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SILICA-ALUMINA SUPPORTED TRANSITION METAL OXIDE CATALYST FOR ALKYLATION OF AROMATIC COMPOUNDS

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Abstract: Titanium oxide on silica-alumina support is described to be an efficient regenerable catalyst for alkylation of aromatic compounds with alkyl halides, alcohols and olefins, and the reaction is proposed to be initiated by the protonated metal active species present in the catalyst.

Transition metal oxides on silica and/or alumina supports[1] are used in some cases for olefin oligomerizations, polymerizations and for metathesis. Until recently, there existed no direct evidence regarding the nature of the active propagating centres in catalysts of this type. However, there were early reports of acid sites being present on these catalyst surfaces[2]. Our recent investigations on the mechanism of oligomerization of styrene[3] and castor oil fatty acid esters[4,5] over molybdenum oxide on silica-alumina gave compelling evidence for a protonated metal active species being present on the catalyst surface to initiate the reaction. In addition, the polymerization of ethene over Cr_2O_3/silica has been recently investigated to be initiated by H (or D) from the catalyst surface to form an ethyl group bonded to the Cr^{2+}-ion[6]. M-H species has been identified spectroscopically in a number of active catalyst systems[7,8]. It is thus likely that the protonated metal active sites could initiate other reactions which are catalysed by acidic catalysts like Lewis acids and mineral acids. Infact, many of the reactions of oligomerization and olefin metathesis catalysed by these catalyst systems often lead to side reactions including alkylation of the aromatic solvents which are popularly treated as cationic processes[9,10]. Our attempts to develop a transition metal oxide catalyst for alkylation of aromatic compounds resulted in a titanium oxide on silica-alumina catalyst providing promising results with a variety of alkylating agents like alcohols, bromides and olefins.

The reactions were carried out at 180°C in a continous column fixed bed glass reactor of 1" diameter. The reactants were premixed at an aromatic substrate to alkylating agent molar ratio of 1:3 and added dropwise into the reactor at a liquid hourly space velocity of 0.5. The reaction of isoprene with toluene was carried out in a batch process at 80°C in a three necked reaction flask, the isoprene to toluene volume ratio being 1 : 10. The products were identified by b.pt, IR, NMR and MS. The results are tabulated in Table I.

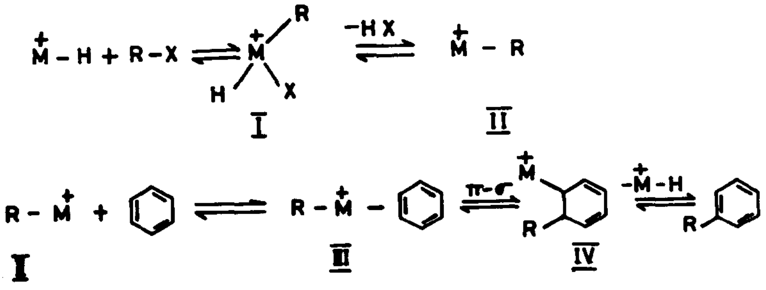
Table I: Yield of products during alkylation

Aromatic substrate	Alkylating agent	Product	% Yield *
Benzene	Ethyl bromide	Ethyl benzene	8
Benzene	Ethanol	Ethyl benzene	15
Benzene	n-propyl bromide	Propyl benzene	20
Benzene	n-propanol	Propyl benzene	20
Benzene	Isopropyl bromide	Isopropyl benzene	66
Benzene	Isopropanol	Isopropyl benzene	70
Benzene	n-butanol	n-butyl benzene	18
Benzene	Isobutanol	Isobutyl benzene	30
Benzene	t-butanol	t-butyl benzene	40
Toluene	Isopropanol	p-methyl isopropyl benzene	60
Chlorobenzene	Isopropanol	p-isopropyl chloro benzene	17
m-Xylene	Isopropanol	1,3 dimethyl 4-isopropyl benzene	80
Toluene	Isoprene	p-methyl p'-3(methyl-2-butenyl) benzene + Oligomer.	20

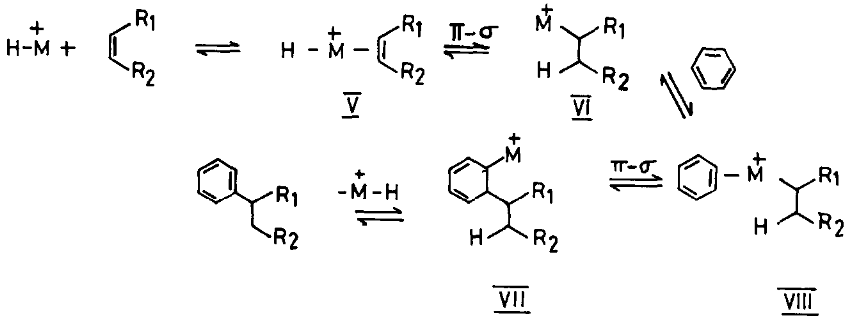
* The yield is from the amount of alkylating agent converted, when 0.16 moles of it is continuously fed into the reactor packed with 15 gms of the catalyst at a liquid hourly space velocity of 0.5.

There exist excellent experimental results suggesting the protonation of hetero and homogeneous transition metal catalyst systems^{7,8,2}. Further, our previous experimental results provided evidence for the presence of protonated metal active sites on transition metal oxide catalyst supported on silica-alumina base^{3,4,5}. These active sites have been shown to initiate the oligomerization reactions and based on this finding, a general mechanism for transition metal catalysed oligomerization reactions was previously proposed^{4}. Availability of the $\overset{+}{M}$-H species, π-complexation of the olefin to this active species & π-σ rearrangements are the key steps in this mechanism. The alkylation reaction being promoted by the identical catalyst system, the mechanism of the reaction, could be proposed to take place as follows:

For halides and alcohols:



Similarly, for Olefins:



The nucleophilicity of the aromatic substrate predictably influences the ease of alkylation reaction. Alkyl substituted benzenes undergo alkylation with higher yield compared to benzene, and chlorosubstituted benzene undergoes alkylation with much lesser yield (table I). This is expected from the proposed mechanism, as the protonated metal attacks the aromatic compound and the higher the nucleophilicity of the aromatic compound, the greater will be the stability of the intermediates III,IV,VII & VIII. The electron donating ability of the alkylating moiety is also expected to have effect on the alkylation reaction and increased electron donation is expected to increase the stability of all the intermediates I-VIII. Thus the nature of the alkylating agent could affect the ease of the reaction in the order tertiary > secondary > primary. However, table I shows the reactivity order to be secondary > tertiary > primary indicating possible additional competitive steric factors influencing the reaction. The reaction could also depend upon the percentage of transition metal oxide on the support, the number of active sites, and also on other factors like porosity, surface area etc. which are normally associated with heterogenous catalysis. The catalyst is prepared by coprecipitation of silica gel, aluminium hydroxide and titanic acid from a solution of sodium silicate, aluminium sulphate and titanium tetrachloride by first acidification and then neutralisation with ammonium hydroxide. The resulting gel is washed free of inorganic ions using distilled water, extruded into an average size of 3mm dia & 15 mm length and dried at 100°C for 12 hours. This is sintered at 650°C for 6 hours. The catalyst employed for the present set of experiments contains 66% silica, 33% aluminium oxide and 1% titanium oxide.

The activity of the catalyst decreases regularly with conversion and the potential utility of these catalysts is enhanced by their regenerable nature. The catalyst is reactivated by further sintering at 650°C in a stream of oxygen. Figure I indicates the life of the catalyst in the first run, where the percentage conversion is plotted versus the amount of alkylating agent, which is being fed continuously. Figure II and III indicate the same plot after the first and second regenerations. These results indicate only negligible reduction in the activity of the catalyst after two regenerations. Similar supported catalysts retain their activity for several regenerations and the experiments are continued in this case to establish the catalytic activity with respect to regenerations.

This and possible similar catalysts are expected to have wide industrial utility and employment due to their ease of separation and purification of the product, high catalytic activity and efficiency due to their easy regenerable catalytic activity.

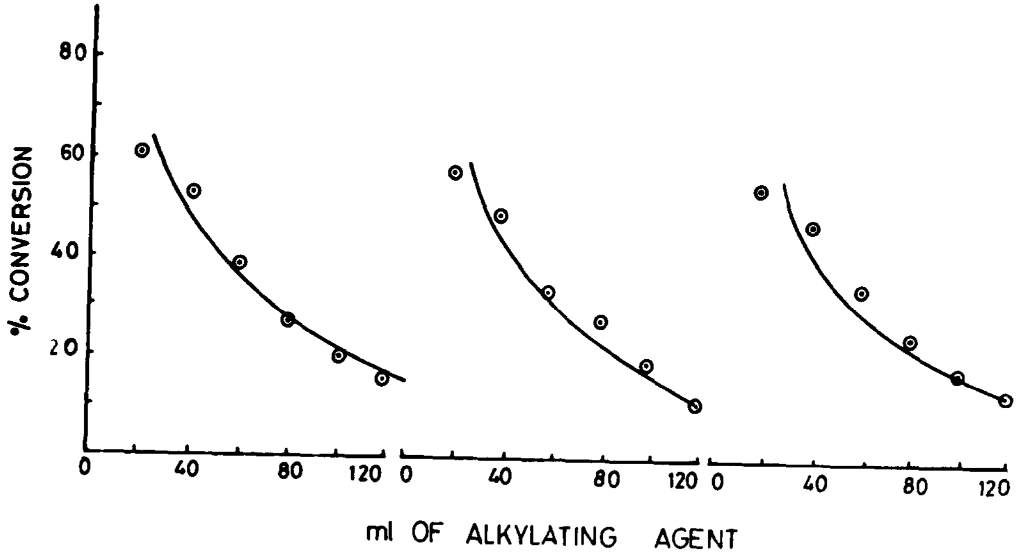


Fig I　　Fig II　　Fig III

Plot of percentage conversion vs. volume of isopropyl bromide over the fresh catalyst (Fig I) and after first (Fig II) and second regenerations (Fig III).

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