

Note

Hydrotalcite-like compounds for liquid-phase oxidation of benzylic hydrocarbons[†]

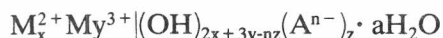
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Hydrotalcite-like compounds (HTlcs – The homogeneously dispersed mixed metallic oxides) have been devised and used for the liquid-phase oxidation of benzylic hydrocarbons for the first time, as an alternative to the heterogeneously dispersed mixed oxides and supported metal catalysts, as an exploratory work. HTlcs such as calcined ZnCrCO₃, NiAlCO₃, CuZnAlCO₃ and MgAlCO₃ (hydrotalcite) have been used in our studies and ZnCrCO₃ system is the best, both in terms of turnover number and conversion.

The use of clays for the design of experimentally clean and environmentally safe catalytic methodologies is of great topical concern. In the past, the cationic smectite clays have shown great potentials as efficient catalysts for various organic transformations¹. The complementary class of anionic clays which are relatively inexpensive and unlike cationic clays allow a great degree of variation in the nature of metal ions, types of anion, the size and morphology of clay particles and their chemical and physical properties are yet to be explored^{2a}. The hydrotalcite-like compounds generically belong to this anionic clay family and can be represented by the formula^{2b}:



where M²⁺ is a divalent metal; M³⁺ is a trivalent metal; Aⁿ⁻ is an n-valent anion; and x, y and z are numbers which satisfy the following:

$$1/2 \leq x/x+y \leq 1, 1/4 \leq nz/x+y < 1/2$$

The solid solutions obtained by the thermal treatment of HTlcs offer certain interesting features such as high surface area, mildly basic nature and exceptionally good homogeneous metal dispersion^{2c}. In view of these unique properties, HTlcs present themselves as a practical alternative to the

heterogeneously dispersed mixed oxides and supported metal catalysts³. Earlier, we reported the interesting results on the utility of calcined ZnCrCO₃-HTlc for the hydroperoxidation of aralkanes^{4a}, oxidation of benzyl amines to Schiff bases^{4b} and oxidation of alkyl- and benzyl-pyridines to pyridyl ketones^{4c}.

Benzylic oxidation of aralkanes is an industrially important organic transformation. Although numerous methodologies have been reported to effect this transformation, they suffer from drawbacks such as use of soluble chromium reagents/catalysts which are toxic and environmentally hazardous and expensive *tert*-butyl hydroperoxide (TBHP) as an oxidant⁵. Earlier we have reported an efficient catalytic methodology⁶ for liquid-phase benzylic oxidation using chromium polyoxometallate cations pillared onto montmorillonite which is a cationic smectite clay. This system overcomes all the disadvantages associated with the earlier systems, but involves the use of TBHP as an oxidant. The recent method of Clark⁷ involves the use of transition metals supported on alumina as the heterogeneous catalyst for the oxidation of aralkanes. However, metal leaching is an inherent problem associated with supported metal systems rendering the process inefficient for recycling, in the liquid-phase reactions. On the other hand, the mixed oxides⁸ which show great potential for hydrocarbon oxidation, also possess certain disadvantages such as, the dissolution of the oxide in the reaction medium to become a homogeneous catalyst. Hence, we herein devise calcined ZnCrCO₃-HTlc⁹, a homogeneously dispersed bimetallic oxide, as a heterogeneous catalyst for the liquid-phase oxidation of aralkanes, as an exploratory work and also compare the efficacy of the system with three more aluminium based systems.

Results and Discussion

The reactions proceed smoothly at a temperature of 130°C to give the corresponding ketones in good yields (Table I). High turnovers are obtained especially in the case of activated aromatic hydrocarbons (Table I, entries 3 and 4). A comparison in the activity of various catalytic systems (Table II) shows that the ZnCrCO₃ system is the most efficient one, in terms of both product conversion and ketone selectivity. Although the turn-

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Table I — Oxidation of benzylic hydrocarbons to ketone

Entry	Substrate	mmols of substrate loaded	Conversion (%) ^a		Selectivity for ketone (%) ^b		Turnover number	
			Zn-Cr	Ni-Al	Zn-Cr	Ni-Al	Zn-Cr ^c	Ni-Al ^d
1	Ethyl benzene	16	39	18.1	75	87	29.8	3.7
1.1	Cycle-1	"	28	—	73	—	—	—
1.2	Cycle-2	"	27	—	73	—	—	—
1.3	Cycle-3	"	24	—	71	—	—	—
1.4	Cycle-4	"	21	—	65	—	—	—
2	1-Butyl benzene	13	20	13.5	88	69	12.2	2.3
3	Diphenylmethane	12	64	59.5	86	90	36.7	9.1
4	Fluorene	18	65	55.6	95	94.5	55.5	12.8
5	Indan	17	25	40.2	60	86	20.3	8.8
6	Tetralin	15	47	36	44	50	34	6.9
7	2-Ethyl naphthalene	13	10.4	—	78	—	6.4	—
8	1-Propyl benzene	14	10.7	—	85	—	7.1	—
9	2-Propyl benzene	14	22	19.7	60	60	14.8	3.5

^aIsolated combined yields.^bCalculated based on isolated yields.^cBased on chromium content.^dBased on nickel content.

Table II — Oxidation of ethyl benzene with various catalytic systems

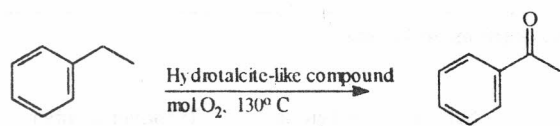
Entry	Catalyst	Conversion (%) ^a	Selectivity (%) ^b	Turnover number	Time (h)
1	Uncalcined ZnCrCO ₃ -HTlc	24	70	—	48
2	Calcined ZnCrCO ₃ -HTlc	39	75	29.8 ^c	"
3	NiAlCO ₃ -HTlc	18.1	87	3.7 ^d	"
4	MgAlCO ₃ -HT	2.6	85	—	"
5	CuZnAlCO ₃ -HTlc	3.4	90	—	"

^aIsolated combined yields.^bCalculated based on isolated yields.^cBased on chromium content.^dBased on nickel content.

overs obtained in the NiAlCO₃-HTlc⁹ system is low, the conversions of hydrocarbons and selectivity for ketone are comparable with the ZnCrCO₃-HTlc system; hence a detailed study has been undertaken with this system also. The MgAlCO₃-HT⁹ system, devoid of any oxidizing metal, has shown very little activity, and could be considered as a control experiment in our studies.

The calcined catalysts have shown better activity when compared to the uncalcined samples (Table II, entries 1 and 2).

In the present system the catalyst is heterogeneous and hence can be easily separated from the reaction medium by simple filtration and reused. One of the salient features of thermally treated HTlc species is the memory effect, which allows the formation of original hydrotalcite species, when in contact with solution containing various anions. The recovered catalyst is also found to show diffuse hydrotalcite pattern in XRD. The reusability of this recovered catalyst for 4 recycles with consistent activity and selectivity has been



Scheme I

demonstrated (Table I, entry 1). The chromium content of the reused catalyst has remained constant as is evident by the analysis of both fresh and used catalysts by atomic absorption spectroscopy. These results show that there is no metal leaching during the reaction.

A temperature of 130°C was found to be optimum for obtaining good conversions and selectivity. Reactions conducted at lower temperatures resulted in poor conversions, whereas reactions conducted at higher temperatures resulted in higher conversions but selectivity for ketone was highly reduced, resulting in the formation of aromatic acids.

Increase in pressure (500 psi at 60°C) did not show any improvement in yield and also resulted in a number of side products.

The reactions conducted in various solvents like dioxan, DMF, THF, etc. resulted in oxidations of solvents themselves; hence neat reactions were preferred.

The plausible mechanism could involve a hydroperoxide intermediate which decomposes at 130°C to give the oxidized products (Scheme I).

On summing up, the present HTlc displayed advantages such as good conversion, good selectivity, memory effect allowing the reusability of the catalyst and consistent activity in the oxidation of benzylic hydrocarbons. Therefore, the said HTlc catalytic system could become a possible alternative to the conventional catalytic systems such as supported metal catalysts and mixed oxides, in future, especially in liquid-phase reactions.

Experimental Section

General procedure for the benzylic oxidation of hydrocarbons. The calcined HTlc (100 mg) was added to the hydrocarbon taken in a reaction flask and stirred at a temperature of 130°C for 48 hr in an oxygen atmosphere. The reaction mixture was then filtered, concentrated and column chromatographed to give the product. The products obtained were characterised by ¹H NMR (200

MHz), mass spectroscopy and compared with authentic samples.

Wherever reusability of the catalyst is mentioned (Table I, entry 1), the used catalyst was collected, dried thoroughly over vacuum/P₂O₅ for 18 hr and reused. Both the reused and fresh catalysts were analysed for chromium content by atomic absorption spectroscopy.

In case of fluorene (entry 4, Table I) which is a solid (m.p. 115°), the vapours collected at cooler part of the reaction flask tend to solidify. Hence constant scratching is required to ensure contact with the catalyst in liquid phase.

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