

Enhanced Aniline Alkylation Activity of Silica-supported Vanadia Catalysts over Simple Oxides

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A very high aniline alkylation activity under vapour-phase conditions by silica-supported vanadia catalyst is reported.

Alkylation is an industrially important chemical reaction. For example, aniline alkylation gives *N*-ethylanilines, which are used as chemical intermediates in dyes and pharmaceuticals; the *C*-alkylated product, 2,6-diethylaniline, is a precursor for the herbicide, Butachlor. These reactions have generally been carried out under liquid-phase conditions using corrosive acids such as HF as the catalyst. To overcome the disadvantages of this expensive route, involving recycling the products, solid-acid catalysts such as alumina^{1,2} and more recently zeolites^{3,4} have been tried under vapour-phase conditions. No attempt has so far been made on the study of supported vanadia catalysts for the industrially important aniline alkylation reaction. This preliminary communication highlights the advantage of using supported vanadia for aniline alkylation over simple vanadium oxide and silica.

Vanadia is prepared by the calcination of ammonium metavanadate (NH_4VO_3) in air at 773 K for 6 h. Silica support is of commercial origin (AKZO Chemie Si2-5P). Different loadings of vanadia on silica (5–20 wt % of V_2O_5) are prepared by wet impregnation of the support with appropriate concentration of ammonium metavanadate in oxalic acid.

Catalyst particles of size 400–500 μm (ca. 0.5 g) are loaded in a vertical-flow glass reactor. The catalyst sample is activated in a nitrogen flow at 773 K for 3 h. Vapour-phase alkylation of aniline is carried out at atmospheric pressure by injecting from the top, a calibrated volume of aniline–ethanol mixture, (ratio 1:5 wt/wt). Ethanol-free aniline feed is maintained at $9 \times 10^{-3} \text{ mol h}^{-1}$ and nitrogen is used as a carrier gas. The reaction is carried out at 523–673 K. The liquid products collected in a trap are analysed by a gas chromatography [8 foot SS column, 1/8 inch o.d. packed with 10% Apizon L treated with 2% KOH on Chromosorb AW (80/100)]. The products contained mainly *N*-ethylaniline (NEA) along with *N,N'*-diethylaniline (*NN'*-DEA) and traces of *C*-alkylated products (others).

The BET (Brunauer, Emmett and Teller) surface area of bulk vanadia is 30 $\text{m}^2 \text{g}^{-1}$ and silica support is 190 $\text{m}^2 \text{g}^{-1}$. Addition of vanadia to silica up to 15 wt % of V_2O_5 has no significant effect on the surface area of the catalyst. However, 20 wt % catalyst shows a decrease in the surface area by 23%. These results suggest that vanadia may be present as a monolayer on silica support up to 15 wt% of vanadia and start forming crystallites beyond 20 wt%. Vanadia is crystalline according to X-ray diffraction (XRD) patterns showing the characteristic peaks. However, V_2O_5 - SiO_2 samples with vanadia content 5 to 20 wt% do not show any characteristic peak and are found to be highly amorphous. The absence of vanadia peaks even at high concentrations, though surprising,

may indicate a high dispersion of vanadia on the silica support. Even if the crystallites are formed, the particle size may be less than 4–5 nm which is below the detection limit of XRD.

The amount of oxygen chemisorbed on a pre-reduced vanadia surface was measured volumetrically following the method of Parekh and Weller.⁵ The dispersion of vanadia is calculated as the number of V_2O_5 molecules present on the surface from the number of chemisorbed oxygen atoms on the assumption that one oxygen atom corresponds to two vanadium atoms.⁶ The dispersion values listed in Table 1 indicate that 5 and 10 wt% vanadia-silica catalysts have dispersion in the range of 25–29% and at higher loading it decreases probably owing to agglomeration of vanadia crystallites.

All catalysts show increased activity with temperature, reaching a maximum around 673 K. Vanadia and silica are more or less equally active (around 35% conversion) at 673 K. Addition of vanadium to silica by the impregnation technique

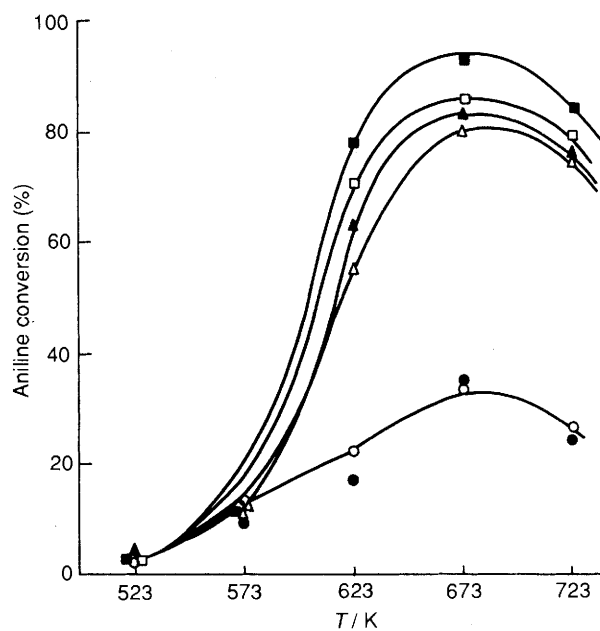


Fig. 1 Temperature effect on aniline alkylation at atmospheric pressure and feed rate of $9 \times 10^{-3} \text{ mol h}^{-1}$. —○— V_2O_5 ; —●— SiO_2 ; —△— 5% V_2O_5 : SiO_2 ; —▲— 10% V_2O_5 : SiO_2 ; —□— 15% V_2O_5 : SiO_2 ; —■— 20% V_2O_5 : SiO_2 .

Table 1 Comparison of conversion and selectivity of catalysts at 673 K

Catalyst	BET area/ $\text{m}^2 \text{g}^{-1} \text{ cat}$	Dispersion (%)	Conversion (%)	Selectivity (%)		
				NEA	<i>N,N'</i> -DEA	Others
V_2O_5	30	—	33	71	20	9
SiO_2	190	—	35	81	14	5
5% V_2O_5 : SiO_2	185	25	81	69	24	7
10% V_2O_5 : SiO_2	185	29	83	72	21	7
15% V_2O_5 : SiO_2	183	13	86	79	13	8
20% V_2O_5 : SiO_2	145	11	93	70	16	14

has undoubtedly improved the conversion level to 80–90%. The selectivity of these catalysts at 673 K are also compared in Table 1. As can be seen from Table 1, supported vanadia enhances conversion dramatically when compared with simple vanadia and silica. However, this does not have any significant effect on the selectivity. The selectivity of *N*-ethylaniline is between 70–80% on all the catalysts irrespective of the conversion. The selectivity for *N,N'*-diethylaniline and *C*-alkylated anilines did not change much.

Several investigations carried out on multiple mixed oxide catalyst systems reveal that there is an interaction at the solid–solid interface in the two-dimensional metal oxide overlayer on the second oxide surface.^{7,8} The physicochemical properties of the support material affect the dispersion of vanadia and hence the catalytic activity. A lot of effort has been expended to develop methods for the uniform dispersion of vanadium oxide as a monolayer on support materials.⁹ However, the study of the interface interaction between solids, dispersion and the type of active species available on the surface for catalytic activity is still a subject of great interest. A simple and logical explanation based on surface area, XRD and dispersion can be postulated at the present juncture. Pure vanadia and silica are more or less equally active. However, the disproportionate increase in the activity of silica-supported vanadia can only be attributed to a well-dispersed vanadium oxide species on the silica surface. The enhanced dispersion of vanadia results in the formation of V^{4+} species on the silica surface. This is evidenced by the appearance of hyperfine splitting in the ESR spectra of supported vanadia even at room temperature compared with bulk vanadia (unsupported), which gives only a singlet. It is believed that even though SiO_2 is relatively a non-interacting

support, a weak interaction probably exists between vanadia and SiO_2 with the formation of V–O–Si species. It may be deduced that the active species for the reaction may be the V^{4+} species resulting from the interaction between V_2O_5 and SiO_2 . A more detailed explanation based on the interaction between the two oxides and the acid–base properties awaits further investigation. It may however, be said that supported vanadia catalysts may be used for aniline alkylation under vapour-phase conditions in place of conventional acid catalysts such as HF and BF_3 . The present study is the first of its kind with respect to the use of silica-supported vanadia catalysts for aniline alkylation.

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