

Letter

Aniline synthesis from cyclohexanol and ammonia over mixed oxide catalysts

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Abstract

Aniline is obtained by amination of cyclohexanol followed by oxidative dehydrogenation over $\text{MoO}_3/\text{Al}_2\text{O}_3$, $\text{V}_2\text{O}_5\text{--}\text{MoO}_3/\text{Al}_2\text{O}_3$ and $\text{NiO--MoO}_3/\text{Al}_2\text{O}_3$ mixed oxide catalysts in the presence of ammonia and air in vapour phase at 623–723 K under atmospheric pressure. © 1998 Elsevier Science B.V.

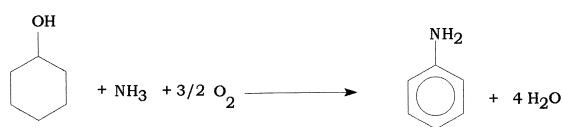
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Aniline is a starting material for the synthesis of many commodity chemicals like cyclohexylamine, alkyl anilines, acetanilide and diphenylamine. It can also be used in the production of rubber additives such as vulcanization accelerators and antioxidants [1]. Commercially aniline is synthesized by reduction of nitrobenzene in the presence of Fe/HCl or fixed bed hydrogenation over a nickel sulfide catalyst [2]. Aniline can also be synthesized by ammonolysis of chlorobenzene and phenol using suitable heterogeneous catalysts [3–5]. Limited yields of aniline are reported on CuX and CuY zeolites by ammonolysis of chlorobenzene [6]. Freeman and Unland showed that adsorption of benzene on zeolites withdraw electrons from aromatic nucleus making it susceptible to nucleophilic sub-

stitution [7]. Warawdekar and Rajadhyaksha studied amination of anisole and phenol over cation exchanged zeolite-Y and correlated the activity with acidity of the zeolites [8,9]. Rearrangement of *N*-methyl aniline over HZSM-5 and HY also yields aniline [10].

Aniline was also synthesized from cyclohexanol over Ni-based zeolites but most of the literature exists in the patented form [11]. Amination followed by non-oxidative dehydrogenation are the basic steps in this process. The non-oxidative dehydrogenation needs high temperature and reversible which limits the yields of the product. To overcome these thermodynamic limitations there is need to switch over to oxidative dehydrogenation which can be carried out on oxides of Mo, V, Sb, Sn and Bi [12]. In this work an attempt is made to synthesize aniline from cyclohexanol by amination followed by oxidative dehydrogenation over mixed oxide catalysts.

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The catalysts used in the present study are prepared by the conventional wet impregnation technique. Ammonium heptamolybdate is the source of molybdenum (Loba Chemie, GR grade), ammonium metavanadate is the source of vanadium (Loba Chemie, GR grade). Alumina in powder form (Harshaw Al-III-61, γ - Al_2O_3 , surface area $204 \text{ m}^2 \text{ g}^{-1}$; ACC, India, γ - Al_2O_3 , SA $104 \text{ m}^2 \text{ g}^{-1}$) is used as support. The V–Mo/ Al_2O_3 catalyst (Mo:V = 1:2 and total 15 wt%) was prepared by co-impregnation of alumina (SA $104 \text{ m}^2 \text{ g}^{-1}$) with stoichiometric solutions of ammonium heptamolybdate and ammonium metavanadate. Another 12 wt% Mo on γ -alumina (Harshaw, SA $204 \text{ m}^2 \text{ g}^{-1}$) was prepared by wet impregnation using requisite quantity of ammonium heptamolybdate. The impregnated samples were dried at 393 K for 12 h and calcined in air at 723 K for 6 h. A commercial Ni–Mo/ Al_2O_3 (Harshaw HT-500 E, SA $200 \text{ m}^2 \text{ g}^{-1}$) catalyst is also used in the present investigation. The BET surface area of the catalysts was determined by N_2 adsorption at 77 K. Surface acidity was obtained by adsorption of ammonia gas at 423 K by double isotherm method on a static volumetric high vacuum set-up [13]. Surface acidity results together with BET surface areas are presented in Table 1.

Catalytic tests were carried out in a fixed bed microreactor at atmospheric pressure as de-

scribed earlier [14]. For each run about 1 g of the catalyst sample was packed between two plugs of Pyrex glass wool inside the glass reactor (Pyrex glass tube 10 mm i.d.) and the products were analysed by gas chromatography using OV-17 column. Cyclohexanol was fed by a metering pump, air and ammonia were fed directly from pressure cylinders at a space velocity of 2500 h^{-1} with molar ratios of cyclohexanol, air and ammonia = 1:1.8:8.8. The reaction products were collected after establishing steady state conditions (about 2 h). The reaction was carried out in the temperature range 623 to 723 K and no loss in activity was observed upto 8 h on stream.

The activities and selectivities of various catalysts studied in the temperature range of 623 to 723 K are presented in Tables 2–4. For all catalysts conversion of cyclohexanol was found to increase with increase in temperature. However, the selectivity towards aniline was decreased and selectivity towards cyclohexene increased. As can be noted from Table 2 the maximum yields of aniline is observed at 698 K on Ni–Mo/ Al_2O_3 catalyst. On V–Mo/ Al_2O_3 catalyst the maximum yield of aniline is observed at 648 K (Table 3). However, on Mo/ Al_2O_3 sample the maximum yield of aniline is noted at 723 K (Table 4). More yields of aniline are observed only at higher temperatures on Ni–Mo/ Al_2O_3 and Mo/ Al_2O_3 catalysts when compared to V–Mo/ Al_2O_3 sample. More formation of cyclohexene was noted on V–Mo/ Al_2O_3 sample when compared to other samples, especially at higher temperatures. Very interestingly, more ammonia uptake sites are

Table 1
The N_2 BET surface area and ammonia uptake measurements on mixed oxide catalysts

Catalyst	Surface area ($\text{m}^2 \text{ g}^{-1}$)	NH_3 uptake ($\mu\text{mol g}^{-1}$)
NiO– MoO_3 / Al_2O_3 (Harshaw Catalyst)	200	421
V_2O_5 – MoO_3 / Al_2O_3 (V:Mo = 2:1; total 15 wt%)	174	453
12% MoO_3 / Al_2O_3	147	260

Table 2

Conversion and product selectivities in amination of cyclohexanol to aniline over NiO–MoO₃/Al₂O₃ catalyst

Temperature (K)	Conversion ^a (%)	Selectivity ^b (%)	Selectivity ^c (%)	Yield of aniline ^d (%)
623	25	71	25	18
648	37	60	35	22
673	45	60	36	27
698	58	93	3	54
723	56	32	63	18

^aConversion (%) = number of moles of cyclohexanol reacted × 100/number of moles of cyclohexanol fed.^bSelectivity = number of moles of aniline formed × 100/number of moles of cyclohexanol reacted.^cSelectivity = number of moles of cyclohexene formed × 100/number of moles of cyclohexanol reacted.^dYield of aniline = conversion^a × selectivity^b.

noted on this sample (Table 1). Cyclohexene formation from cyclohexanol is an acid catalyzed reaction [15].

The reaction was also carried out at different molar ratios of air and ammonia. The conversion of cyclohexanol and the aniline yield were maximum when the ammonia to air ratio was 5. Aniline was not produced in the absence of air. There was a drastic decrease in the yield of aniline for the deviation from the above molar composition of ammonia to air.

Amination of phenol to aniline over Cu–Y zeolite [9] involves interaction of ammonia with Bronsted acid sites and the aromatic ring with cationic sites leading to nucleophilic substitution. In other words, the substituent of the aromatic species interacts with the cation of the zeolite while the ammonia adsorbed on the Bronsted site replaces the hydroxyls with NH₂. The reaction occurs by a nucleophilic attack of the –NH₂ species on the aromatic nucleus. Similarly, in the amination of cyclohexanol am-

Table 3

Conversion and product selectivities in the amination of cyclohexanol to aniline over V₂O₅–MoO₃/Al₂O₃ catalyst

Temperature (K)	Conversion ^a (%)	Selectivity ^b (%)	Selectivity ^c (%)	Yield of aniline ^d (%)
623	17	80	15	14
648	22	74	21	16
673	23	48	47	11
698	24	40	55	10
723	86	8	87	7

^aConversion (%) = number of moles of cyclohexanol reacted × 100/number of moles of cyclohexanol fed.^bSelectivity = number of moles of aniline formed × 100/number of moles of cyclohexanol reacted.^cSelectivity = number of moles of cyclohexene formed × 100/number of moles of cyclohexanol reacted.^dYield of aniline = conversion^a × selectivity^b.

Table 4

Conversion and product selectivities in the amination of cyclohexanol to aniline over 12% MoO₃/Al₂O₃ catalyst

Temperature (K)	Conversion ^a (%)	Selectivity ^b (%)	Selectivity ^c (%)	Yield of aniline ^d (%)
623	11	24	71	3
648	12	54	40	6
673	14	67	28	9
698	16	40	55	6
723	36	38	56	14

^aConversion (%) = number of moles of cyclohexanol reacted × 100/number of moles of cyclohexanol fed.^bSelectivity = number of moles of aniline formed × 100/number of moles of cyclohexanol reacted.^cSelectivity = number of moles of cyclohexene formed × 100/number of moles of cyclohexanol reacted.^dYield of aniline = conversion^a × selectivity^b.

monia interacts with Bronsted acid sites facilitating nucleophilic substitution of $-\text{NH}_2$ in place of $-\text{OH}$ and hydrocarbon part is adsorbed on cationic site undergoing oxydehydrogenation. In the case of $\text{V-Mo}/\text{Al}_2\text{O}_3$ catalyst adsorption may be taking place on Mo site and the vanadium ion present by the side of Mo is carrying out the oxydehydrogenation step. Oxygen required for this process is supplied by air. This is probably a reason for non formation of aniline in the absence of air. Vanadium is known to catalyze oxydehydrogenation reactions [16].

Higher yields of aniline over $\text{Ni-Mo}/\text{Al}_2\text{O}_3$ catalyst may probably be due to higher surface area and greater dehydrogenating ability of Ni apart from higher acidity. The higher the acidity of the catalyst the greater is the interaction with ammonia leading to greater nucleophilic substitution. Nickel is found to have higher dehydrogenating ability over vanadium. When amination of cyclohexanol was carried out on a $10\% \text{V}_2\text{O}_5/\text{MgO}$ catalyst aniline is not formed; instead cyclohexanone in small amount is observed. This further proves that for amination acidic sites are required and a transition elements like V or Ni for oxydehydrogenation in presence of air is necessary.

Amination of cyclohexanol followed by oxydehydrogenation was carried out at lower temperatures unlike Ni-incorporated zeolites which need higher temperatures [11]. The Ni–

$\text{Mo}/\text{Al}_2\text{O}_3$ catalyst shows better performance than other samples.

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