, and transmetalation observed, leading to a metal doped alumoxane and



Fig. 3 ¹³C CP MAS NMR spectrum of Hacac modified material. a: Hacac peaks; b: butanol peaks; c: Al(acac)₃ peaks.

elimination of $Al(acac)_3$.²⁷ No evidence of transmetalation in the $Zn(acac)_2$ modified system [leading to formation of $Al(acac)_3$] was observed by ¹³C CP MAS NMR or MS.

SEM/Nitrogen adsorption studies

Addition of Hacac or $Zn(acac)_2$ to the aluminosilicate system has a significant effect on the textural properties of the materials, as shown by SEM and nitrogen adsorptiondesorption studies. The SEM of the unmodified material [Fig. 5(a)] has a highly open, amorphous texture, which alters significantly upon addition of Hacac or $Zn(acac)_2$. In the $Zn(acac)_2$ material [Fig. 5(b)], agglomerates of ZnO are visible on the surface of the particle. In the Hacac modified material, these agglomerates [presumably Al_2O_3 from $Al(acac)_3$ decomposition] are even more prominent [Fig. 5(c)].

Nitrogen adsorption-desorption isotherms for the three



Fig. 4 Thermal analysis of materials. a: Untreated; b: Hacac treated; c: $Zn(acac)_2$ treated. The line descending continuously from left to right is the weight loss curve, and the other is the energy plot.



Fig. 5 SEM analysis of catalysts. a: Untreated; b: $Zn(acac)_2$ treated; c: Hacac treated

materials are shown in Fig. 6. The type II adsorptiondesorption isotherm of the unmodified material indicates that the material is either non-porous or macroporous.²⁸ The SEM analysis previously described suggests the latter. Upon addition of Hacac or $Zn(acac)_2$ into the aluminosilicate



Fig. 6 Nitrogen adsorption–desorption isotherms for materials. (---) Untreated; (---) Zn(acac)₂ treated; (----) Hacac treated.

system, the isotherm switches to type IV, indicative of a mesoporous structure. The nature of the hysteresis associated with the adsorption–desorption branches of the isotherm suggests that the mesopores are interparticulate voids rather than framework pores.²⁸ Pore size distributions calculated using the BJH method of analysis are shown in Fig. 7. The Zn(acac)₂ modified material shows a sharp pore size distribution centred around 8.42 nm, and the Hacac modified material a broader distribution centred around 13.93 nm.

In a zirconia based system modified with Hacac, dynamic quasi-elastic light scattering was used to show the modification of the textural properties of the materials. Hacac addition was found to prevent aggregation of nanosized zirconia particles. The effect of Hacac on nitrogen adsorption properties in a sol-gel system has not previously been reported, although the mesoporous nature of a silica system has been modified using Pt(acac)₂.²²

Varying sol-gel preparation conditions

Ageing. The effect of varying ageing treatments is illustrated in Table 2 (entries 1–5) for the system modified with $Zn(acac)_2$ (1.00 g per sample). After preparation, samples were aged under varying thermal treatments before final treatment at 500 °C. Allowing the sample to dry completely at room tem-



Fig. 7 BJH pore distribution plots for materials. (----) Untreated; (-----) $Zn(acac)_2$ treated; (.....) Hacac treated.

 Table 2
 Effect of varying preparation conditions on physical properties and catalytic activity of various materials

preparation condition		surface area /m ² g ⁻¹	pore volume /cm ³ g ⁻¹	conversion (%)		
Zn(acac) ₂ mo	dified system	.1 \				
ageing (ove	rnight/subsequen	tly)				
1	RT/RT	426.70	0.36	5		
2	50 °C/50 °C	424.75	0.66	21		
3	RT/50°C	449.59	0.43	18		
4	150°C/150°C	446.70	0.94	41		
5	RT/150°C	428.36	0.74	29		
amount of Zr	$n(acac)_2$					
6	1.0 g	425.16	1.19	36		
7	1.5 g	386.20	0.99	25		
8	2.0 g	341.71	0.90	26		
9	5.0 g	227.87	0.69	48		
amount of Hacac (ZnCl ₂ loaded at 7.5 mmol g^{-1})						
10	0.5 ml	578.10	1.37	24		
11	1.0 ml	462.42	1.45	46		
12	1.5 ml	392.30	1.79	73		
13	2.0 ml	335.04	1.82	74		



Fig. 8 Nitrogen adsorption-desorption isotherms for room temperature dried material (entry 1 in Table 2). (---) adsorption; $(---\diamond--)$ desorption.

perature before activation gives a material with poor activity, the nitrogen adsorption isotherm for which exhibits a type II hysteresis loop (Fig. 8). This has been associated with 'inkbottle' type pores, having narrow necks and wide bodies, where the mechanism of condensation and evaporation is different, although this is now believed to be an over simplified model.²⁸ Allowing the materials to age at lower temperatures results in materials with lower pore volumes, and lower pore



Fig. 9 Effect of ageing on pore size distributions. (---) room temperature; $(--\diamond)$ 50 °C; $(--\diamond)$ RT overnight, then 50 °C; $(--\diamond)$ 150 °C; $(--\diamond)$ RT overnight, then 150 °C.



Fig. 10 Effect of $Zn(acac)_2$ loading on pore size distribution. ($\square\square$) 1.0 g $Zn(acac)_2$; ($\square \diamondsuit$) 1.5 g $Zn(acac)_2$; ($\square \circlearrowright$) 2.0 g $Zn(acac)_2$; ($\square \circlearrowright$) 5.0 g $Zn(acac)_2$.



Fig. 11 Effect of amount of Hacac added on pore size distributions. (-+-) 0.5 ml Hacac; $(--\diamond-)$ 1.0 ml Hacac; $(--\diamond-)$ 1.5 ml Hacac; $(--\Delta-)$ 2.0 ml Hacac.

diameters (Fig. 9), resulting in lower-levels of benzyl chloride conversion. The most active catalyst with the largest pore diameter was dried at $150 \,^{\circ}$ C immediately after preparation. It is likely that heating, particularly for a wet gel where precursors are still partly in solution, increases the interaction between acac and the sol-gel resulting in the greatest effect on the system.

Amount of additive. The effect of varying the amount of $Zn(acac)_2$ is illustrated in entries 6–9 of Table 2, and the effect of varying Hacac in entries 10-13. For both systems, surface areas initially increase compared to the untreated material, then steadily decrease. For the $Zn(acac)_2$ system, pore volumes decrease, presumably as a result of filling with ZnO, although the pore diameter increases slightly and the distribution broadens somewhat (Fig. 10). No obvious trend in catalytic performance is observed, possibly as a result of reduced pore volume countering the effects of increasing the amount of Zn^{2+} in the system. In the Hacac system, pore volumes increase with the amount of additive, although the relative increase is much less at higher Hacac levels. Conversion of benzyl chloride in the model reaction appears to correlate well with total pore volume, rather than the pore diameter (Fig. 11). This contrasts to previous studies which suggested that the pore diameter (8-10 nm) was the most significant factor,¹¹ although the most active catalysts also had the greatest total pore volumes. With increasing amounts of additive, the pore diameter increases and broadens significantly such that at the higher levels, no definite maximum in pore diameter is evident.

Other metal-acac complexes. A number of metal-acac complexes were also studied for both their effect on the textural properties of the materials and their catalytic ability (Table 3, Fig. 12). Each was incorporated into the aluminosilicate framework at the same molar ratio as $Zn(acac)_2$. With the exception of Fe, V and Mn, all gave broad mesoporous distributions up to 25 nm. Generally, surface areas and pore volumes are comparable to the $Zn(acac)_2$ modified aluminosilicate, although in some cases pore volumes are significantly greater. Interestingly, a number of the resulting supported metal oxides show reasonable activity as Friedel–Crafts alkylation catalysts. K10 supported copper and magnesium chlorides have been used as Friedel–Crafts alkylation catalysts⁹ and the corresponding oxides are also shown to be active in the present study.

Other β-diketones and ketones

A number of other organic modifiers in addition to Hacac were investigated (Table 4). Catalytic activity after loading with zinc chloride (5.0 mmol g^{-1}) correlates well with the total

 Table 3
 Effect of varying metal acetylacetonate complex on physical properties and catalytic activity of various materials

	metal complex	surface area /m ² g ⁻¹	pore volume /cm ³ g ⁻¹	pore diameter /nm ^a	conversion (%)
1	$Zn(acac)_2$	392.89	1.00	8.42	99
2	Fe(acac) ₃	396.32	1.43		2
3	V(acac) ₃	431.66	2.07		0
4	Cr(acac) ₃	414.86	1.06	10.75	26
5	$Mg(acac)_2$	432.79	0.93	8.94	55
6	$Ni(acac)_2$	553.14	1.09	7.64	55
7	$Mn(acac)_2$	362.65	1.74		3
8	$Cu(acac)_2$	480.72	1.09	8.94	63
9	$Co(acac)_2$	440.01	0.98	6.34	44
10	$Al(acac)_3$	448.69	1.26	11.95	33

^a Where pore diameters are not listed they covered a very wide range.



Fig. 12 Effect of metal acetylacetonate complexes on pore size distributions

pore volume of the support, which in many cases is significantly greater than that of Hacac, although surface areas are generally on the same order. Only the β -diketones, which are capable of complexing to transition metals through keto-enol tautomerization, gave materials with type IV isotherms, the corresponding BJH pore size distributions for which are shown in Fig. 13. Other additives including ketones and noncomplexing diketones gave type II isotherms similar to those of the unmodified aluminosilicate. MS analysis of the materials dried at 150 °C showed only residual solvent for the materials exhibiting type II isotherms. Organic additives have been used to alter the pore volumes and pore size distribution of sol-gel derived materials either in conjunction with tetraalkylammonium tempates²⁹ or as drying control chemical additives (DCCAs).¹⁴ DCCAs such as dimethylformamide which are less volatile than the solvent replace the solvent in pores during the final stages of drying, and the different surface tension in the final drying stages controls pore distributions.³⁰ It is possible that the ketones and noncomplexing diketones are acting as DCCAs, although generally up to half of the solvent is replaced by the DCCA.¹⁴ In the present work only a small amount of additive (approximately 5% by volume) produces a significant effect in the resulting sol-gel. For the materials exhibiting type IV isotherms, MS indicated the presence of aluminium diketonate (L) complexes for 3-methylpentane-2,4-dione (AlL₂⁺ m/z(L) completes for 5-methylperiale-2,+doine $(AL_2^2 - m/z) = 253$, $AL_3^+ - m/z = 366$), 2,2,6,6-tetramethylheptane-3,5-dione $(AL_2^+ - m/z) = 393$, $AL_3^+ - m/z) = 576$ and dibenzoyl-methane $(AL_2^+ - m/z) = 473$, $AL_3^+ - m/z) = 696$). For the



Fig. 13 Effect of β -diketones on pore size distributions. (—+—) Hacac; (— \diamond —) 1,1,1,5,5,5-hexafluoropentane-2,4-dione; (— \times —) 3methylpentane-2,4-dione; (— ∇ —)2,2,6,6-tetramethyl-heptane-3,5dione; (— Δ —)dibenzoyl methane.

Table 4	Effect of varying	organic additive on	physical	properties and	l catalytic activit	y of various materials	;
	20	6		1 1	~		

	additive	surface area /m ² g ⁻¹	pore volume /cm ³ g ⁻¹	pore diameter /nm ^a	conversion(%)
1	Hacac	526.63	1.09	8.58	26
2	1,1,1,5,5,5-hexafluoropentane-2,4-dione	340.29	0.83	7.64	11
3	3-methylpentane-2,4-dione	521.90	1.76		80
4	pentane-2,3-dione	480.42	2.22	_	75
5	hexane-2,5-dione	457.91	2.26	_	78
6	2,2,6,6-tetramethylheptane-3,5-dione	476.63	0.97	7.64	15
7	dibenzoylmethane	561.53	1.25	7.11	42
8	propanone	429.83	1.54	_	89
9	pentan-2-one	471.77	2.39	_	83
10	heptan-4-one	443.28	2.21	_	87
11	acetophenone	438.33	1.61	_	65
12	2-hydroxy-4,6-dimethylacetophenone	442.72	1.67	—	79

^a Where pore diameters are not listed they covered a very wide range. $ZnCl_2$ loadings were 7.5 mmol g⁻¹.

Conclusions

Metal acetylacetonate complexes can be heated within a sol-gel derived aluminosilicate to generate supported metal oxides with significantly altered textural porosity which have catalytic activity in Friedel–Crafts alkylation. β -Diketones may also be incorporated into the aluminosilicate gel where complexation to sol-gel derived aluminium species again results in a metal diketonate complex, which generates a mesoporous aluminosilicate framework with a higher pore volume than the unmodified material. This material provides a suitable support onto which zinc chloride may be loaded at higher levels than Clayzic (K10 supported zinc chloride) or the unmodified material resulting in significantly greater catalytic activity.

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