Aniline alkylation with ethanol over zeolites and vanadium modified zeolites prepared by solid state exchange method

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Abstract

Vapour phase aniline alkylation was carried out over HX, HY, HZSM-5, *H*-mordenite and over zeolites solid state ion-exchanged with vanadium. Calcination of V_2O_5-zeolite mixture in nitrogen reduced V_2O_5 to VO^{2+} ion and these species migrated into the cationic positions in the zeolite channels. Three-dimensional and mildly acidic zeolites (ZSM-5, Y and X) showed higher catalytic activities for aniline alkylation than did unidimensional and strongly acidic mordenite. Addition of vanadia enhanced the alkylation activity of all the four zeolites studied. © 1998 Elsevier Science B.V.

Keywords: Aniline alkylation; Zeolite; V_2O_5; Solid state ion exchange; Acidity by STPD of ammonia; Mechanism of alkylation

1. Introduction

Alkylanilines are valuable intermediates for the manufacture of pharmaceuticals, drugs, dyes and agrochemicals. These compounds may be prepared by catalytic alkylation of aniline with various alkylating reagents: alcohols [1,2] dimethyl carbonate [3] and olefins [4]. Most of the projects carried out so far have used methanol as an alkylating reagent [5–9]. There are only a few reports available in the literature [10], mainly our own references on aniline alkylation over zeolites using ethanol as an alkylating reagent. We have also described the use of several oxides [11] mixed oxides [11,12] clays [13,14] and zeolites [15–17] for producing alkylanilines selectively under different experimental conditions.

Vanadium oxide on supports acts as a good catalytic system for alkylation of aniline [11,12]. It has been suggested that a type of interaction exists between V_2O_5 and the support, leading to the formation of an active and selective monolayer of vanadia species spread over the support, enhancing the acidity and activity [13,14]. Previous studies revealed that the major factor influencing the activity and selectivity is the acidity of the solid acid catalysts. For a zeolite with a given structure, the selectivity towards N- and C-alkylation depends on the acido-basic properties.

Studies on alkylation of aniline with methanol by Kikhtyanin et al. [6] have shown that the catalytic properties are strongly affected by the structure of the zeolite, in addition to its acido-basic character. Faujasite zeolites X and Y, mordenite and MFI widely differ in their channel structure, Si/Al ratios and acidity distribution. Therefore, it is interesting to

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compare these zeolites in reference to their catalytic properties. We have chosen aniline alkylation reaction for this study. The zeolites were modified with vanadium by a solid state exchange method. The modified zeolite catalysts were characterised by XRD, ESR and surface area measurements. Incorporation of vanadium ions into the cationic sites of HZSM-5 has been observed when the solid state reaction proceeded between the zeolite and the corresponding salts or oxides at elevated temperatures [18,19]. There are only a few reports on VZSM-5 prepared by isomorphous substitution for aniline alkylation with methanol [7]. Vanadium zeolites modified by solid state exchange have been studied for the first time for aniline alkylation with ethanol and the results are reported here. A mechanism of aniline alkylation over zeolites and vanadium-modified HZSM-5 zeolites has been proposed in the present investigation.

2. Experimental

2.1. Catalyst preparation

Zeolites HX, HY, HM and HZSM-5 used in this study are of commercial origin as shown in Table 1. Zeolites containing 5% vanadium (V_2O_5=8.9%) were prepared by a solid state exchange method, in which a physical mixture of the two was thoroughly ground in a mortar for 1 h and then heated in a nitrogen flow (50 cm^3 min^{-1}) at 673 K for 7 h.

2.2. Characterisation

The calcined samples were characterised by XRD, ESR and surface area measurements. XRD patterns of

the samples were taken using a Philips diffractometer (PW-1051) and CuK_α radiation (λ=1.54014 Å). ESR spectra were taken at room temperature with a Bruker ESR 200D SRD X-band spectrometer at a microwave frequency of 9.7 GHz and a modulation frequency of 100 KHz. Before taking the spectra, the powdered sample (Ca. 30 mg) was dried overnight at 393 K in an impurity-free ESR tube.

The surface area of the sample was measured by single point method on a Micromeritics pulse chemisorb 2700 unit using nitrogen as adsorbate at 77 K. The sample was preheated at 723 K for 3 h before nitrogen adsorption.

2.3. Acidity measurements

Surface acidity was measured by ammonia adsorption–desorption technique using a Micromeritics pulse chemisorb 2700 unit. The sample (Ca. 125 mg) was degassed at 723 K for 3 h in helium flow before ammonia adsorption. A known volume of ammonia corresponding to the loop volume was passed over the catalyst in several pulses at 393 K till it got saturated. The saturation of the sample with ammonia was evidenced by the appearance of a constant peak area recorded on a strip chart recorder. The sample was flushed with helium for 30 min at 393 K to remove any physically adsorbed ammonia. The desorption temperature of the sample was then raised slowly in three steps (A, B, C) representing three temperature regions: 393–523, 523–623, 623–723 K respectively. Ammonia amounts desorbed in these temperature regions were taken as a measure of weak, medium and strong acid sites. The detailed procedure of the stepwise temperature programmed desorption (STPD) of ammonia has been described in our earlier paper [14].

Table 1
Physical parameters of the zeolite and modified zeolites

Catalyst	Origin	SiO_2/Al_2O_3	Effective pore diameter (A°)	Surface area (m^2g^{-1})	
				Zeolites [a]	V-zeolites [b]
HX (Union carbide)	Linde	4.74	7.9	900	700
HM (Norton)	Zeolon 100H	10	8.9	440	368
HY (PQ Corpn)	CBV 720	26	7.4	720	578
HZSM-5 (PQ Corpn)	CBV 3020	35	5.5	397	368

[a] As given by the supplier.
[b] Measured by us.

2.4. Catalytic activity

Catalytic experiments were carried out at atmo-
spheric pressure on Ca. 500 mg of sample taken in
a tubular down flow glass reactor. The catalyst sample
was preheated for 4 h at 723 K in nitrogen flow.
Aniline–ethanol mixture of 1:10 mol ratio was fed
from the top of the reactor using a calibrated motor-
ized syringe. Nitrogen (50 cm^3 min^{-1}) was used as a
carrier gas. The reaction was carried out at 673 K for
4 h, at a feed rate of 12 cm^3 aniline–ethanol mixture
h^{-1} g^{-1} of the catalyst. The liquid products were
collected every 45 min and analyzed by a Chemito
3865 gas chromatograph with an 8 ft. SS column of
1/8″ o.d packed with 10% Apeizon L treated with 2%
KOH on Chromosorb AW (80/100). The alkylated
products were identified as N-ethylaniline (NEA),
N,N-diethylaniline (NN'DEA) and others.

3. Results and discussion

3.1. Physical characteristics

Physical characteristics of the samples are given in
Table 1. Zeolites HX and HY possess larger surface
area than those of HM and HZSM-5 zeolites. The
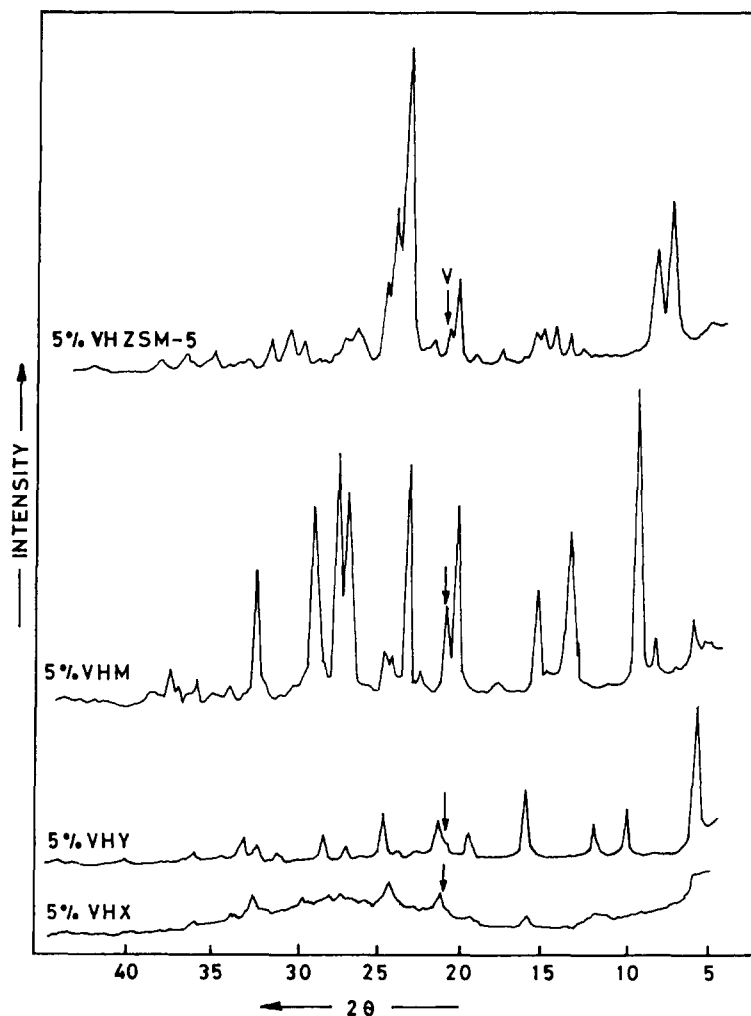surface area of the samples decreases on vanadia

Fig. 1. XRD patterns of vanadium-modified zeolites.

addition, suggesting that the oxide disperses over the zeolites and blocks the zeolite pores.

3.2. XRD

XRD patterns of the vanadium modified zeolites are given in Fig. 1. Addition of 5% vanadium (8.9% V_2O_5) to the zeolites did not alter the structure of zeolites, and the spectra showed the characteristic peak of vanadia around $2\theta = 20.25$. The intensities of the zeolite peaks in HX and HY are relatively small compared to HM and HZSM-5. Qualitatively, the intensity of vanadia peak was more in HM than in HX, HY and HZSM-5. Vanadia may be present as small particles in HX, HY and HZSM-5. In the case of HM, relatively more vanadia may remain on the external surface as large crystallites.

3.3. ESR

ESR spectra of vanadium-modified zeolites are shown in Fig. 2. Calcination of mechanical mixtures of V_2O_5 with zeolites at 673 K in nitrogen flow resulted in the appearance of weak V^{4+} esr signals at room temperature. This is in contrast to V_2O_5/SiO_2 and V_2O_5/Al_2O_3 systems containing nearly 5–10 wt.% vanadia, where the hyperfine splitting is well resolved [11,12]. It has been reported in the literature that the preparation of vanadium-modified zeolites by solid state exchange method results in hyperfine splitting [20] caused by the interaction of a free electron of V^{4+} ($3d^1$) and nuclear magnetic moment of ^{51}V nuclei ($I = 7/2$) and to the anisotropic effect of the vanadium complex in the magnetic field. This type of signal has been attributed to VO^{2+} ions embedded in X and Y zeolites and to VO^{2+} ions in thin V_2O_5 layers supported on various inorganic carriers [20,21]. In this case even though our esr spectrum is not well resolved because it is taken at room temperature, we presume that a kind of interaction takes place during the process of the preparation of V_2O_5-modified zeolites by solid state ion-exchange method. We could get a better resolved esr spectra with hyperfine splitting for 10% vanadium loading (17.80% V_2O_5). The V_2O_5 HZSM-5 showed a better esr spectrum than that of V_2O_5 HM. This may be due to the reason that, in high
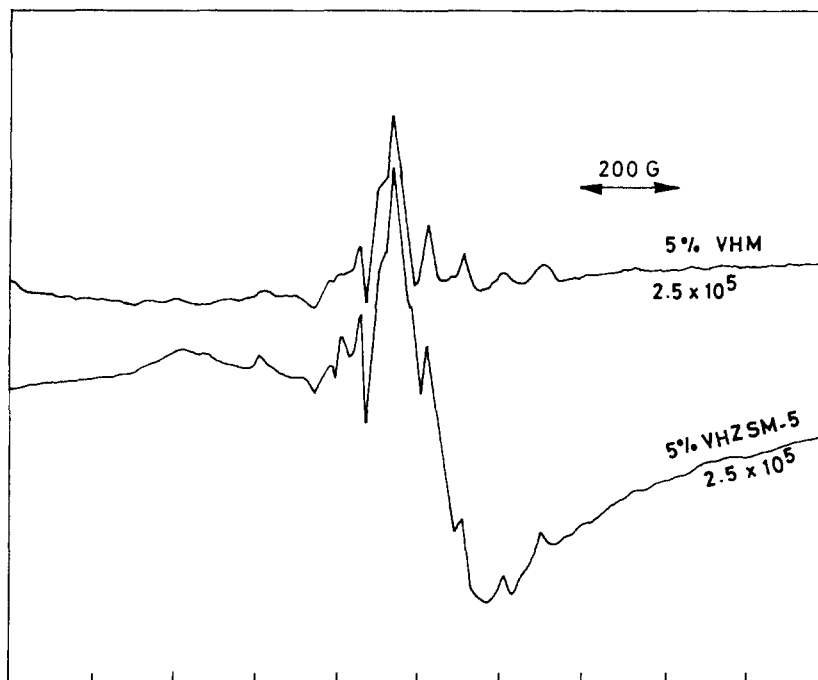

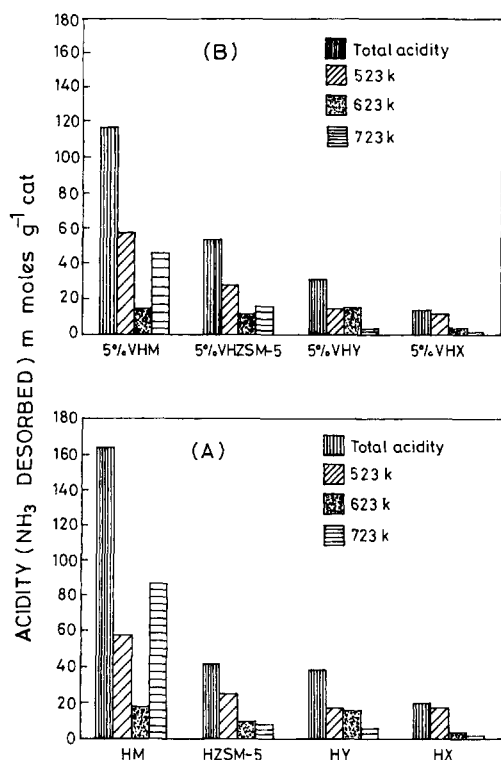Fig. 2. ESR spectra of vanadium-modified HZSM-5 and HM zeolites.

Fig. 3. Acidity of (A) zeolites (B) vanadium-modified zeolites. [|||]
Total acidity [///] 523 K, [••] 623 K, [≡] 723 K.

temperature programmed desorption (STPD) of ammonia. *H*-mordenite shows high total acidity. The numbers of both weak and strong acid sites are also more than on other zeolites. A similar observation is reported by Komorek et al. [20] The acidity of the zeolites measured follows the order HM>HZSM-5>HY>HX. Addition of vanadia to zeolite generally decreased the acidity of each zeolite, and the decrease was most effective for mordenite. On the other hand, the acidity of HZSM-5 increased slightly on vanadia addition. Calcination of oxide–zeolite mixture in nitrogen leads to the reduction of some V_2O_5 to VO^{2+} species, which may stabilize in/or on the zeolite as a result of V_2O_5 and zeolite interaction [22]. The VO^{2+} ion migration into the zeolite reduces the number of structural protons, resulting in a considerable decrease in acid site concentration. At the same time, new acid sites may also be created as a result of polyvalent ion location in the coordinatively unsaturated environment [23]. The formation of VO^{2+} species and their stabilization has also been noticed in V_2O_5/SiO_2 and V_2O_5/Al_2O_3 systems [11,12].

4. Catalytic activity

The catalytic activity and selectivity for aniline alkylation over various zeolites are shown in Fig. 4(a) and (b). As shown above *H*-mordenite possessed higher acidity in all the three strength regions than other materials. However, it showed almost no catalytic activity commensurate with either total or strong acidity. Kikhtyanin et al. [6] reported that the widepore zeolites, although possess strong Bronsted and Lewis acid sites, they do not show any increase in the alkylation of aniline with methanol. Recent reports on STPD of NH_3 and aniline alkylation with ethanol on Mont K10-supported vanadia catalysts reveal that only weak to moderate acid sites are required to catalyze this reaction. The presence of surplus acidity does not alter the activity, and there is no linear relationship between acidity and activity [14]. It is probably just enough to have weak/medium acidity to start the reaction, and the acid sites may be self-generating, especially with alcohol as the alkylating agent. An excess of strong acidity may
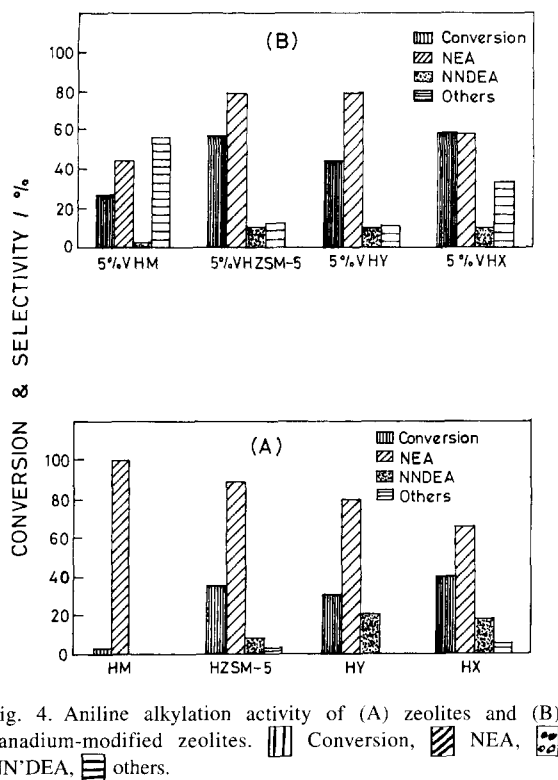
silica HZSM-5, the distance between the Al atoms in the framework is large, whereas in *H*-mordenite, the dipole–dipole interaction between closely arranged V^{4+} cations results in not well resolved hfs in esr spectrum. Heat treatment of oxide and zeolite mixture in nitrogen leads to the reduction of some V_2O_5 to VO^{2+} species which are stabilised in and/or on the zeolite [22]. VO^{2+} species formed may be present on the terminal Si–OH groups of the outer zeolite crystal and on the cationic site of zeolite, where they replace structural protons. However, formation of vanadyl complexes in the second vanadium surface layers similar to those found on inorganic carriers cannot be excluded at higher vanadium oxide loadings.

3.4. Acidity

Fig. 3(a) and (b) gives acidity of zeolites and vanadia-modified zeolites as measured by stepwise

Fig. 4. Aniline alkylation activity of (A) zeolites and (B) vanadium-modified zeolites. ⦀ Conversion, ▨ NEA, ⊡ NN'DEA, ▤ others.

be disadvantageous, as it may cause cracking of alcohol and hence some would not be available for the reaction. Inspite of the differences in acidity, HX, HY and HZSM-5 showed almost the same activity, with a marginal increase in the case of HZSM-5. The above results indicate that the three-dimensional framework zeolites (ZSM-5, HX and HY) with mild acidity are more suitable for aniline alkylation compared to unidimensional framework H-mordenite having more strong acidity. The formation of N-alkylanilines could possibly proceed easily in intersections of zeolite channels with geometrical dimensions larger than those of pore openings.

Vanadium-modified HZSM-5 showed the enhanced acidity and catalytic activity. VHX, VHY and VHM, in spite of a decrease in acidity mainly in the strong region (shown by 723 K desorption in STPD), showed an increase in alkylation activity. This indicates that reduction of strong acid sites enhances the alkylation activity. The product selectivities are

similar to the observations reported earlier [12,13]. At low conversions, NEA is formed, and at high conversions NN'DEA and other products are formed. The catalytic activity is maintained up to 5 h for HY and HZSM-5 zeolites and V_2O_5 HY and V_2O_5HZSM-5, whereas V_2O_5HY and V_2O_5HM deactivated with time on stream (Fig. 5). This could be due to the formation of more C-alkylated products in these catalysts which act as coke precursors. The coke formed is deposited on acid sites of the zeolites, leading to decreases in the number of available active sites by site coverage or by blocking of pores. The unidimensional nature, and added to that, the presence of strong acid sites, may lead to easy deactivation and blocking in HM. Generally it is expected that strong acid sites are responsible for the formation of C-alkylated products. However, in the present case, even though addition of vanadia has decreased, the strong acid sites in HX and HM zeolites gave more C-alkylated products. This may be due to high aniline conversion in vanadia-modified HX and HM. Aniline alkylation under vapour phase conditions proceeds in a consecutive mechanistic pathway reaction. Generally at low conversion level, NEA is the primary product, and at high conversion levels, the secondary products, namely NN'DEA and C-alkylated products, are formed. Thus formation of more C-alkylated products at high conversions in vanadia-modified HX and HM was responsible for deactivation.

We have proposed a mechanism of aniline alkylation involving Bronsted and Lewis acid sites [24]. It has been proposed in the literature that N-alkylation of aniline takes place by dehydrogenation of alcohol, followed by the formation of an imine, which is finally hydrogenated to alkylaniline [25,26]. Here we propose a possible mechanism of aniline alkylation over zeolites and vanadium-modified zeolites.

In the case of zeolites [Scheme 1], the activation of ethanol is initiated by hydrogen bonding between Bronsted hydroxyl proton of the zeolite and oxygen of alcohol, followed by alcohol protonation and dehydration, releasing the carbocation. The electrophilic substitution of carbocation on aniline takes place, forming NEA. In the case of V-zeolites, VO^{2+} ion formed by the interaction of vanadia and zeolite has one ligand, a free oxygen atom of the
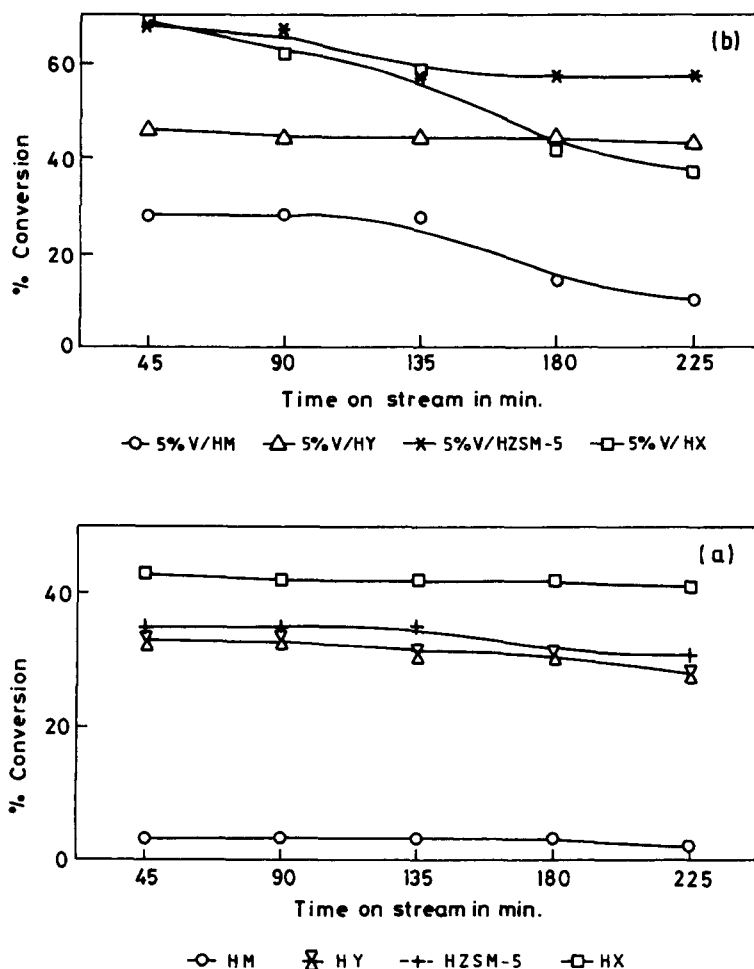
Fig. 5. Effect of time on stream (A) zeolites. ○ HM, ⊗ HY, + HZSM-5, □ HX. (B) vanadium-modified zeolites. ○ 5%V/HM, △ 5%V/HY, X 5%V/HZSM-5, □ 5%V/HX.

V=O bond in the Z direction, in addition with the others (in the xy plane), the framework oxygen atoms; these oxygen atoms may be from SiOH and AlOH or from two SiOH [Scheme 2]. The initial step in vanadium-modified zeolites is the activation of ethanol by V^{4+} ions. In the next step, adsorption of aniline on V^{4+} takes place, which leads to dehydration forming carbocation, and the lone pair of electrons on nitrogen attract the carbocation, forming NEA. Once NEA is formed, the consecutive reaction takes place. The V^{4+} once again helps in the formation of carbocation and the cycle continues.

5. Conclusions

Our study suggests that, in addition to the acid–base properties, geometric effects characteristic of each zeolite govern aniline alkylation. Three-dimensional and mildly acidic zeolites (HZSM-5, HY and HX) are more active than widepore unidimensional and strongly acidic H-mordenite. Vanadium addition certainly improves the activity by (i) blocking the strong acid sites and (ii) by creating V^{4+} species due to vanadium zeolite interaction which act as active sites for alkylation. V^{4+} species may also act as carbonium ion-creating sites, thereby helping aniline alkylation
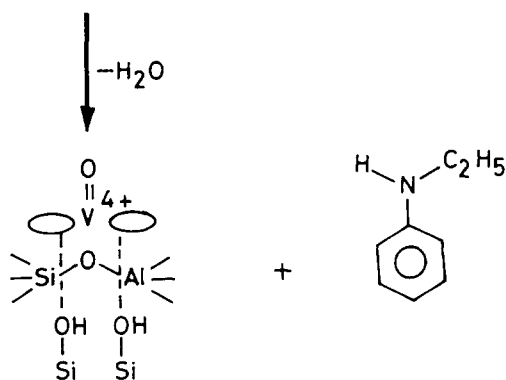
Mechanism of aniline alkylation over zeolites

Mechanism of aniline alkylation over vanadium modified HZSM-5 zeolites
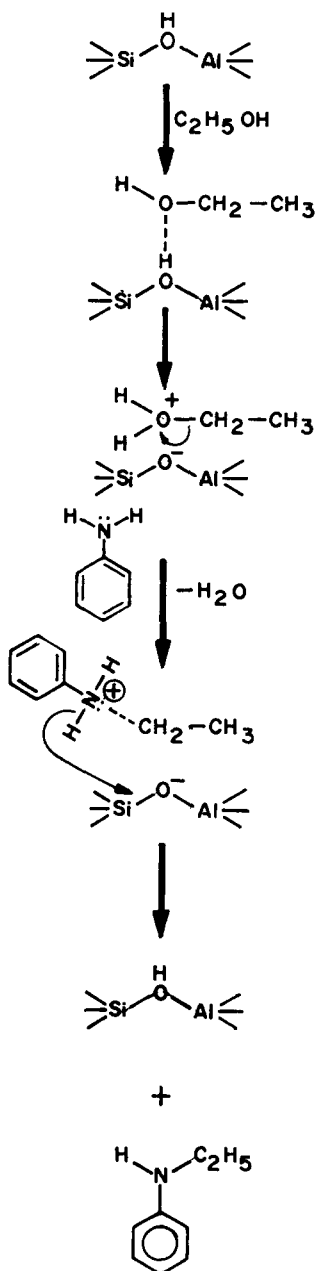
Scheme 1. Mechanism of aniline alkylation over zeolites.
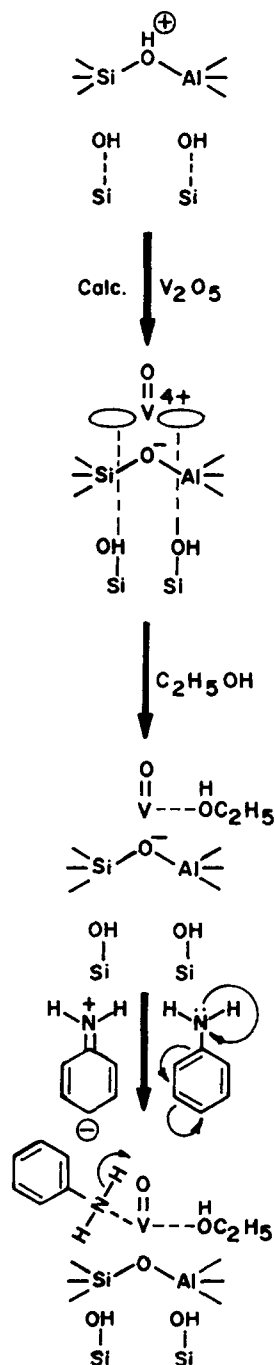
Scheme 2. Mechanism of aniline alkylation over vanadium-modified zeolites (continued on next page).

Scheme 2. (continued)

reaction. Only weak/moderate acid sites may be required to trigger the reaction.

Acknowledgements

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