

Letter

Vapour phase synthesis of quinoline from aniline and glycerol over mixed oxide catalysts

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Abstract

The vapour phase synthesis of quinoline from aniline and glycerol (1:2 mole ratio) in a single step was investigated over ZnO–Cr₂O₃, CuO–ZnO/Al₂O₃, MoO₃–V₂O₅/Al₂O₃ and NiO–MoO₃/Al₂O₃ catalysts in the presence of air at 623–723 K under normal atmospheric pressure. Among these catalysts investigated, the CuO–ZnO/Al₂O₃ combination effectively performed this reaction with high activity and selectivity. © 2000 Elsevier Science B.V. All rights reserved.

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Quinoline and alkylquinolines are important classes of heterocyclic compounds of high industrial importance. These compounds are the starting materials for the design of many pharmaceuticals (mainly antimalarial compounds), herbicides, fungicides, corrosion inhibitors and acid-binding agents [1–4]. Quinolines have also been used as high boiling basic solvents in the laboratory [1,2]. Quinolines are usually recovered from methylnaphthalene fraction of coal tar by extraction with ammonia. They can also be produced by different routes which have many drawbacks: for example, the most widely employed method, Skraup's synthesis, as well as other similar methods utilize high amounts of sulfuric acid and high temperatures [3–5]. Recent unprecedented environmental pressure and

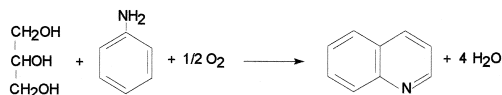
the resulting drive towards clean technologies force the scientific community to develop ecologically friendly alternative routes. In fact, there are several advantages like continuous production, simplified product recovery, catalyst regenerability, absence of acid waste stream, etc. for carrying out this reaction in the vapour phase when compared to the conventional liquid phase routes.

Therefore, the vapour phase route employing an appropriate heterogeneous catalyst system is preferred over the conventional liquid phase methods. However, such attempts are very limited in the literature [6,7]. In a recent publication, Campanati et al. [7] reported the ecofriendly vapour phase synthesis of 2-methyl-8-ethylquinoline from ethylene glycol and 2-ethylaniline over a commercial K 10 montmorillonite catalyst at normal atmospheric pressure. The montmorillonite K 10 is a porous material besides its higher acidity. Due to its high porosity,

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operation in vapour phase reactions for longer times is arduous and no quick diffusion of products formed on the surface is possible. In the present study, an attempt is made to synthesize quinoline from aniline and glycerol in one step over different mixed oxide catalysts.



The catalysts used in the present study are prepared by either the conventional wet-impregnation or by a deposition-precipitation method. The CuO–ZnO/Al₂O₃ catalyst was prepared by a deposition-precipitation method using urea as a hydrolyzing agent [8]. The required quantities of copper nitrate (Fluka, AR grade) and zinc nitrate (Loba Chemie, GR grade) to yield the desired composition of the catalyst were dissolved in deionized water to which an excess amount of urea (Loba Chemie, AR grade) was also added. Alumina support (Harshaw Al-III-61, γ -Al₂O₃, surface area of 204 m² g⁻¹, pore volume of 0.65 cm³ g⁻¹) in fine powder form was then added to this mixture solution and heated to 368 K with vigorous stirring. Precipitation to neutral pH was completed in 3–4 h. The precipitates obtained were filtered off, washed several times with deionized water, dried at 383 K for 16 h and calcined at 723 K in air for 12 h. The MoO₃–V₂O₅/Al₂O₃ catalyst was prepared by co-impregnation of alumina (ACC, India, γ -Al₂O₃, SA 104 m² g⁻¹) with stoichiometric aqueous solutions of ammonium heptamolybdate (Loba Chemie, GR grade) and ammonium metavanadate (Loba Chemie, GR

grade). The excess water was evaporated on a water bath and oven dried at 393 K for 12 h and calcined in an air at 723 K for 6 h. Two commercial NiO–MoO₃/Al₂O₃ (Harshaw HT-500 E) and ZnO–Cr₂O₃ (Harshaw Zn-0312 T) catalysts are also used in the present investigation. The BET surface area of these catalysts was determined by N₂ adsorption at 77 K. Catalyst composition together with that of BET surface areas are presented in Table 1.

Catalytic tests were conducted in a fixed bed microreactor at atmospheric pressure as described earlier [9,10]. A liquid mixture of glycerol and aniline (2:1 molar ratio) was fed by a metering pump at a flow rate of 3–4 ml h⁻¹. The liquid feed was then evaporated in the reactor and subsequently diluted with air, the air flow rate was controlled at 45 ml min⁻¹. For each runabout, 3–4 g (5 cm³ volume) of catalyst was packed between 2 quartz wool plugs inside the reactor (Pyrex glass tube 8 mm i.d.) and the liquid products were analyzed by gas chromatography with a 10% OV-17 on Chromosorb G-AW column (2 m long) and flame ionization detector. The reaction products were collected after establishing steady state conditions (about 2 h). The main reaction products observed were quinoline, 1,2-dihydroquinoline, acrolein, alkylated quinolines, and CO and CO₂ in addition to small quantities of unknown products, respectively. More details of the experimental procedure and the method of activity calculation have been described elsewhere [10].

A decrease in the conversion of aniline during the initial reaction period was observed for all the catalysts used, but stable activities were obtained within few hours. The activities and

Table 1
Composition and specific surface areas of various catalysts

Catalyst	Composition	Surface area (m ² g ⁻¹)
MoO ₃ –V ₂ O ₅ /Al ₂ O ₃	Mo:V = 1:2 mole ratio and total 15 wt.%	174
NiO–MoO ₃ /Al ₂ O ₃ (Harshaw)	NiO = 3.5 wt.%; MoO ₃ = 15.5 wt.%	200
CuO–ZnO/Al ₂ O ₃	Cu:Zn:Al = 1:2.3:2.7 mole ratio	80
ZnO–Cr ₂ O ₃ (Harshaw)	Cr ₂ O ₃ = 21 wt.%; ZnO = 74 wt.%	130

Table 2

Conversion and product selectivities in the synthesis of quinoline from aniline and glycerol over CuO–ZnO/Al₂O₃

Temperature (K)	Conversion ^a	Selectivity ^b (%)	Selectivity ^c (%)	Yield of quinoline ^d (%)
623	63	80	19	50
648	65	80	19	52
673	76	84	14	64
698	78	83	16	65
723	79	71	27	56

^aConversion (%) = number of moles of aniline reacted × 100/number of moles of aniline fed.^bSelectivity = number of moles of quinoline formed × 100/number of moles of aniline reacted.^cSelectivity = number of moles of side products formed × 100/number of moles of aniline reacted.^dYield of quinoline = Conversion^a × Selectivity^b.

selectivities of various catalysts studied in the temperature range of 623–723 K are presented in Tables 2–5. For all the catalysts, conversion of aniline and selectivity of quinoline was found to increase with increase in temperature. As can be noted from Tables 2 and 3, the maximum yield of quinoline was obtained at 698 K on CuO–ZnO/Al₂O₃ and NiO–MoO₃/Al₂O₃ catalysts. Over ZnO–Cr₂O₃ and MoO₃–V₂O₅/Al₂O₃ catalysts, maximum yield of

Table 3

Conversion and product selectivities in the synthesis of quinoline from aniline and glycerol over NiO–MoO₃/Al₂O₃

Temperature (K)	Conversion ^a	Selectivity ^b (%)	Selectivity ^c (%)	Yield of quinoline ^d (%)
623	61	49	49	30
648	68	55	43	37
673	73	80	18	58
698	76	79	20	60
723	78	65	34	51

^aConversion (%) = number of moles of aniline reacted × 100/number of moles of aniline fed.^bSelectivity = number of moles of quinoline formed × 100/number of moles of aniline reacted.^cSelectivity = number of moles of side products formed × 100/number of moles of aniline reacted.^dYield of quinoline = Conversion^a × Selectivity^b.

Table 4

Conversion and product selectivities in synthesis of quinoline from aniline and glycerol over ZnO–Cr₂O₃

Temperature (K)	Conversion ^a	Selectivity ^b (%)	Selectivity ^c (%)	Yield of quinoline ^d (%)
623	60	69	29	41
648	61	80	19	49
673	63	91	8	57
698	65	85	13	55
723	65	80	19	52

^aConversion (%) = number of moles of aniline reacted × 100/number of moles of aniline fed.^bSelectivity = number of moles of quinoline formed × 100/number of moles of aniline reacted.^cSelectivity = number of moles of side products formed × 100/number of moles of aniline reacted.^dYield of quinoline = Conversion^a × Selectivity^b.

quinoline was noted at 673 K (Tables 4 and 5). More yield of quinoline was observed only at higher temperatures over CuO–ZnO/Al₂O₃ and NiO–MoO₃/Al₂O₃ when compared to ZnO–Cr₂O₃ and MoO₃–V₂O₅/Al₂O₃ catalysts. The more formation of 1,2-dihydroquinoline and acrolein including small quantities of alkylated quinolines (methyl and ethyl substituted, confirmed by GC/MS) in addition to some unknown products were noted at lower tempera-

Table 5

Conversion and product selectivities in synthesis of quinoline from aniline and glycerol over MoO₃–V₂O₅/Al₂O₃

Temperature (K)	Conversion ^a	Selectivity ^b (%)	Selectivity ^c (%)	Yield of quinoline ^d (%)
623	36	30	68	11
648	40	38	60	15
673	64	68	30	43
698	42	60	37	25
723	48	66	31	32

^aConversion (%) = number of moles of aniline reacted × 100/number of moles of aniline fed.^bSelectivity = number of moles of quinoline formed × 100/number of moles of aniline reacted.^cSelectivity = number of moles of side products formed × 100/number of moles of aniline reacted.^dYield of quinoline = Conversion^a × Selectivity^b.

tures over ZnO–Cr₂O₃ and V₂O₅–MoO₃/Al₂O₃ catalysts.

The reaction was also investigated at different molar ratios of aniline and glycerol. The conversion of aniline and selectivity of quinoline was more when the glycerol to aniline mole ratio was two. There was a drastic decrease in the yield of quinoline for the deviation from the above molar composition of glycerol to aniline. When glycerol to aniline ratio was less than two, the conversion of aniline was less with reasonably good selectivity of quinoline. When this ratio was increased to higher than the said composition, more side products were noted to have less selectivity of quinoline, however, the conversion of aniline was high. Air appears to be the desired carrier gas for this reaction, because only small quantities of quinoline were observed when air was replaced by nitrogen. Furthermore, considerable amounts of 1,2-dihydroquinoline were also noted when N₂ was used as the carrier gas. Aniline adds to acrolein via the Michael addition across the vinyl group to give aniline propanal. This is followed by the electrophilic attack of protonated aniline propanal on the aromatic ring results in the ring closure. Subsequent dehydration leads to 1,2-dihydroquinoline, which on oxidation results in quinoline formation [11]. In the present study, the quinoline is presumably formed by oxidative dehydrogenation of 1,2-dihydroquinoline by involving oxygen molecule from air, which was used as the carrier gas. This may be the reason for the preferential formation of quinoline in the presence of air as carrier gas instead of nitrogen.

In a recent publication, Bezouhanova and Al-Zihari [12] reported that CuO and NiO oxides are highly effective in the dehydrogenation of cyclohexanol to phenol. ZnO is considered as a solid base [11,13] but some acidic properties have also been established [14]. The CuO–ZnO/Al₂O₃ [8] and NiO–MoO₃/Al₂O₃ [9] catalysts are highly active in the dehydrogenation of cyclohexanol to cyclohexanone and the oxidative dehydrogenation of cyclohexylamine

to aniline, respectively. The formation of quinoline in higher yields over CuO–ZnO/Al₂O₃ and NiO–MoO₃/Al₂O₃ catalysts than on ZnO–Cr₂O₃ and MoO₃–V₂O₅/Al₂O₃ catalysts may presumably be due to the higher dehydrogenation ability of CuO, NiO [12,15] and ZnO [13] materials than the Cr₂O₃ and V₂O₅, apart from higher surface areas (Table 1). It is a well-established fact in the literature that the Al₂O₃ is an effective catalyst in the dehydration of alcohols to the corresponding olefin compounds. In the present case, glycerol is bringing forth acrolein by dehydration over Al₂O₃, which is a support material. Thus, produced acrolein may be condensing with aniline to generate 1,2-dihydroquinoline. Metal oxides like V₂O₅, MoO₃, Cr₂O₃, etc., are known to be highly active for oxidative dehydrogenation [9,13] since these materials show good redox properties. These metal oxides present on the surface of the Al₂O₃ support may be involved in the oxidative dehydrogenation of the generated 1,2-dihydroquinoline to produce quinoline. In the case of ZnO–Cr₂O₃ and MoO₃–V₂O₅/Al₂O₃ catalysts, formation of more side products were noted especially at lower temperatures and occasionally, small quantities of alkylquinolines were also noted at higher temperatures. Chromia and vanadia are known to exhibit higher acidity than the copper, nickel and molybdenum oxides [12,15,16]. The higher the acidity of a catalyst is, the greater is the interaction of aromatic ring carbon atoms with the electrophiles generated in the reaction, leading to substituted aromatic products [16–18]. However, the mechanism in the formation of alkylated quinolines in the present case is not fully understood.

Thus, the formation of quinoline from aniline and glycerol mixtures in the vapour phase over a mixed oxide catalyst in a single step is a reaction of much importance. Very interestingly, the CuO–ZnO/Al₂O₃ catalyst exhibits better conversion and product selectivity than other catalyst systems. Further studies are highly essential to understand the mechanism of this reaction and the role of acid–base properties of

the catalyst on the conversion and product selectivity.

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