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Letter

Mechanism of aniline alkylation over vanadia and supported vanadia

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Abstract

The mechanism of aniline alkylation reaction over solid acid catalysts viz., montmorillonite K10, silica and supported vanadia catalysts is explained on the basis of presence of Brønsted and Lewis acid sites.

Keywords: Alkylation; Aniline; Acidic sites; Mechanism; Solid acids; Silica; Montmorillonite; Supported catalysts; Vanadia

Ecofriendly solid acid catalysts are the answer for alkylation reactions involving corrosive and polluting traditional Lewis acids and mineral acids. In light of this we [1–6] have studied aniline alkylation reaction over many solid acid catalysts like oxides, mixed oxides, zeolites and clays. Over the solid acid catalysts studied [8,9], it is observed that *N*-ethylaniline is the main product and the reaction depends on acidity of the catalysts, though, the strength of acid sites responsible for the reaction is still a matter of discussion. This has motivated us to propose a mechanism for the formation of *N*-ethylaniline over the surface of a solid acid catalyst. We have tried to explain the mechanisms based on the experimental results obtained in catalyst systems studied and draw inference on the type of acid sites responsible for the reaction.

It has been proposed in the literature that, *N*-alkylation of aniline takes place by dehydrogenation of alcohol to carbonyl, followed by the

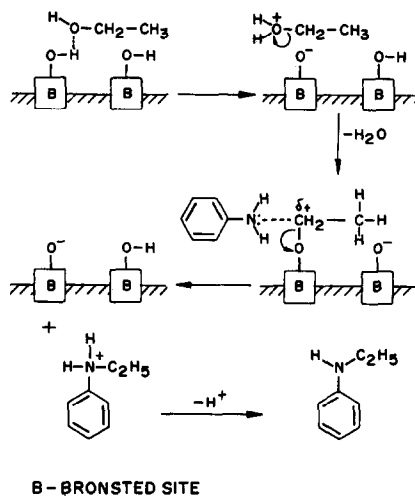
formation of an imine, which is finally hydrogenated to alkyl aniline [10,11]. Alkylation with alcohols and haloalkanes proceed analogously to those with olefins, by generation of electrophiles from heterolysis of carbon–oxygen or carbon–halide bonds [12]. For aniline alkylation, we envisage a situation where the presence of both the types of acid sites on the catalyst surface would enhance the product formation.

The acidity of the catalysts was measured by *n*-butylamine titrations as well as by stepwise temperature programmed desorption (STPD) of ammonia. The desorbed ammonia was estimated by back titration with an acid [4]. We have also carried out STPD of ammonia using Micromeritics Pulse Chemisorb 2700 unit. The details of the experiment are given in our paper [7]. Vapour phase aniline alkylation was carried out over the catalysts as described earlier [6]. The results of a typical experiment on the catalysts is given in Table 1. The products formed contained mainly *N*-alkylated aniline. Reaction is a sequential one,

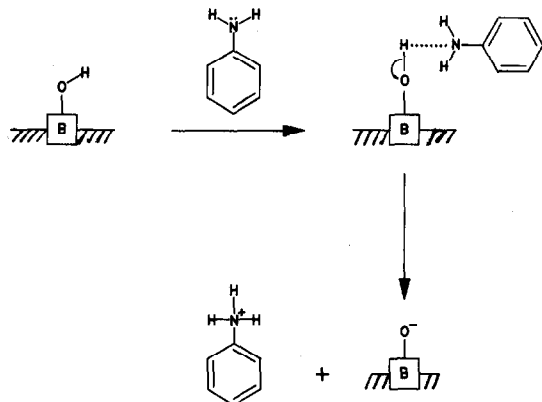
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Table 1
Aniline alkylation at 673 K, $12 \text{ cm}^3 \text{ h}^{-1} \text{ g}^{-1}$ catalyst and 1 bar

Catalyst	Total NH_3 , desorbed (353–723 K) $\text{mmol g}^{-1}/10^{-2}$	Aniline conversion/%	Selectivity/%		
			NEA	NNDEA	Others
SiO_2	2.41	35	81	14	5
V_2O_5	0.51	35	70	20	10
Montmorillonite K10	20.28	77	64	25	11
$10\text{V}_2\text{O}_5\text{-SiO}_2$	34.88	83	72	21	7
$10\text{V}_2\text{O}_5\text{-Mont K10}$	47.10	97	48	37	15



Scheme 1. Aniline alkylation on catalyst having only Brønsted acid sites.



Scheme 2. Aniline alkylation on catalyst having only Brønsted acid sites.

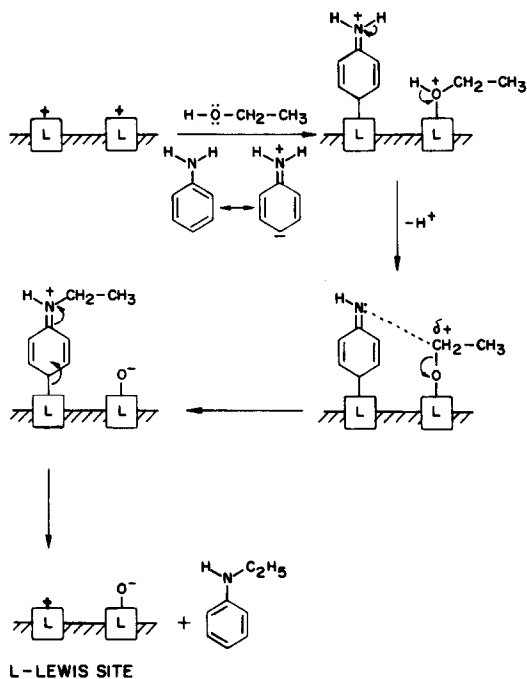
with N,N' -diethylaniline being formed by alkylation of N -ethylaniline (NEA).

The reaction mechanisms have been proposed, for the formation of primary product, viz., NEA over the solid acid catalysts under different conditions of the catalyst containing:

1. only Brønsted acid sites;
2. only Lewis acid sites;
3. both Brønsted and Lewis acid sites.

Scheme 1 depicts aniline alkylation on catalyst having only Brønsted acid sites. The suggested Scheme 1 is very similar to the situation present in silica catalyst. Weak Brønsted acidity of silica has been well established [13]. Dehydration of alcohol involved in the reaction helps in maintaining slight acidity of silica even at high reaction temperature of 673 K. Brønsted acidity helps the reaction by dehydrating the alcohol to give carbocation. On the other hand aniline gets protonated to anilinium ion bringing down the rate of reaction (Scheme 2). This may be the reason for comparatively low aniline alkylation activity of silica. However, the absence of deactivation of silica surface for the reaction period of 4 h indicates that the anilinium ion may be washed down by the excess of alcohol used in the feed. The activation of ethanol is initiated by hydrogen bonding between Brønsted hydroxyl proton and oxygen of alcohol. It leads to the alcohol protonation and dehydration, releasing the carbocation. Formation of NEA on silica surface may be explained by the electrophilic substitution of the released carbocation, on the unadsorbed base molecule, i.e. aniline (Scheme 1).

Scheme 3 describes the reaction on a catalyst surface possessing only Lewis acid sites. Aniline being a stronger base than ethanol gets adsorbed preferentially on the Lewis site. However, the presence of a large excess of alkylating agent, does not rule out the possibility of ethanol getting adsorbed on the acid sites. Having a catalyst sys-



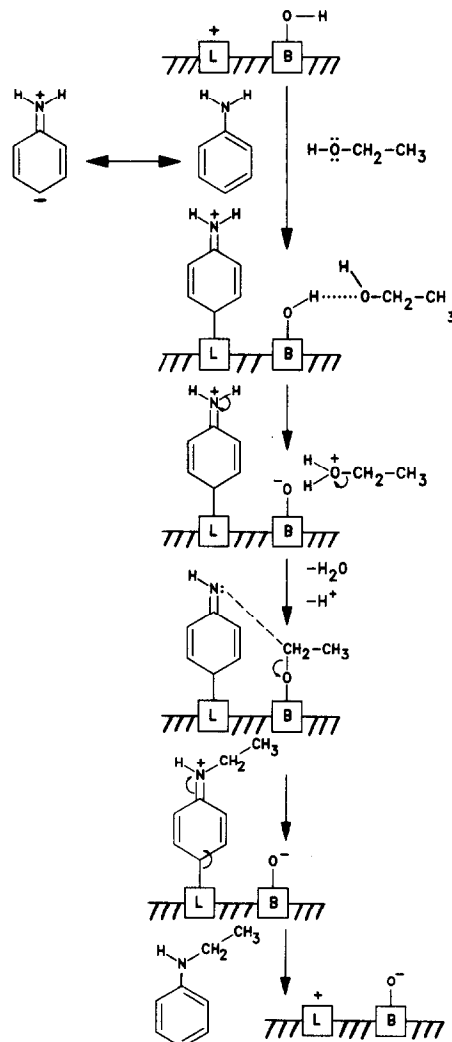
Scheme 3. Aniline alkylation on catalyst having only Lewis acid sites.

tem with exclusively Lewis sites is rather unlikely under the reaction conditions involving dehydration of alcohol. Even if the catalyst does not possess Brønsted hydroxyls to start with, it may eventually develop them during the course of alkylation.

Mechanism of aniline alkylation on a catalyst system containing both Lewis and Brønsted sites is depicted in Scheme 4. Aniline being a stronger base than ethanol, gets preferentially adsorbed on Lewis sites, while high electronegativity of oxygen of ethanol leads to hydrogen bonding with hydroxyl proton of Brønsted sites. Protonation of alcohol, dehydration and subsequent formation of ether of the released carbocation with the conjugate base of Brønsted acid site may follow. On the Lewis site, the adsorbed aniline loses a proton to balance the positive charge developed on the nitrogen. The high electronegativity of oxygen in the ether linkage results in the development of a partial positive charge on the C moiety of the ethyl side chain. The lone pair of electrons on nitrogen attract the alkyl side chain, initiating heterolytic cleavage of polar O–C bond and the shift of alkyl carbocation to nitrogen.

The three catalyst systems (Table 1), viz., 10 wt% vanadia impregnated silica (10V–SiO₂), montmorillonite K10 and 10 wt% vanadia impregnated montmorillonite K10, are believed to possess both Lewis and Brønsted acidity. Aniline alkylation on these catalyst systems is proposed to go by Scheme 3.

V₂O₅ is weakly acidic. Ammonia STPD measurement indicated acidic sites on V₂O₅ which desorbed ammonia only in the temperature region 353 to 423 K. Weak acidity of bulk V₂O₅ has been reported [14]. Bulk V₂O₅ does not show a catalytic activity comparable to the supported vanadia. However, when V₂O₅ was impregnated on SiO₂,



Scheme 4. Aniline alkylation on catalyst having both Brønsted and Lewis acid sites.

a well dispersed catalyst system with vanadia probably in (+IV) oxidation state was obtained [15] showing high catalytic activity.

Acidity as measured by STPD of ammonia shows an increase in acidity on vanadia impregnation on SiO₂. 10V–SiO₂ shows almost 14 times more acidity than SiO₂. Creation of new acid sites with higher strength on V₂O₅ impregnated SiO₂, than pure silica or bulk V₂O₅ have been identified by microcalorimetric measurements [14]. In fact deposition of various oxides on silica seems to enhance the acidity of the catalyst system [16]. Ammonia adsorption by infrared spectroscopy using the diffuse reflectance mode (DRIFT) of V₂O₅/SiO₂ catalyst has shown it to be a medium acidic material possessing both Lewis and Brønsted acid sites of equal strength [17]. These sites seem to be of suitable strength and number, for aniline alkylation enhancing the conversion compared to silica.

Montmorillonite is a layered aluminosilicate. Isomorphous substitution of Si(IV) by Al(III) in tetrahedral layers of montmorillonite is responsible for both Lewis and Brønsted acidity. The excess negative charge on the oxygen is delocalised over the whole clay surface by simple proton hops. Presence of interlamellar cations to maintain electroneutrality of the layers add to Brønsted acidity by polarising water molecules pinched between negatively charged oxygens of the sheet and positively charged counter ions [18]. Facile proton movement helps in dehydroxylation at Al(III) and the formation of Lewis sites above 363 K [19]. Acid activation not only increases the surface area of clay but also the acidity by replacing interlamellar cations with protons and by leaching Al(III) from the octahedral layer [20]. Protons add to Brønsted acidity and Al(III) to Lewis sites. Montmorillonite K10 is a commercially acid activated clay. It has its laminar structure intact to a considerable extent [21]. FTIR studies on pyridine adsorbed montmorillonite K10 showed the presence of both the types of acid sites [22]. For commercial clay catalysts, Cseri et al. [23] have given the relative intensities of the I R bands corresponding to Lewis and

Brønsted acidity on montmorillonite K10 to be 1.91:2.23.

Vanadia impregnation on montmorillonite K10 increases the acidity of the system. But a proportional increase in the alkylation activity is not observed. Probably the acid sites present on montmorillonite K10 itself are sufficient for the reaction and any additional sites created by vanadia impregnation do not drastically affect the reaction unlike in the case of vanadia–silica.

In conclusion, it may be said that:

1. In presence of Brønsted sites carbocation is formed, but the aniline molecule gets protonated reducing the effective concentration of reactant.
2. Having a catalyst system with exclusively Lewis sites is unlikely for the alkylation reaction which involves dehydration of alcohol.
3. The presence of a combination of Brønsted and Lewis acid sites on the catalyst surface favours aniline alkylation reaction.

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