Montmorillonite Supported Transition Metal Salts as Friedel–Crafts Alkylation Catalysts[1,2]

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Montmorillonite supported zinc and nickel chlorides are highly active and selective reagents for the catalysis of Friedel–Crafts alkylations.

There has been a considerable growth in interest in recent years in the catalysis of organic reactions by inorganic reagents supported on high surface area inorganic materials.[3] These reactions often proceed with greater selectivity and under milder conditions than analogous homogeneous reactions. For these reasons we have become interested in the use of supported reagents as catalysts for Friedel-Crafts alkylations. Strongly acidic reagents are normally employed in such reactions, and polyalkylations and rearrangements are generally difficult to avoid.[4]

The clay, montmorillonite K10, slowly catalyses the reaction of benzene and benzyl chloride to form diphenylmethane. Thus, rapid stirring of a mixture of K10 (33 g) and benzyl chloride (0.1 mol) in benzene (2 mol) at room temperature gives 57% conversion to diphenylmethane (g.c.) after 24 h. At this time no benzyl chloride remains, the other major products being dibenzylbenzenes. The effect on the Friedel–Crafts activity and selectivity of supported $ZnCl_2$ and $NiCl_2$ is dramatic. For example, using a 1 mmol g^{-1} loading of $ZnCl_2$ on K10 (clayzic) activated at 280 °C, all of the benzyl chloride reacts in less than 15 min at room temperature, giving an isolated yield of diphenylmethane of 80%. Further results for other supported metal salts are shown in Table 1. Interestingly, the effect of supporting other metal ions such as Ca^{2+}, Ce^{3+}, Ba^{2+}, or Na^+ is to reduce the Friedel–Crafts activity of the clay.

Table 1. Formation of diphenylmethane using montmorillonite K10 supported reagents.[a]

Supported reagent[b]	Conversion of $PhCH_2Cl$[c]/%	Ph_2CH_2 yield[d] /%
K10	12	—
$NiCl_2$	96 (0.25 h)	67
$CuCl_2$	51	41
$ZnCl_2$	100 (0.25 h)	80[e]
$ZnBr_2$	95	68
ZnI_2	100 (0.25 h)	80
$Zn(PO_4)_2$	66 (0.25 h)	59
$Zn(NO_3)_2$	60	49
$ZnSO_4$	30	24
$Zn(OAc)_2$	15	13
$AgNO_3$	14	12
$CdCl_2$	40	32

[a] All reactions at room temperature using 1 mmol g^{-1} reagents, pre-treated at 280 °C: 1.6 mol benzene, 0.09 mol $PhCH_2Cl$ and 8 g catalyst. [b] Supported NaCl, $MgCl_2$, $AlCl_3$, $CaCl_2$, $CrCl_3$, $MnCl_2$, $FeCl_3$, $CoCl_2$, ZnF_2, YCl_3, $ZrCl_4$, $RuCl_3$, $SnCl_2$, $BaCl_2$, and $CeCl_3$ all give $\leqslant 6\%$ conversion in 1 h. [c] Conversion at 1 h determined by g.c. [d] G.c. yield. [e] Isolated.

The remarkable activity of the zinc supported reagent is in marked contrast to unsupported zinc chloride, which is

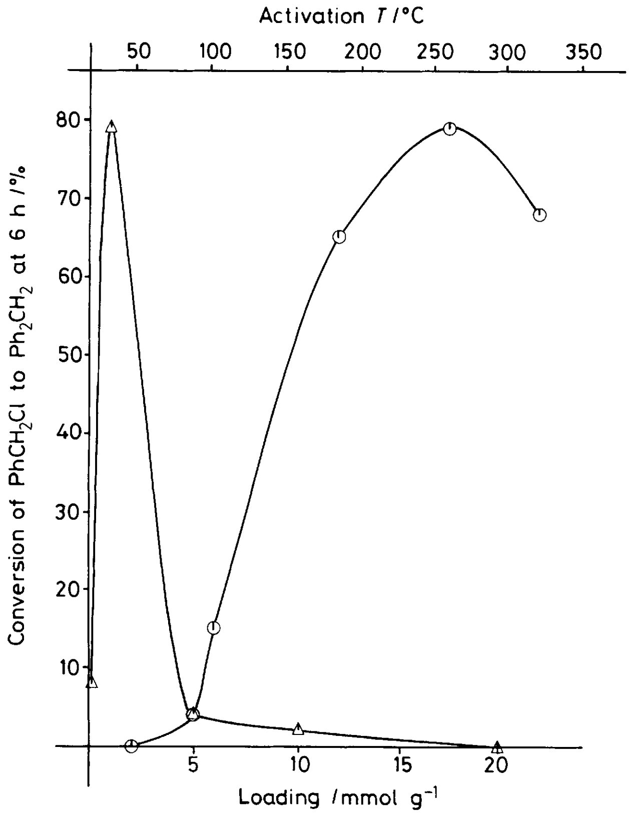

Figure 1. The formation of diphenylmethane using claycuc. Comparison of △ various loadings of $CuCl_2$ on K10 (activated at 280 °C), and ○ claycuc activation temperatures (1 mmol g^{-1} $CuCl_2$ on K10). All reactions: 2 mol benzene, 0.1 mol benzyl chloride with 17 g catalyst, stirred at room temperature.

generally regarded as one of the weakest Friedel–Crafts catalysts. Thus, using zinc chloride often requires elevated temperatures and pressures and also the addition of a co-catalyst such as HCl.[4] Other, usually powerful, Lewis acid catalysts such as $AlCl_3$ are less effective as supported reagents than the $ZnCl_2$.

The Friedel–Crafts activity and selectivity of clayzic is considerably greater than that recently reported using ion-exchanged K10.[5] Thus, for example, using ion-exchanged K10–Zn^{II} the authors report 100% (60% diphenylmethane) conversion of benzyl chloride in 1.5 h at reflux, whereas clayzic achieves 80% monoalkylation at room temperature in less than 15 min. We have prepared a Zn^{II} ion-exchanged catalyst following the procedure described in ref. 5 and found that using our reaction conditions only 8% conversion is achieved in 1 h.

The activity of the clay supported Friedel–Crafts reagents reported here is highly dependent upon the reagent loading and activation temperature. These effects are illustrated for claycuc K10–$CuCl_2$ in Figure 1 (this catalyst is illustrated since the reaction proceeds at a slower rate, such that variations may be observed readily). There is also an anion dependence for the supported reagents. In the benzene/benzyl chloride reaction with zinc(II) salts on K10 the following order of activity is found: $Cl^- \approx I^- \gg PO_4^{2-} > Br^- > NO_3^- > SO_4^{2-} > AcO^- > F^-$.

We have successfully employed the most active of these catalysts in a variety of Friedel–Crafts alkylation reactions. For example, difluorodiphenylmethane is formed from 4-fluorobenzyl chloride and fluorobenzene in 100% conversion with 86% regioselectivity to the 4,4′-isomer, in 6 h at room temperature using claycuc. Dibromomethane reacts with benzene in the presence of clayzic to give 60% conversion to diphenylmethane in 6 h at 80 °C. Isobutyl chloride reacts with benzene at reflux in 6 h to give 90% t- and 10% s-butylbenzenes and is therefore also an example of the catalysts' ability to promote rearrangements.

Alkylating agents other than halides have also been tested, including benzyl alcohol which undergoes a considerably slower reaction with benzene than the benzyl chloride using clayzic (8% in 6 h). Of particular interest is the use of paraformaldehyde as the alkylating agent. Thus, using clayzic, paraformaldehyde reacts at 80 °C with benzene to form diphenylmethane (70% isolated in 5 h), and phenol to form dihydroxydiphenylmethane (75% in 6 h; 2 : 13 : 5 mol ratio of 4,4′- : 4,2′-: 2,2′-isomers).

We believe that these new supported reagents represent an important breakthrough in the development of solid acid catalysts and further details of the catalysts and their applications (including acylation catalysis) will be described elsewhere. Work in another laboratory on chemisorbed $AlCl_3$ has also demonstrated the value of such materials for hydrocarbon cracking.[6] The high reactivity and specificity of our catalysts coupled with their ease of use and recovery, and low waste (*cf.* $AlCl_3$ processes) and environmental problems makes them attractive alternatives to homogeneous acidic reagents.

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