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# Highly Selective Liquid-Phase Benzylation of Anisole with Solid-Acid Zeolite Catalysts

Raju Poreddy, Shunmugavel Saravanamurugan and Anders Riisager\*

## Abstract

Zeolites were evaluated as solid acid catalysts for the liquid-phase benzylation of anisole with benzyl alcohol, benzyl bromide, and benzyl chloride at 80 °C. Among the examined zeolites, H-mordenite-10 (H-MOR-10) demonstrated particular high activity (>99%) and excellent selectivity (>96%) to the monobenzylated products, *ortho/para* benzyl anisole, using benzyl alcohol as reagent (anisole/alcohol molar ratio = 28). Analogous reactions with benzyl halides resulted in lower yields of the desired monobenzylated products. The conversion of benzyl alcohol was confirmed to be proportional to the amount of added H-MOR-10, and the linear free-energy relationship relating the conversion of substituted benzyl alcohol and substituent constants as well as the orientation effect of substituents of anisole on the distribution of *ortho/para/meta* isomers was evaluated.

**KEY WORDS:** solid-acid catalysis; zeolites; benzyl alcohol; aromatic benzylation; substituted anisole.

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## Introduction

Alkylation of aromatics is an important class of acid catalysed processes applied on industrial scale for the production of various chemicals used in pharmaceuticals and agro chemistry [1]. Alkylation of anisole, being a model compound of lignin, has in this context also recently come into focus as a technology for converting a bio-based compound into commodity chemicals [2]. Alkylated anisole compounds are, for example, constituents of lubricants with interesting

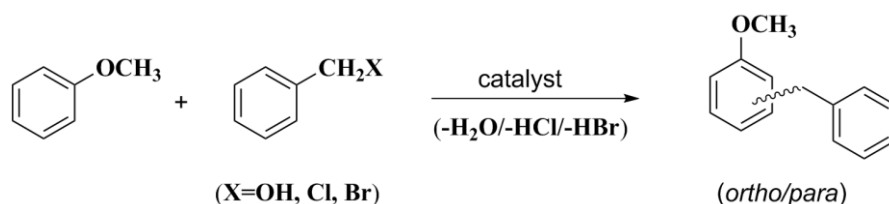
properties such as improved thermal oxidation and hydrolytic stability [3]. Conventional alkylations are carried out via electrophilic substitution reactions using stoichiometric and/or sub-stoichiometric amounts of Lewis acids or strong mineral Brønsted acids such as, e.g.  $\text{AlCl}_3$ ,  $\text{FeCl}_3$ ,  $\text{BF}_3$ ,  $\text{ZnCl}_2$ ,  $\text{HF}$  or  $\text{H}_2\text{SO}_4$  [4,5,6]. However, the use of these homogeneous systems needs laborious efforts to recover and reuse the catalyst. In addition, high toxicity, low atom-efficiency and the corrosive nature prevents these catalytic systems to find widespread use [6a]. These inevitable drawbacks make it attractive to replace the commonly used homogeneous acid catalysts by solid acid catalysts, which are easy to reuse and more environmentally benign.

Owing to their strong acidity, thermal stability and possible shape selectivity particular zeolites, as well as heteropoly acids and inorganic metal oxides, have been extensively studied as solid acid catalysts for alkylation of aromatic compounds with alcohols [7,8,9,10], alkyl halides [11,12] and ethers [13]. Hence, a wide variety of zeolites have been used for the alkylation of arenes [14,15]. However, less work has been reported on benzylation reactions since size of the benzylating agent and/or the benzylated product may not be compatible with zeolites, as diffusion of reactant molecules through the micropores may be limited. This can result in poor selectivity and loss of catalyst lifetime [14,15]. Creation of additional mesopores in zeolites is a possible method to circumvent this problem. Accordingly, Sang-Eon *et. al* studied the effect on selectivity of meso- and micro porous ZSM-5 catalysts in the benzylation of benzene, toluene, anisole and mesitylene with benzyl alcohol. Here higher conversions as well as higher selectivities toward the desired monobenzylated products were observed with meso-ZSM-5 prepared by microwave-induced assembly method [16]. Besides the zeolites, ordered mesoporous silica molecular sieves, designated as M41S, have also been applied for these reactions as alternatives to the micro porous zeolites [17,18,19,20,21]. Inadequate activity of these materials further led to the introduction of other metals into the framework of mesoporous silica materials resulting in modified catalysts such as, e.g. sulphated zirconia-stabilized on MCM-41[13], Ga exchanged silicates [12], Zr-SBA-15 [22] and Ga-Al alloy supported on SBA-15 [23]. However, uniform pore sizes, thin pore walls, poor hydrothermal stability and weaker acidity compared to zeolites make these alternative materials impractical as heterogeneous catalysts.

Recently, Ramesh Kumar *et al.* have also reported benzylation of anisole with benzyl alcohol over heteropolyacid salts [9,10], titania-supported aluminium [24] and samarium exchanged heteropoly tungstate [25]. In addition, niobium oxide [8] ( $\text{Nb}_2\text{O}_5$ ), niobium phosphate ( $\text{H}_3\text{PO}_4\text{-WO}_3\text{-Nb}_2\text{O}_5$ ) [11,26], phosphated and sulfated mesoporous niobium oxide [27] as well as alumina-supported niobium oxides [28] have also been reported to be active catalysts – but not very selective - for the

benzylation of benzene, toluene and anisole. Silver nanoparticles supported on silica are also reported as heterogeneous catalyst for the alkylation of arenes [29]. However, low yield of monobenzylated product and use of a transition metal is not attractive for practical use. Therefore, the use of zeolites seems to be preferred catalyst for alkylation of arenes.

From the literature survey above it is evident that alkylation of anisole with many alkylating agents has been reported. However, to the best of our knowledge no studies have correlated zeolite-catalysed alkylation of substituted anisole with aromatic substituted and unsubstituted benzyl alcohol to Hammett studies. Hence, in this work we report the alkylation of both substituted and unsubstituted anisole with benzyl alcohol with and without substituents over various zeolites, and sulphonic acid-containing resin (Dowex) and SBA-15 (**Scheme 1**). The reaction kinetics, effect of temperature, catalyst loading and substrate scope have been investigated along with the Hammett correlation studies.



**Scheme 1.** Reaction scheme for benzylation of anisole with benzyl alcohol, benzyl chloride or benzyl bromide.

## Experimental

### *Catalysts and Materials*

The zeolites beta-12.5, USY-6, Y-2.6, ZSM-5 and mordenite (MOR)-10 were purchased from Zeolyst as the  $\text{NH}_4$ -forms. The materials were converted to the H-forms by calcination at 500 °C for 6 h. Sulfonated SBA-15 mesoporous silica ( $\text{SO}_3\text{H-SBA-15}$ ) was prepared according to the literature [30]. The ion exchange resin Dowex as well as all other chemicals were purchased from Sigma-Aldrich.

### *Synthesis of silicate-1 and titanium silicate-1*

Zeolite silicate-1 (S-1) and modified titanium silicate-1 (TS-1) were prepared according to a slightly modified procedure of the originally patented procedure [31]. Tetrapropyl ammonium hydroxide (3.44 g) was added to a Teflon vessel together with deionized water (0.516 g). Tetraethyl orthosilicate (TEOS) (3.87 g) was then added drop wise to the solution and

stirred for 1 h until it become viscous (0.042 g of tetraethyl orthotitanate was added to 3.87 g of TEOS for the synthesis of TS-1 with Si/Ti ratio = 101). The Teflon vessel was then positioned in an autoclave, sealed and heated to the crystallization temperature (180 °C) for 24 h. The autoclave was subsequently cooled to room temperature and the mixture filtered to recover the solid product. The solid was then washed with deionized water three times and dried at room temperature for 24 h. Finally, the solid was calcined at 550 °C with a ramp and dwell time of 4 and 24 h, respectively.

### *Catalyst characterization*

Nitrogen physisorption was performed with the synthesized S-1 and TS-1 at liquid nitrogen temperature using a Micromeritics ASAP 2020 instrument equipped with an automated gas adsorption surface area and porosimetry analyzer. The samples were outgassed in vacuum at 200 °C prior to measurement. The surface areas were determined by the Brunauer-Emmett-Teller (BET) method.

X-ray powder diffraction (XRPD) analysis was carried out on a Huber (Rimsting, Germany) G670 diffractometer operated in transmission mode with  $\text{CuK}\alpha_1$  ( $\lambda = 1.54 \text{ \AA}$ ) irradiation from a focusing quartz monochromator. The catalyst samples were fixed between two pieces of scotch tape and rotated during data collection. The diffraction patterns of the samples were recorded at room temperature in the  $2\theta$  range 3-100° in steps of 0.005°.

Temperature programmed desorption of ammonia ( $\text{NH}_3$ -TPD) experiments were conducted on a Micromeritics Autochem-II instrument for surface acidity measurements of both synthesized and commercial catalysts. In a typical experiment, 80 mg of the dried sample was placed between two quartz wool beds in one arm of a U-shaped quartz tube and preheated in a He flow (75 mL/min) for 1h at 100 °C followed by treatment with anhydrous  $\text{NH}_3$  gas (Air Liquide, 5%  $\text{NH}_3$  in He). The sample was then flushed with He (50 mL/min) for 100 min at 100 °C to remove physically adsorbed  $\text{NH}_3$ . The TPD operation was finally carried out by heating the sample from 100 to 700 °C (10 °C/min) under He flow (50 mL/min).

### *Standard alkylation reaction procedure*

In a typical experiment, anisole (28 mmol), benzyl alcohol (1.0 mmol), mesitylene (internal standard, 0.1 mmol) were charged into a reaction tube and connected to a reaction station (Radley Carrousel 12 Plus), which provided stirring, heating and atmospheric air at ambient pressure. The reaction tubes were heated to the desired temperature where after 60 mg of catalyst was added. Unless otherwise noted, the reactions were performed at 80 °C for 45 min.

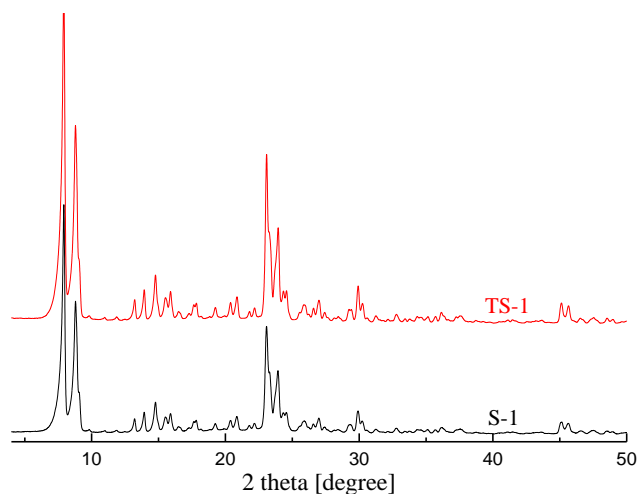
### *Product analysis*

During the alkylation reactions, aliquots of the reaction mixture were periodically collected, filtered and analysed by GC-FID (Agilent, 6890N, HP-5 capillary column 30.0m x 320  $\mu$ m) using N<sub>2</sub> as the carrier gas with a total flow rate of 90.2 mL/min. The GC oven temperature was ramped from 40 to 250 °C with 15 °C/min and maintained here for 6 min during analysis. The reported conversions were calculated from the conversion of benzyl alcohol using mesitylene as an internal standard. The reaction product, monobenzylated anisole, and the by-product dibenzyl ether were quantified using mesitylene as an internal standard. The reaction products were identified by analyzing the samples on GC-MS (Agilent, 6850N).

## Results and Discussion

### *Catalyst characterization*

The synthesized S-1 and TS-1 materials were characterized by nitrogen physisorption, XRPD and NH<sub>3</sub>-TPD. In the XRPD patterns (**Figure 1**) the characteristic diffraction peaks were assigned to the S-1 and TS-1 orthorhombic MFI structure, thus confirming a high degree of crystallinity with no evidence for presence of other crystalline phases or amorphous material [32].

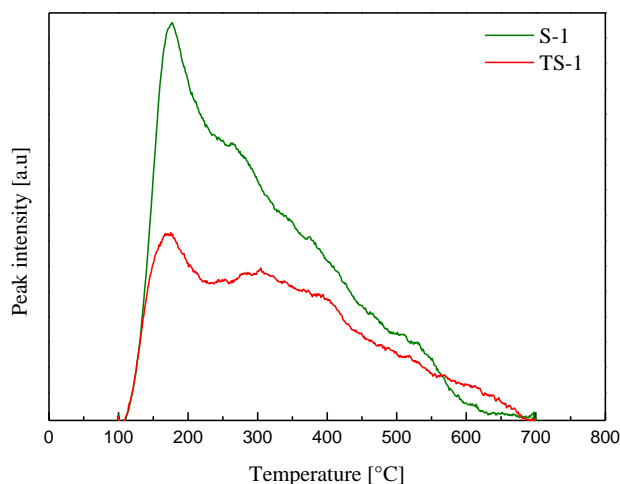


**Figure 1.** XRPD patterns of synthesized silicate-1 (S-1) and titanium silicate-1 (TS-1)

The measured BET surface areas of the synthesized S-1 and TS-1 materials are reported in **Table 1** along with BET surface

areas of the other used catalysts. The BET surface areas of S-1 (283 m<sup>2</sup>/g) and TS-1 (324 m<sup>2</sup>/g) revealed that the materials were microporous and the values were comparable to the zeolitic crystals reported in [33]. The micropore volumes of S-1 and TS-1 were determined using the t-plot method at relative pressure ( $P/P_0$ ) = 0.97 as 0.07 and 0.11 cm<sup>3</sup>/g, respectively.

To provide a fingerprint of the distribution of the strength of the acidic sites in the synthesized S-1 and TS-1 materials, NH<sub>3</sub>-TPD curves were also measured (**Figure 2**). The NH<sub>3</sub> desorption curves for both materials had similar irregular shapes displaying two peaks located around 175 and 290-310 °C, respectively, with the S-1 catalyst having larger intrinsic acidity (peak intensity) than TS-1. The variation in the position of the second desorption peaks clearly showed, that the two materials had a different distribution of strengths of acidic sites (entries 8 and 9, **Table 1**).



**Figure 2.** NH<sub>3</sub>-TPD curves of the microporous S-1 and TS-1 materials

### *Reaction of benzyl alcohol and anisole*

For the benzylation of anisole with benzyl alcohol different classes of catalysts were carefully chosen to represent different types of porous systems (i.e. large, medium and meso) and solid Brønsted acid catalysts (SO<sub>3</sub>H-SBA-15 and Dowex).

Entry	Catalyst	Pore type	Surface area [m <sup>2</sup> /g]	Acid sites type 1 [100-270 °C] [μmol/g]	Acid sites type 2 [270-500 °C] [μmol/g]	Total acid sites [μmol/g]	Conv. <sup>b</sup> [%]	Yield benzyl anisole [%]		Yield DBE [%]
								<i>ortho-</i>	<i>para-</i>	
1	H-MOR-10	large	500	726	1045	1771	>99	45	51	2

2	H-USY-6	large	730	461	374	835	>99	48	46	2
3	H-Y-2.6	large	730	699	252	951	>99	50	45	0
4	H-USY-30	large	720	182	165	347	>99	49	45	0
5	H-beta-12.5	large	680	563	292	855	>99	40	55	3
6	H-ZSM-5-11.5	medium	425	920	573	1493	98	38	52	8
7	SO <sub>3</sub> H-SBA-15	meso	NA	NA	NA	NA	>99	39	51	5
8	TS-1	medium	324	65	167	232	0	0	0	0
9	S-1	medium	283	135	211	346	0	0	0	0
10	Dowex (IER)	NA	NA	NA	NA	NA	>99	48	47	2
11	Na-MOR-10	large	425	1754	0	1754	6	0	0	5
12	No catalyst	-	-	-	-	-	0	0	0	0

**Table 1** compiles the results obtained from benzylation of anisole at 80 °C in 45 min along with some physicochemical properties of the catalysts. H-MOR-10, H-USY-6, H-Y-2.6, H-USY- 30 and H-beta-12.5 (entries 1-5) representing large pore zeolites gave excellent yield of 90-96% of mono-benzylated anisole in 45 min reactions regardless of the total number of acid sites and the ratio of weak (type 1) to strong (type 2) acid sites. In our previous work, the amount of Brønsted and Lewis acid sites for some of the chosen zeolites (**Table 1**, Entries 2-6) were quantified using pyridine adsorption studies and a decent correlation was found to the type 2 and 1 acid sites, respectively [34]. With the higher surface area zeolites H-USY-6, H-Y-2.6, H-USY- 30 (entries 2-4) traces of bulky poly-alkylation products of anisole were found (confirmed by GC-MS), which potentially could lead to pore blocking during prolonged usage. Interestingly, none of such products were formed with H-MOR-10 and H-beta-12.5. Similarly, the medium pore zeolite H-ZSM-5-11.5 (entry 6) did not reveal formation of such products. However, in contrast to any of other catalysts the latter yielded relatively more dibenzyl ether (DBE) by-product formed by self-condensation of benzyl alcohol, which probably relates to the materials relatively high Brønsted acidity. The other medium pore catalysts S-1 and aluminium-free Lewis acid-containing TS-1 showed no activity at all under the examined reaction conditions (entries 8 and 9) despite being moderately acidic.

Entry	Catalyst	Pore type	Surface area [m <sup>2</sup> /g]	Acid sites type 1 [100-270 °C] [μmol/g]	Acid sites type 2 [270-500 °C] [μmol/g]	Total acid sites [μmol/g]	Conv. <sup>b</sup> [%]	Yield benzyl anisole [%]		Yield DBE [%]
								<i>ortho-</i>	<i>para-</i>	
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2	H-USY-6	large	730	461	374	835	>99	48	46	2
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7	SO <sub>3</sub> H-SBA-15	meso	NA	NA	NA	NA	>99	39	51	5
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10	Dowex (IER)	NA	NA	NA	NA	NA	>99	48	47	2
11	Na-MOR-10	large	425	1754	0	1754	6	0	0	5
12	No catalyst	-	-	-	-	-	0	0	0	0

**Table 1.** Benzylation of anisole<sup>a</sup> with different solid acid catalysts and their textural and acidic properties

<sup>a</sup> Reaction conditions: anisole (28 mmol), benzyl alcohol (1 mmol), mesitylene (0.1 mmol), catalyst (60 mg), 80 °C, 45 min. <sup>b</sup> With respect to benzyl alcohol. NA = not available. DBE = dibenzyl ether.

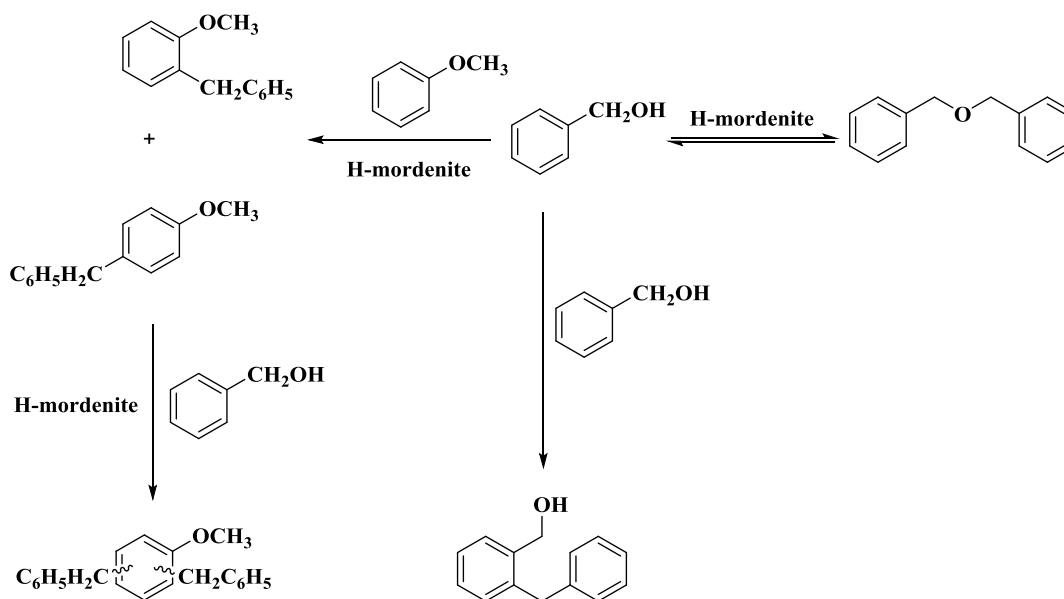
To assure that Brønsted acid sites were necessary for the selective production of mono-benzylated anisole, Na-MOR-10 without Brønsted acidity was also examined for the benzylation reaction (entry 11). As expected, no benzyl anisole was formed and the observed conversion of 6% benzyl alcohol to DBE may be attributed to the presence of basic sites from Na. This observation led us to further examine catalysts with strong Brønsted acidity such as sulphonated mesoporous SBA-15 (SO<sub>3</sub>H-SBA-15, entry 7) and Dowex (Ion-exchanged resin, entry 10). Both catalysts were found to be equally active for the benzylation of anisole (90-95% yield), but their strong Brønsted acidity resulted also in formation of polyalkylated anisoles as well as DBE. Thus formed DBE may also act as a secondary alkylating agent after it is formed in the reaction. Furthermore, a control experiment without added catalyst was carried out to confirm the inevitability of the catalyst under the given reaction conditions. As expected, no conversion of benzyl alcohol was achieved in the given reaction time (entry 12).

In order to validate the difference in activity among the best performing zeolites from

Entry	Catalyst	Pore type	Surface area [m <sup>2</sup> /g]	Acid sites type 1 [100-270 °C] [μmol/g]	Acid sites type 2 [270-500 °C] [μmol/g]	Total acid sites [μmol/g]	Conv. <sup>b</sup> [%]	Yield benzyl anisole [%]		Yield DBE [%]
								<i>ortho-</i>	<i>para-</i>	
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10	Dowex (IER)	NA	NA	NA	NA	NA	>99	48	47	2
11	Na-MOR-10	large	425	1754	0	1754	6	0	0	5
12	No catalyst	-	-	-	-	-	0	0	0	0

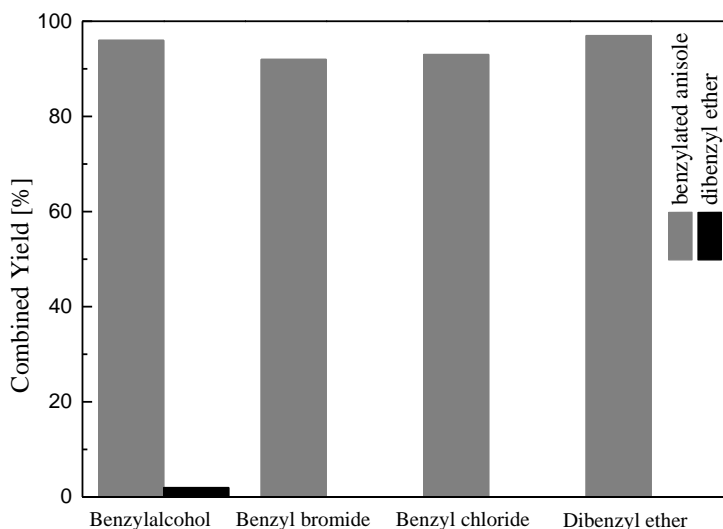
**Table 1**, the benzylation reaction was also performed at lower temperature (40 °C). Here H-MOR-10 provided 29% yield of mono-benzylated products (>99% selectivity), while the other zeolites only yielded ≤18% mono-benzylated anisole with 99% selectivity. Thus, in view point of activity and selectivity even at lower temperatures, H-MOR-10 was confirmed to be the best catalyst for anisole benzylation with benzyl alcohol, and the following reactions were accordingly performed using this catalyst. It can be speculated that a combination of a high total number of acid sites and mesoporosity in H-MOR-10 might be responsible for the superior performance. A general reaction scheme for the formation of mono- and dibenzylated products and other by-products is presented in **Scheme 2**.



**Scheme 2.** Reaction pathways in connection with the benzylation of anisole

### Effect of benzylating agents

The benzylation reaction with H-MOR-10 was further studied by reacting anisole with different alkylating agents under identical reaction conditions (**Figure 3**). The yields of mono-benzylated products of anisole with the examined benzylating agents were all found to be high but following the order of: dibenzyl ether > benzyl alcohol > benzyl chloride > benzyl bromide. This order can be rationalized by the size of the leaving groups, thus supporting formation of benzyl carbocations from reaction between the surface Brønsted acid sites of H-MOR-10 and the alkylating agent to be the rate determining step in the reaction [29]. The selectivity of benzyl alcohol and DBE to mono-alkylated products was slightly higher than for the benzyl halides, suggesting the alcohol or the ether to be the preferred alkylating agent under the given reaction conditions.



**Figure 3.** Benzylation of anisole with different benzylating agents over H-MOR-10. Reaction conditions: Anisole (28 mmol), benzylation agent (1 mmol), mesitylene (0.1 mmol), catalyst (60 mg), 80 °C, 45 min.

### Effect of reaction temperature and time

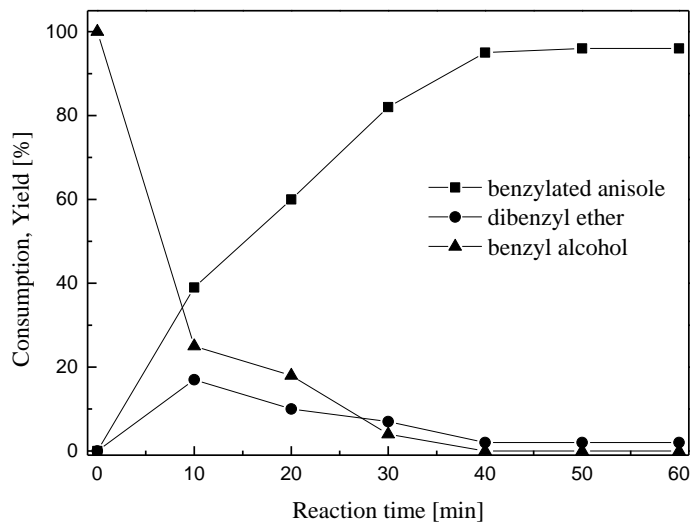
The influence of reaction temperature and reaction time on the performance of the H-MOR-10 catalyst was investigated by conducting the reaction with benzyl alcohol between RT and 100 °C (**Table 2** and **Figure 4**). The catalyst activity gradually increased with the reaction temperature (as expected) enabling the conversion of the benzyl alcohol to increase from 11 to 100% after 1 h, when the temperature was increased from 40 to 100 °C (**Table 2**). Quantitative conversion of benzyl alcohol was achieved even after 15 min when the reaction was performed at 100 °C and after 45 min at 80 °C (entries 4 and 5).

When the reaction was done at room temperature no conversion was observed even after 72 h of reaction time (entry 1). During the reaction performed at 80 °C intermediate formation of DBE (yield up to 17%) was observed, especially in the initial phase when the concentration of benzyl alcohol was still relatively high (**Figure 4**). Furthermore, a gradual shift in the *ortho/para* isomer ratio from 0.4 to 0.9 was also observed as the reaction proceeded, indicating that the reaction is driven towards the *ortho* isomer (results not shown).

**Table 2.** Effect of temperature on H-MOR-10 catalyst performance for benzylation of anisole.<sup>a</sup>

Entry	Temperature [°C]	Time [h]	Conversion [%]	Yield [%]		Dibenzylether [%]
				<i>ortho</i> -	<i>para</i> -	
1	25	72	0	0	0	0
2	40	1	11	2	3	6
3	60	1	30	11	13	5
4	80	0.75	>99	45	51	3
5	100	0.25	>99	47	51	0

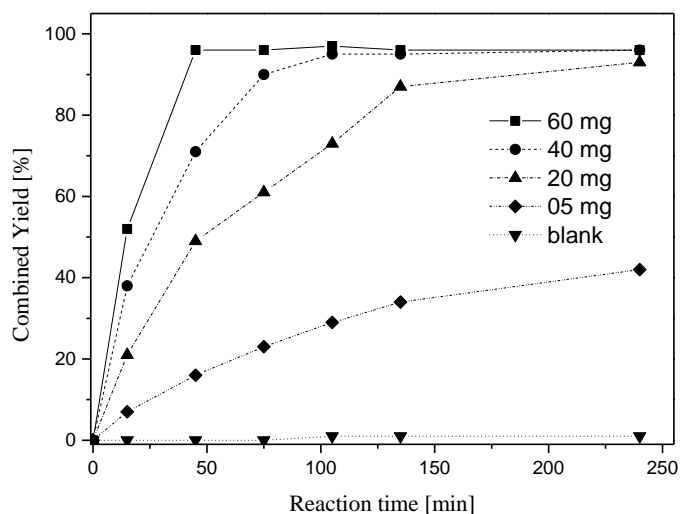
<sup>a</sup> Reaction conditions: anisole (28 mmol), benzyl alcohol (1 mmol), mesitylene (0.1 mmol), H-MOR-10 (60 mg). <sup>b</sup> With respect to benzyl alcohol.



**Figure 4.** Benzylation of anisole and auto-etherification (self-condensation) with time over H-MOR-10 catalyst. Reaction conditions: Anisole (28 mmol), benzyl alcohol (1 mmol), mesitylene (0.1 mmol), H-MOR-10 (60 mg), 80 °C.

### Effect of the amount of catalyst

The benzylation of anisole with benzyl alcohol was also studied under standard reaction conditions with different amounts of H-MOR-10 catalyst present. The yields of benzylated products obtained as a function of time are shown in **Figure 5**. As expected, the overall reaction rate was found to increase with more catalyst being present (i.e. more acid sites available). More detailed analysis further indicated that the initial reaction rate increased almost linearly with the increasing amount of catalyst, suggesting a first order rate dependency with respect to the amount of catalyst. Hence, after 45 min of reaction 18% of monobenzylated anisole was obtained with 5 mg of H-MOR-10 catalyst, 49% with 20 mg catalyst (91% yield after 6 h), 71% with 40 mg and 96% with 60 mg. In all reactions the selectivity towards the monoalkylated product remained high and unaffected at 95-96%.

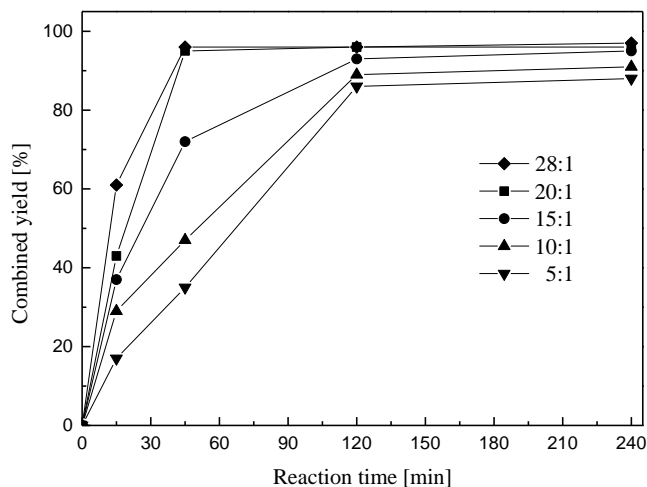


**Figure 5.** Effect of H-MOR-10 catalyst loading on benzylation of anisole. Reaction conditions: Anisole (28 mmol), benzyl alcohol (1 mmol), mesitylene (0.1 mmol), 80 °C.

### Effect of anisole/alcohol mole ratio

The mole ratio of anisole and benzyl alcohol was varied to verify the effect on the catalyst selectivity. The combined yield of *ortho/para* benzylated anisole increased from 17 to 61% after 20 min reaction, when the ratio of anisole to benzyl alcohol was increased from 5:1 to 28:1 (**Figure 6**). In all reactions, a trace amount of poly-alkylated product was observed, and the selectivity to benzylated anisole decreased gradually with lower anisole:alcohol mole ratios. However, the *ortho/para* ratio of benzylated anisole varied only slightly between 0.84 and 0.9 when the anisole to alcohol ratio was varied. The anisole to

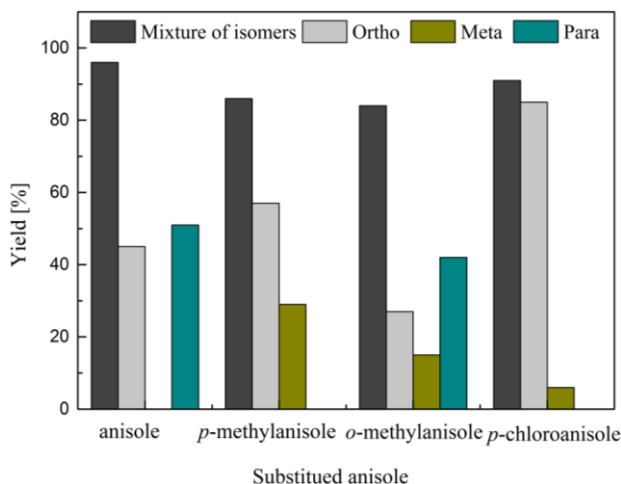
alcohol ratio did not only affect the selectivity towards DBE and benzylated anisole, but apparently also the selectivity towards the undesired product 9,10-dihydroanthracene (qualitative validation from GC-MS data), which was formed when reactions were conducted with high anisole to alcohol ratios where benzylation of benzyl alcohol occurred.



**Figure 6.** The effect of anisole to alcohol mole ratio on benzylation of anisole over H-MOR-10. Reaction conditions: Mesitylene (0.1 mmol), H-MOR-10 (60 mg), 80 °C.

### *Effect of substituents on anisole and benzyl alcohol*

Benzylation of anisole with electron-donating as well as withdrawing substituents was performed with benzyl alcohol in order to evaluate the electronic effects on catalyst performance. The conversion of benzyl alcohol was completed in 45 min irrespective of the substituents on anisole, however the distribution of *ortho*, *meta*, and *para* isomer products was altered (**Figure 7**). The obtained distribution of isomers was in close agreements with the orientation abilities of substituents on anisole [29].



**Figure 7.** Benzylation of substituted anisoles with benzyl alcohol using H-MOR-10. Reaction conditions: Anisole (28 mmol), benzyl alcohol (1 mmol), mesitylene (0.1 mmol), H-MOR-10 (60 mg), 80 °C.

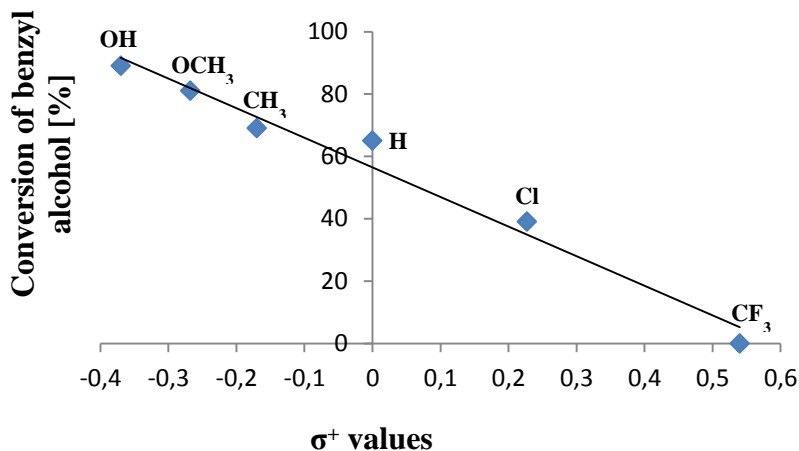
Since the benzylation reaction is expected to follow an electrophilic substitution pathway (similar to Friedel-Craft reactions) the stability of the benzyl carbocation (electrophile) should play a major role in the rate of the benzylation reaction. To study the effect of substituents on the conversion rate and selectivity towards benzylated product different substituted benzyl alcohols were accordingly compared with unsubstituted benzyl alcohol (**Table 3**). As expected, the substituents which increased the electron density on the aromatic ring (i.e. electron donating) and stabilized the carbocation, demonstrated higher conversions (entries 2-4) than the electron-withdrawing substituents which destabilized the carbocation (entries 5 and 6). The *ortho* to *para* isomer ratio remained however unchanged (0.8-0.9).

**Table 3.** Benzylation of anisole with substituted benzyl alcohols over H-MOR-10 catalyst.<sup>a</sup>

Entry	Alcohol substrate	Substituent	Conversion [%]	Yield [%]		Dibenzylether [%]
				<i>ortho</i> -	<i>para</i> -	
1	Benzyl alcohol	-H	65	29	33	2
2	<i>p</i> -methylbenzyl alcohol	-CH <sub>3</sub>	69	32	34	1
3	<i>p</i> -hydroxybenzyl alcohol	-OH	89	40	48	0
4	<i>p</i> -methoxybenzyl alcohol	-OCH <sub>3</sub>	81	38	40	1
5	<i>p</i> -chlorobenzyl alcohol	-Cl	39	15	18	5
6 <sup>b</sup>	<i>p</i> -trifluoromethylbenzyl alcohol	-CF <sub>3</sub>	0	0	0	0

<sup>a</sup> Reaction conditions: Anisole (28 mmol), benzyl alcohol (1 mmol), mesitylene (0.1 mmol), H-MOR-10 (60 mg), 80 °C, 30 min. <sup>b</sup> 22 h was needed to reach 71% yield with 99% selectivity (*ortho* to *para* isomer ratio 0.91).

The linear free-energy relationship was also studied by relating the conversion of substituted benzyl alcohols and the Brown-Okamoto parameter ( $\sigma^+$ ). As shown in **Figure 8**, benzyl alcohols with electron donating groups (*p*-CH<sub>3</sub>, *p*-OCH<sub>3</sub>, and *p*-OH) were more reactive than those with electron withdrawing groups (*p*-Cl, *p*-CF<sub>3</sub>). This linear correlation clearly indicated the importance of stabilizing the built-up positive charge at the benzylic position during reaction, thus demonstrating the reaction to be sensitive to electronic substituent effects [35].

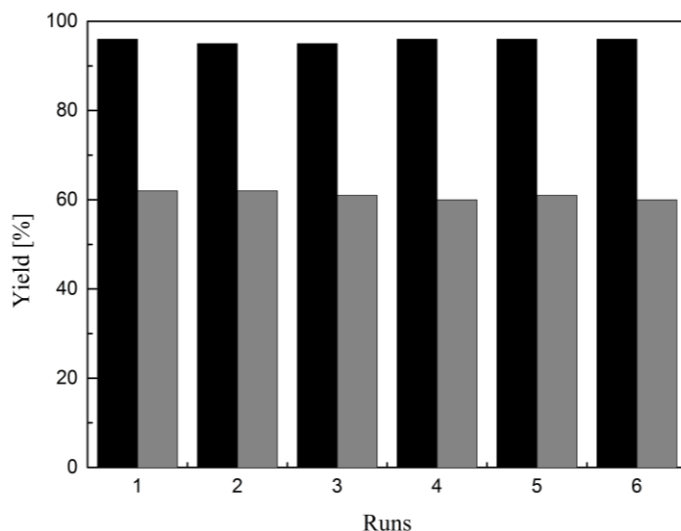


**Figure 8.** Hammett plot relating conversions and Brown-Okamoto parameters ( $\sigma^+$  values).

### Catalyst regeneration

Lastly, reuse of the H-MOR-10 catalyst was investigated by performing five consecutive benzylations of anisole with benzyl alcohol with a recovered catalyst. After the first reaction the catalyst was collected by filtration, washed with acetone, dried at 80 °C and re-activated by calcination at 500 °C in air for 8 h. Then the catalyst was applied for four consecutive reactions in a similar manner. The combined yields of *ortho* and *para* benzylated anisole remained constant at 95% after 45 min for all of the six reactions (**Figure 9**). Also at shorter reaction time of 20 min (with lower conversions) did the catalyst yield identical initial activity resulting in a 60% product yield. If the catalyst was only dried at 80 °C (without calcination) 20% of the catalyst activity was lost from the first to the second reaction run, confirming that re-activation by calcination is indeed required to maintain a high catalyst durability.





**Figure 9.** Reusability of H-MOR-10 in five consecutive benzylations of anisole with benzyl alcohol after 45 min (■) and after 20 min (■). Reaction conditions: Anisole (28 mmol), benzyl alcohol (1 mmol), mesitylene (0.1 mmol), H-MOR-10 (60 mg), 80 °C.

## Conclusions

Commercial available zeolites (large and medium pore), synthesized S-1 and TS-1 (medium pore) as well as SO<sub>3</sub>H-SBA-15 (mesoporous) and ion-exchanged resin (Dowex) were examined as efficient solid acid catalysts for the benzylation of unsubstituted as well as substituted anisole to produce the corresponding mono-benzylated anisoles. Among the examined zeolites, H-MOR-10, with adequate acidity was found to be an especially promising and reusable catalyst for the formation of benzylated anisole (98% yield) after only 15 min of reaction under relative mild reaction condition and a high molar ratio of anisole to benzyl alcohol. H-MOR-10 did - despite its inherent Lewis acidity - not catalyse self-condensation of benzyl alcohol to form dibenzyl ether to the same extent as compared to the other examined zeolites. The demonstration of H-MOR-10 as an efficient solid acid benzylation catalyst suggests, that it might have potential in other alkylation reactions of industrial relevance as well.

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