

# Single-step synthesis of 2-methylquinoxaline from 1,2-phenylenediamine and 1,2-propanediol over modified HY zeolites<sup>☆</sup>

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## Abstract

The cyclization reaction of 1,2-phenylenediamine and 1,2-propanediol for the synthesis of 2-methylquinoxaline (2-MQ) was carried out over the HY, LaHY, PbHY, CuHY and CrHY zeolites at 350 °C. The catalytic activity towards the yield of 2-MQ followed the order: PbHY > MnHY > CrHY > LaHY > HY > CuHY. The medium acidic catalysts like Pb- and Cr-modified HY zeolites gave high activity. The high acidity of the catalyst and high reaction temperatures decrease the yield and selectivity of the product. The maximum yield of 82.1% of 2-MQ with 99.2% conversion of 1,2-phenylenediamine was obtained over a PbHY catalyst at 350 °C. © 2001 Elsevier Science B.V. All rights reserved.

*Keywords:* 2-Methylquinoxaline; 1,2-Phenylenediamine; 1,2-Propanediol; Cyclization; HY zeolite

## 1. Introduction

2-Methylquinoxaline (2-MQ) and its derivatives are important intermediates in the production of biologically active antimicrobial compounds and germicides. Many substituted 2-methylquinoxalines have shown fungicidal and antiviral activity [1]. 2-MQ *N,N*-dioxides substituted in the 3-position (e.g., with amide, amidino, hydrazino carbonyl and ester groups) are potent bactericides. Antibiotics of the triosin and quinomycin series

have been shown to contain a quinoxaline 2-carboxylic acid residue [2]. Among several routes for the preparation of 2-MQ, reacting 1,2-phenylenediamine with pyrovaldehyde sodiumbisulfide, reacting the diamine with hydroxyimino acetate and the alkylation of preformed quinoxaline are commonly employed [1,2]. However, these multi-step methods for the synthesis lead to several by-products. Application of zeolites in the field of heterogeneous catalysis for fine chemical synthesis is more interesting due to their high thermal stability, crystalline pore structure, uniform size, and availability of many active centers and eco-friendly in nature [3–5]. A large volume of the literature has been published in the applications of zeolites like HZSM-5, HM, H $\beta$ , HY, etc., for the synthesis of heterocyclic compounds [5–9]. We are reporting here the synthesis of 2-MQ in vapor-phase for the

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first time over zeolite catalysts from 1,2-phenylenediamine and 1,2-propanediol.

## 2. Experimental

HY (Si/Al = 2.6) was obtained from PQ, USA. The catalyst powder was pelletized, crushed, and sieved into 2 mm size. The HY zeolite was modified by an impregnation method with 3 wt% metal cations such as La, Pb, Cr and Cu. The required quantity of metal nitrate salts was dissolved in distilled water and added to the zeolite and the mixture was allowed to stay overnight with stirring at room temperature. It was then dried in an oven at 100 °C to evaporate the residual water and later calcined in air between 400 and 420 °C for 4 h to obtain the finished form of the catalyst.

The vapor-phase cyclization reaction was carried out in a continuous fixed-bed glass reactor. Four grams of 2 mm sized catalyst was placed in the middle of the reactor. The 1,2-phenylenediamine and 1,2-propanediol in the 1:3 mole ratio was used as a feed. The need for an excess of 1,2-propanediol is because of the side reactions, which lead to the formation of acetone and lower hydrocarbons. The reactants were fed from the top of the reactor using a syringe pump (Perfusor, B. Braun). The products were collected from an ice-cold water trap at the bottom of the reactor. The products were analyzed on a Gas Chromatograph (HP-6890 series) using HP-1 capillary column and confirmed by GC/MS and NMR spectroscopy. The conversions were given with respect to 1,2-phenylenediamine. The catalytic activity data comparison is made between different catalysts at the 4th hour run duration period.

## 3. Results and discussion

The X-ray diffraction patterns of the modified zeolites clearly indicated that the crystallinity was not affected by modification. The framework of the modified zeolites was also checked by FT-IR spectroscopy and the crystallinity found to be retained even after modification. The surface areas of the modified and unmodified zeolites were measured by N<sub>2</sub> adsorption at 77 K (BET method). The surface areas of the zeolite catalysts decreased (except Pb- and Mn-modified HY has only a marginal decrease) on modification, and the values are shown in Table 1. Acidity of the zeolites and modified zeolites was measured by the method of stepwise temperature programmed desorption of ammonia, as reported earlier [10], and the values of the zeolites are given in Table 1. The three peaks observed at 150–250, 250–350 and 350–450 °C correspond to the desorption of NH<sub>3</sub> gas related to weak, medium and strong acid sites, respectively, as observed also by several other groups [10–12]. The total acidity observed decreased in the order LaHY > HY > CrHY > PbHY > CuHY. The HY catalyst modified by rare earth cation like La showed a slightly higher acidity than unmodified zeolites [11,12]. The acidity of LaHY can be attributed to its coordinating ability of La with water to generate strong acidic sites by dissociation [13,14].

### 3.1. Catalytic activity

The cyclization reaction of 1,2-phenylenediamine and 1,2-propanediol for the synthesis of 2-methylquinoxaline was carried out over the HY, LaHY, PbHY, CuHY and CrHY zeolites and the

Table 1  
Acidified and surface area of the modified HY zeolite catalysts

Catalyst	Surface area (m <sup>2</sup> g <sup>-1</sup> )	Acidity (mmol g <sup>-1</sup> )			Total acidity (mmol g <sup>-1</sup> )
		150–250 °C	250–350 °C	350–450 °C	
HY	457.2	1.73	0.64	0.45	2.82
LaHY	355.7	1.87	0.85	0.69	3.41
CrHY	411.4	1.09	0.38	0.62	2.09
CuHY	393.8	0.44	0.68	0.05	1.17
MnHY	449.0	1.33	0.37	0.28	1.98
PbHY	448.3	0.89	0.54	0.12	1.55

Table 2  
Synthesis of 2-methylquinoxaline from 1,2-phenylenediamine and 1,2-propanediol over modified HY zeolites

Catalyst	TOS (h)	Conversion of 1,2-phenylenediamine (%)	Yield of 2-methylquinoxaline (%)	Others (%)
HY	1	91.4	58.4	33.0
	4	92.6	44.2	48.4
LaHY	2	89.6	64.8	24.8
	4	85.7	63.2	22.5
PbHY	3	99.2	82.1	17.1
	4	93.2	77.0	16.2
CrHY	4	93.7	66.8	26.9
CuHY	1	97.4	63.4	34.0
	4	94.8	45.7	49.1
MnHY	2	96.1	81.8	14.3
	4	92.9	70.1	22.8

Temperature = 350 °C; feed = 1,2-phenylenediamine: 1,2-propanediol = 1:3 (mole ratio); weight hour space velocity (WHSV) = 0.5 h<sup>-1</sup>; others = polyalkylquinoxalines, isomers of phenylenediamine, etc.

results are given in Table 2. The catalytic activity towards the yield of 2-MQ followed the order: PbHY > MnHY > CrHY > LaHY > HY > CuHY. The medium acidic Mn and Pb-modified HY zeolite catalysts have shown high yield and selectivity of 2-MQ. The maximum yield of 77.0% of 2-MQ with 93.2% conversion of 1,2-phenylenediamine was obtained over 3 wt% PbHY zeolite. The low yield of 2-MQ over La-modified HY zeolite is due to its high acidity resulting in the formation of side products like polyalkyl quinoxalines. A decreased yield of 2MQ over CuHY may be due to the reductive nature of Cu ions, which leads to the formation of dihydro and tetrahydro-2-MQ. In order to get more insight into the reaction mechanism, the effect of various reaction parameters like temperature, weight hour space velocity (WHSV) and time on stream product distribution studies have been carried out.

The effect of temperature on the synthesis of 2-MQ was studied in the range 300–420 °C and the results are shown in Fig. 1. The maximum yield of 2-MQ was obtained at 350 °C. Below 350 °C the catalytic activity is low. This may be due to the non-availability of suitable acid sites for the cyclization reaction. Amines are assumed to be adsorbed on the acid sites of the catalyst thus blocking the active sites required for the cyclization reaction [15,16]. The high reaction tempera-

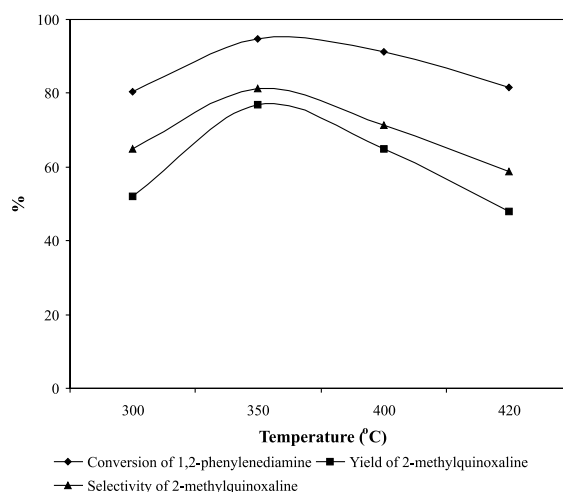


Fig. 1. Effect of reaction temperature on the synthesis of 2-methylquinoxaline. Catalyst = 3 wt% PbHY; feed = 1,2-phenylenediamine: 1,2-propanediol = 1:3 (mole ratio); WHSV = 0.5 h<sup>-1</sup>; time on stream = 4 h.

tures above 350 °C result in low conversion and yield. The strong acid sites at high reaction temperatures appear due to desorption of amines [17,18], which enhance the formation of polyalkyl products and coke [19].

The effect of variation on WHSV was studied in the range 0.25–1 h<sup>-1</sup> and the results are shown in Fig. 2. The conversion of 1,2-phenylenbediamine

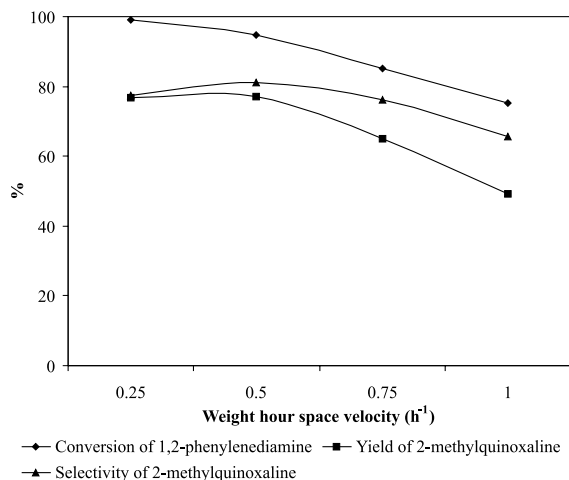


Fig. 2. Effect of WHSV on the synthesis of 2-methylquinoxaline. Catalyst = 3 wt% PbHY; feed = 1,2-phenylenediamine: 1,2-propanediol = 1:3 (mole ratio); temperature = 350 °C; time on stream = 4 h.

and the yield of 2-MQ decreased with the increase of WHSV from 0.25–1 h<sup>-1</sup>. This may be due to the low contact time between the reactants and the catalyst. The maximum yield of 78.4% of 2-MQ with 97.7% conversion of 1,2-phenylenediamine was obtained at 0.25 h<sup>-1</sup> WHSV.

The effect of time on stream on the product distribution has been studied for 10 h at 350 °C and 0.5 h<sup>-1</sup> WHSV and the results are shown in

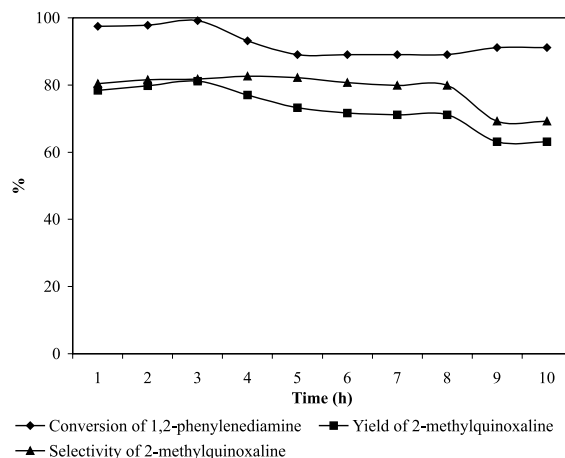
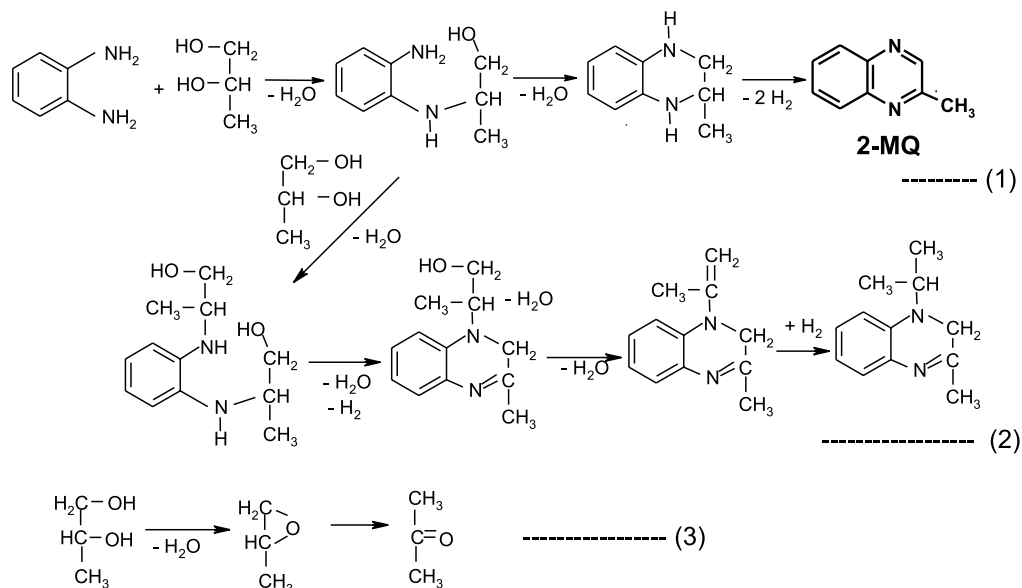


Fig. 3. Effect of time on stream on the synthesis of 2-methylquinoxaline. Catalyst = 3 wt% PbHY; feed = 1,2-phenylenediamine: 1,2-propanediol = 1:3 (mole ratio); temperature = 350 °C; WHSV = 0.5 h<sup>-1</sup>.

Fig. 3. The catalytic activity was almost constant during the initial 4 h and later the catalyst deactivation was observed. The deactivation of catalytic activity with time on stream may be due to the coke formation.

The plausible reaction mechanism for the formation of various products during the synthesis of 2-MQ from vapor-phase cyclization of 1,2-phenylenediamine and 1,2-propanediol was depicted in



Scheme 1. A plausible reaction mechanism for the formation of various products during the synthesis of 2-methylquinoxaline over zeolite catalysts.

Scheme 1 with three routes. The dehydrocyclization of 1,2-phenylenediamine with 1,2-propanediol gives rise to 1,2,3,4-tetrahydro-2-methylquinoxaline followed by subsequent dehydrogenation leading to the formation of 2-MQ as shown in route 1. The substituted 2-methylquinoxalines and acetone are the major side products formed during the reaction as depicted in routes 2 and 3, respectively.

#### 4. Conclusions

The 2-methylquinoxaline was synthesized in high yields from the cyclization reaction of 1,2-phenylenediamine and 1,2-propanediol over modified HY zeolites at 350 °C. The medium acidic catalysts like Pb- and Cr-modified HY zeolites gave high activity. The high acidity of the LaHY catalyst and high reaction temperatures decrease the yield and selectivity of the product. The maximum yield of 82.1% of 2-MQ with 99.2% conversion of 1,2-phenylenediamine was obtained at 350 °C with 0.5 h<sup>-1</sup> WHSV.

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