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Synthesis of hierarchical ZSM-5 using glucose as a templating precursor†

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Devaki Nandan,[ab] Sandeep K. Saxena[b] and Nagabhatla Viswanadham*[ab]

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Various hierarchical ZSM-5 materials have been synthesized by adopting a novel concept using glucose as a precursor for the structure directing agent through a steam-assisted crystallization (SAC) process. The effect of the glucose/TEOS weight ratio was studied, and materials exhibiting different properties such as surface area, porosity and acidity were obtained by varying the concentration of glucose in the initial synthesis mixture. All the samples were characterized by XRD, SEM, TPD, and N_2 adsorption–desorption and were studied for their performance towards the tertiary butylation of phenol reaction. The activities of all the hierarchical ZSM-5 materials synthesized by the present method were observed to be higher than that of the conventional ZSM-5. The optimal production of 2,4-di-tertiary butyl phenol over hierarchical ZSM-5 occurred at a reaction temperature of 150 °C after 7 h reaction time under solvent free conditions.

1. Introduction

Zeolites, with their inherent porous crystalline acidic nature, possessing uniform pore sizes and large internal surface areas, find a wide range of applications in catalysis, separation and ion-exchange.[1–3] In particular, the medium pore ZSM-5 zeolite has attracted much attention due to its shape-selective features responsible for its excellent performance in selective organic transformations. The narrow pores of this zeolite exhibiting linear selectivity provide a special feature for the synthesis of *para*-xylene from *ortho*- and *meta*-xylenes, which is considered as a milestone in zeolite and heterogeneous catalysis research fields. However, an obvious shortcoming of zeolite materials originates from their intrinsic micropores that strongly inhibit the diffusion of bulky reactants and products, which prevents their wide use in fine chemical and petrochemical processing. Al-containing mesoporous molecular sieves with large and high specific surfaces could be the catalysts for the conversion of bulky reactants.[4–6] However, these materials suffer from poor thermal and hydrothermal stability due to the thin and amorphous nature of their walls. Therefore, the preparation of hierarchical pore zeolite molecular sieves possessing the positive aspects of both micropores (high activity and stability) and mesopores (larger pore size for accommodating bulky molecules) has become a hot point of research recently. The most widely used method to prepare hierarchical pore zeolite is by adopting special chemicals as templates including hard and supramolecular structured compounds. Jacobsen *et al.*[7] did pioneering work on the hard templating method and successfully synthesized mesopore zeolites using carbon materials such carbon nano-tubes. Three-dimensionally ordered mesoporous (3DOM) carbon materials are also used by other researchers for the synthesis of mesoporous zeolite materials.[8] Nevertheless, the templates used in these methods are very costly. Carbon aerogels[9] and ordered mesoporous carbons[10,11] have also been used as templates to prepare hierarchical zeolite, but the preparation process of this carbon template itself is complicated and requires high temperature and an inert gas atmosphere during carbonization. In the supra-molecular templating method, the templates used are mainly cetyltrimethylammoniumbromide (CTABr),[12] poly(ethylene oxide)–poly(propylene oxide)–poly(ethylene oxide) triblock copolymer (P123),[13] and organosilane[14] agents, but these are expensive. Recently, through the combination of conventional soft templates such as TEA, copolymer Pluronic F127, organosilane and the steam-assisted crystallization (SAC) process, hierarchically structured c-TUD-1, TS-1 and ZSM-5 zeolites[15] have been facilely produced, but the use of these templates makes the process costly. Very recently, monosaccharides such as glucose and disaccharides such as sucrose *etc.* have been identified as cheaper potential precursors for mesopore structure-directing agents. Kustova *et al.*[16] synthesized zeolite single crystals with controlled mesoporosity by *in situ* sugar decomposition for the templating of hierarchical zeolites which is a three step process in which they first synthesized a silica–carbon composite in an inert atmosphere and used this composite material as a template upon which crystallization and calcination yields

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[a] *AcSIR-Indian Institute of Petroleum, Dehradun, India*

[b] *Catalyst and Conversion Processes Division, Indian Institute of Petroleum, Council of Scientific and Industrial Research, Dehradun-248005, India. E-mail: nvish@iip.res.in; Fax: +91-135-2525702; Tel: +91-135-2525856*

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Na–ZSM-5. The material was further treated with ammonium nitrate to obtain NH_4–ZSM-5, and the high temperature decomposition finally yielded H–ZSM-5. Ma *et al.*[17] synthesized mesoporous ZSM-5 where a precursor of ZSM-5 is first prepared by a sequential reaction between aluminium sulphate solution, tetrapropylammonium hydroxide and tetraethyl orthosilicate in a specific manner. The resultant ZSM-5 precursor was added to an aqueous solution of glucose followed by heating to the crystallization temperature. The final solid product obtained was calcined to remove the organic template, followed by ion exchange with NH_4NO_3 and calcination treatment to yield H–ZSM-5. A similar method was also reported, the difference being the use of starch derived bread instead of glucose for the synthesis of the hierarchical ZSM-5 (ref. 18). Wang *et al.*[19,20] synthesized hierarchical TS-1 by using sucrose as a meso/macro template in the presence of isopropyl alcohol, using high cost ethylendiamine as a crystallising agent. Previously, we successfully synthesized mesoporous silica by using glucose as a template precursor in an acidic medium.[21] However, the same method is not applicable for the synthesis of mesoporous ZSM-5 due to the fact that the metal to metal (silicon and aluminium) bond formation is difficult in an acidic medium to yield any crystalline material.

Here, we report a novel method for the successful synthesis of hierarchical ZSM-5 zeolite material using environmentally benign glucose in a basic medium created by the addition of low cost aqueous ammonium hydroxide, where the pore size pattern of the synthesized material is significantly influenced by the concentration of glucose in the synthesis mixture. The present work has an advantage over the existing methods as it uses a simple, low cost, non-surfactant common chemical "glucose" as the template precursor that spontaneously gets converted to a hard template during partial carbonization by drying of the synthesis gel at 170 °C in air. Furthermore, the use of ammonium hydroxide as an alkaline agent instead of sodium hydroxide makes it simple to obtain the proton form of ZSM-5 directly and avoids the additional step of ion-exchange of sodium with ammonium ions. The ammonium form of ZSM-5 obtained in the synthesis gets transformed into acidic ZSM-5 (H–ZSM-5) through the simple decomposition of the ammonium ion during calcination. This is the first method of its kind to synthesize crystalline hierarchical aluminosilicate material from a glucose and ammonium hydroxide medium to the best of our knowledge. The catalytic performance of hierarchical ZSM-5 samples was studied for the bulky molecular alkylation reaction of phenol with tertiary butanol.

2. Experimental

2.1. Materials

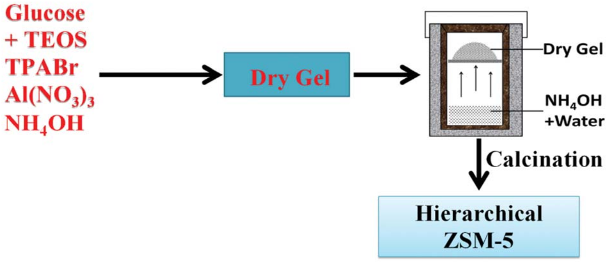
Tetraethyl ortho silicate (TEOS), ammonia solution, 25%, tetrapropylammonium bromide (TPABr), phenol, tertiary butanol and aluminium nitrate were purchased from Merck while glucose was purchased from Rankem, The reference ZSM-5 sample was obtained from Sud-Chemie India Ltd.

2.2. Synthesis of hierarchical ZSM-5 materials

As depicted in Scheme 1, a typical synthesis procedure involves the drop by drop admixing of tetrapropylammonium bromide (TPABr) solution, tetraethyl orthosilicate (TEOS), aluminium nitrate solution and glucose solution with a TPABr : TEOS : aluminium nitrate : glucose : water molar ratio of 1 : 5.2 : 0.215 : 2.4 to 4.9 : 60. The resultant gel is treated at 170 °C in air and the dry gel obtained from the mixture is used for steam assisted crystallization in a specially designed autoclave equipped with a porous metallic boat for holding the dry gel which is allowed to be in contact with the steam produced from the bottom of the autoclave during heat treatment (Scheme 1). In a typical synthesis procedure 12.5 g tetrapropylammonium bromide with the required amount of glucose and water is added to TEOS followed by the addition of 3.75 g of aluminium nitrate solution (in 5 g water). To study the effect of the template precursor (glucose) the synthesis was conducted by varying the glucose to TEOS weight ratio in the initial gel mixture from 0.40 to 0.64. The resultant solution was dried in a water bath by treating at 80 °C for 2 h, and the resulting viscous gel was further heated at 170 °C for 28 h to obtain the dry gel (brown in colour). Finally, the dry gel (solid phase), along with a mixture of aqueous ammonia (25%) and deionized water containing the aqueous phase were transferred into a specially designed autoclave, in which the solid phase was separated from the aqueous phase. The crystallization was carried out at 170 °C for 6 days, and the steam obtained from the aqueous phase came in contact with the upper solid phase to facilitate the crystallization process of the zeolite. At the end of the treatment, the black coloured solid product obtained was collected by filtration, washed with deionized water, dried at 100 °C and calcined at 650 °C for 10 h to remove the template. The final materials obtained in the synthesis are denoted MZ0.40, MZ0.48 and MZ0.64, where the suffix indicates the weight ratio of glucose to TEOS.

2.3. Characterisation

The powder X-ray diffraction patterns of the samples were recorded on a Regaku Dmax III B equipped with a rotating anode and CuKα irradiation. SEM images were recorded for obtaining the particle morphology on a Quanta 200f instrument, Netherlands. Nitrogen sorption isotherms were obtained using a Micromeritics ASAP 2010 unit, USA, operated at −196 °C, where the samples were degassed at 300 °C prior to measurement to determine the specific BET surface area (SBET) and pore volume. The pore size was calculated from the



Scheme 1 Synthesis route of hierarchical ZSM-5 zeolite.

desorption branch of the adsorption–desorption isotherms by the Barrett–Joyner–Halenda (BJH) method. The temperature programmed desorption (TPD) patterns of ammonia on the samples were recorded on Micromeritics 2010 unit, USA, where helium was used as the carrier gas and prior to the ammonia adsorption the samples were degassed at 300 °C for one hour.

2.4. Application of materials for the tertiary butylation of phenol

The catalyst performance studies of the materials were conducted in the present work towards the alkylation of phenol. In a typical reaction procedure, 1 mol of phenol was added to a 2.5 mol of tertiary butyl alcohol and 5 mol% of catalyst. The whole mixture was transferred in to a 25 ml volume capacity Parr reactor autoclave, sealed tightly and pressurised by N_2 up to 2 bar. The reaction was conducted at 150 °C for 7 h and the product obtained at the end of the run was filtered and analysed by GC equipped with a DB wax column and flame ionisation detector (FID).

3. Results and discussion

3.1. Crystallinity, porosity and acidic properties of the synthesised materials

The SEM images of the samples shown in Fig. 1 indicate the formation of uniform crystals in the case of MZ0.40, when compared to those of MZ0.48 and MZ0.64. This can be ascribed to the variation in the concentration of the templating precursor, glucose, in the synthesis gel. The non-uniform distribution of the templating precursor resulting in excess glucose concentration may be the reason for the formation of non uniform semi-crystalline ZSM-5 materials. The powder X-ray diffraction (XRD) patterns of the samples are given in Fig. 2, where a standard ZSM-5 sample of Si/Al = 15 is also shown for comparison. All three synthesized materials depict the characteristic diffraction peaks occurring at 2θ of 8.0, 8.9, 23.2, 24 and 24.5 representing the ZSM-5 framework structure without any crystalline impurity phases. The crystallite size of the materials was estimated from the full width at half maxima of the respective peaks at 2θ values of 7–10, using Scherrer's equation, and the average of the crystallite size is given in Table 1. The data indicate a comparable crystal size of the materials synthesized in this study with that of the conventional ZSM-5 zeolite. The small angle X-ray scattering (SAXS) patterns of the as-synthesized samples (Fig. S1, ESI†) suggest the presence of larger mesopores in the materials,[22] which is indeed confirmed by N_2 adsorption–desorption isotherm curves of the corresponding samples (Fig. 3A). All the samples exhibited the type IV isotherm with an H1 type hysteresis loop which is usually observed for larger mesopores. The sharp uptake in nitrogen adsorption at relative pressures of 0.6–0.9 P/P_0 reveals the capillary condensation of the gas inside the mesopores. A steep increase at relative pressure $P/P_0 < 0.02$ and significant adsorption at high relative pressure P/P_0 0.9–1.0, indicates the co-existence of intrinsic micro, meso and macropores in all three samples. However, the concentration of glucose in the initial synthetic gel was observed to influence the porosity of the samples significantly. At lower glucose concentration, the isotherm exhibited the formation of more micropores (pressure

Fig. 1 SEM images of the synthesized materials.

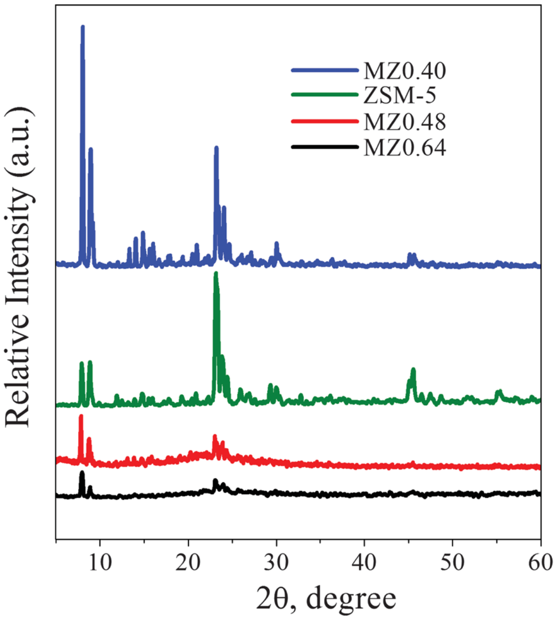


Fig. 2 Wide angle XRD patterns of the synthesized materials.

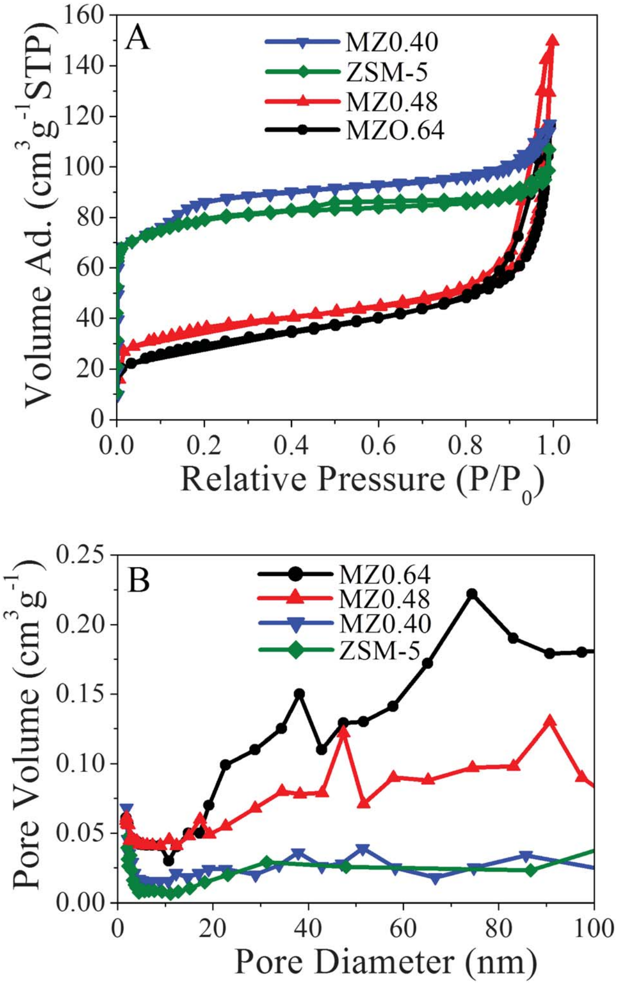


Fig. 3 (A) N_2 adsorption–desorption isotherms of the synthesized materials, (B) pore size distributions of the samples measured by the BJH method.

range of $P/P_0 < 0.02$), while at higher glucose concentration the porosity dramatically shifted into meso/macropores (relative pressure range P/P_0 of 0.6–0.9). This phenomenon of enhanced mesopore/macropore formation at higher glucose concentrations is further reflected in the pore size distribution patterns of the materials (Fig. 3B). All the materials exhibited hierarchical pore size distribution patterns with significant contribution of mesopores as well as macropores (Fig. 3B). However, the population of such hierarchical pores is dramatically increased in the samples using more glucose and the increase follows the glucose concentration. Therefore the order of hierarchical porosity is observed to be as follows: ZSM-5 < MZ0.40 < MZ0.48 < MZ0.64. The finding of increasing hierarchical pore size distribution with increasing glucose concentration can be understood from the XRD results, where the increase in glucose concentration is observed to increase the amorphous nature of the material (lower crystallinity). This is to say that the semi crystalline ZSM-5 material containing a larger amount of amorphous material is forming at a higher glucose concentration and the presence of such amorphous material is contributing to the formation of meso and macropores. Such a material with a lower number of micropores and higher numbers of meso/macropores is expected to give a lower surface area, which is indeed observed in the samples (Table 1). However, it is important to note that the total pore volume as well as the mesopore/macropore volume is increased in the higher glucose based synthesized samples. This results in an overall increase in the average pore diameter of the samples with increasing glucose concentration. The BJH adsorption average pore diameters of the corresponding samples are 2.2, 2.3, 6.7 and 7.2 nm, further suggesting that an increase of glucose concentration leads to a shift of the mean pore diameter to a higher value. Here, glucose undergoes dehydration and partial carbonization to

Table 1 Textural properties of the synthesized materials

Sample	SA_{BET}[a]/m^2 g^{-1}	SA_{mi}[b]/m^2 g^{-1}	SA_{me}[c]/m^2 g^{-1}	V_{tot}[d]/cm^3 g^{-1}	V_{mi}[e]/cm^3 g^{-1}	$V_{me/ma}$[f]/cm^3 g^{-1}	D[g]/nm	Crystallite size[h]/nm
ZSM-5	294	207	87	0.18	0.08	0.10	2.2	50.3
MZ0.40	305	113	192	0.18	0.05	0.13	2.3	51.7
MZ0.48	107	25	82	0.18	0.01	0.17	6.7	57.0
MZ0.64	128	42	86	0.23	0.01	0.22	7.2	47.4

[a] BET surface area. [b] Micropore surface area calculated from *t*-plot. [c] Mesopore surface area calculated as $SA_{BET} - SA_{mi}$. [d] Total pore volume taken from the volume of N_2 adsorbed at $P/P_0 = 0.995$. [e] Micropore volume calculated from *t*-plot. [f] Mesopore/macropore volume calculated by $V_{tot} - V_{mi}$. [g] BJH adsorption average pore diameter. [h] Average crystal size determined using Scherrer's equation for the peaks at 2θ values of 7–10.

form templating carbonaceous species during the heat treatment of the gel at 170 °C, which is responsible for the creation of meso/macropores in the final material upon steam assisted crystallization. The formation of such meso/macropores is increased with an increased concentration of glucose. Overall, the increased formation of meso/macropores with increased glucose concentration clearly demonstrates the meso/macropore directing role of the glucose precursor.

The acidity patterns of the samples measured by TPD (Fig. 4) also followed the crystallinity trend of the samples. All the samples exhibited a two peak pattern with desorption peaks at ~100 °C and ~350 °C representing weak and strong acidity, respectively. The acidity pattern of a reference ZSM-5 sample (Si/Al = 15) is also given for comparison, showing that the acidity of all three samples (Si/Al = 60) in the present study is lower (lower number of acid sites) compared to the reference sample, following the aluminium content. Among the three ZSM-5 samples synthesized in the present study, the acidity is decreased with increasing glucose concentration. This is in accordance with the XRD and porosity patterns, as the increased amorphous nature of the material is expected to give low acidity (lower number of strong acid sites) to the ZSM-5 samples. The results together summarize the role of glucose as a meso/macropore directing agent and the partially crystalline hierarchical ZSM-5 samples obtained at higher glucose loadings exhibit moderate acidity along with a large number of meso/macropores. With the higher pore volume and larger space in the mesopores, the samples are expected to exhibit potential catalytic applications in molecular reactions involving bulky species, such as the tertiary butylation of phenol.

3.2. Catalytic application of the materials

The tertiary butylation of phenol is catalyzed by conventional homogeneous acid catalysts in the liquid phase at lower reaction temperatures, but the acid contamination and difficulty involved in the separation of the product (which also adds to the cost) limits their use. Recently, solid acid catalysts have been applied for solvent-free liquid phase reactions for low cost and environmentally-friendly process, in which the easy separation of catalysts from the reaction system makes it suitable for industrial applications.[23] In this regard, hierarchical ZSM-5 samples are observed to exhibit excellent catalytic properties, especially in terms of the di-alkylated product. The hierarchical mesoporous ZSM-5 samples in the present study, which possess meso/macroporosity along with zeolitic microporosity, are also expected to exhibit promising catalytic activity towards this reaction involving bulky reactants. In the present study we would like to explore the effect of glucose-dependent meso/macroporosity created in the ZSM-5 samples on the conversion and product selectivity towards the tertiary butylation of phenol. All three hierarchical ZSM-5 samples exhibited higher conversions (34–46%) when compared to the microporous ZSM-5 zeolite (Table 2). The lower conversion of microporous ZSM-5 obtained in the reaction in spite of its higher acidity (ESI Fig. S2†) clearly suggests the importance of meso/macropores for this reaction and the lack of such porosity in the standard ZSM-5 sample may be responsible for its lower activity. The catalytic performance of the three hierarchical mesoporous ZSM-5 samples also followed the porosity trend, in which the more meso/macroporous material (MZ0.64) exhibited higher conversion (44%) and higher 4-TBP (tertiary butyl phenol) selectivity (81%). This sample also produced the highest amount of di-alkylated product (2,4-DTBP).

Table 2 *tert*-Butylation of phenol over hierarchical ZSM-5 samples[a]

Catalyst	Conversion of phenol (mol%)	Selectivity of product (%)		
		2-TBP	4-TBP	2,4-DTBP
MZ0.40	34	38.2	57.3	4.5
MZ0.48	46.6	11.1	81.5	5.4
MZ0.64	44	10.6	80.9	8.5
ZSM-5	13.7	63.5	32.84	Nil

[a] Catalyst: 0.5 g, reaction temperature 150 °C, pressure 2 bar N_2; reaction time 7 h; phenol : TBA 1 : 2.5 (molar ratio).

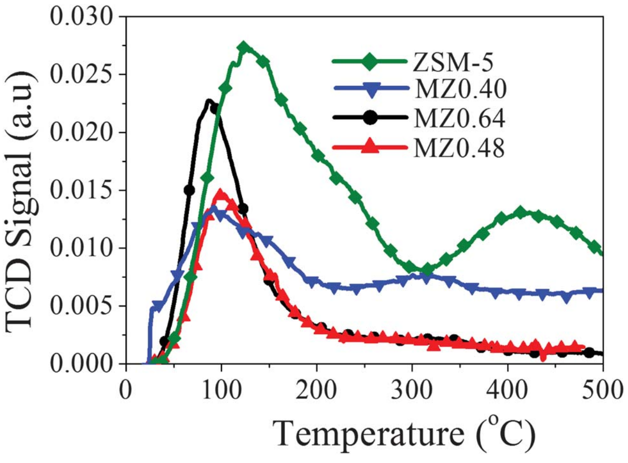


Fig. 4 TPD spectra of synthesised and reference material.

4. Conclusions

In summary, hierarchical ZSM-5 zeolite samples have been successfully synthesized by using the low-cost template precursor glucose in a basic medium that can be directly converted to a hard template during heat treatment of the gel to give glucose-dependent porosity patterns in the samples. This method also provides scope for using other kinds of sugars as template precursors for the synthesis of hierarchical materials. The synthesis method provides an economical path for the production of hierarchical aluminosilicates with tailored meso/macroporosity (controlled by glucose) for various industrial applications and could be extended for the synthesis of other types of zeolites. The materials possessing a well-connected network of micro/meso/macropores could be a source for a variety of molecular reactions involving bulk species and better replacements for conventional ZSM-5. The materials indeed exhibited improved catalytic performance in the tertiary butylation of phenol as a result of overcoming the diffusion limitation of the reactants.

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