

Research Note

# Friedel–Crafts hydroxyalkylation: reaction of anisole with paraformaldehyde catalyzed by zeolites in supercritical CO<sub>2</sub>

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## Abstract

Supercritical CO<sub>2</sub> has been found to be a very convenient reaction medium for the Friedel–Crafts hydroxyalkylation of anisole with paraformaldehyde. The high diffusion coefficients of molecules in the supercritical state are a crucial factor contributing to the catalytic activity when the reaction is carried out with microporous zeolites. Thus, the activity of mordenite for the hydroxyalkylation in supercritical CO<sub>2</sub> at 60 °C is about threefold higher than that observed for the same zeolite in toluene at 110 °C.

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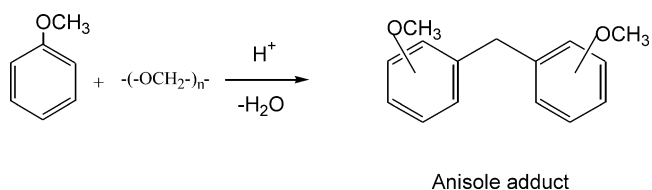
## 1. Introduction

The use of supercritical CO<sub>2</sub> as a solvent in Green chemical synthesis has attracted much interest in recent years [1,2]. Supercritical CO<sub>2</sub> possesses unique properties that make it an inexpensive, nontoxic, and environmentally benign solvent alternative for conventional volatile organic compounds [3–7]. In supercritical fluids, solubility of reactants becomes comparable to that in the liquid state, while molecular diffusivity falls in between that in a liquid and that in a gas [2]. Therefore, processes limited by diffusion in the liquid phase, such as catalysis by microporous solids, should become favored under supercritical conditions.

The majority of the catalytic reactions reported so far using supercritical CO<sub>2</sub> as solvent employ homogeneous catalysts. In these cases, while the medium complies the principles of Green Chemistry in terms of nontoxicity and no-waste production, the catalyst is difficult to separate from the reaction mixture and cannot be easily recovered and reused. In order to conform to the Green Chemistry principles [8,9], it would be more convenient to combine the use of supercritical CO<sub>2</sub> with solid catalysts. Therefore, from this point of view the use of microporous zeolites as heterogeneous and reusable catalysts would be of particular interest. The use of

zeolites as catalysts in supercritical CO<sub>2</sub> seems to be an attractive combination since on one hand the catalytic process will be heterogeneous in nature as the catalyst can be recovered easily and on the other hand fast diffusion provided by the supercritical fluids would play a positive influence in the reaction, helping to overcome diffusion limitations normally encountered in zeolites [10].

To demonstrate the advantages of supercritical CO<sub>2</sub> in zeolite-catalyzed reactions we have selected the hydroxyalkylation of anisole with paraformaldehyde (Scheme 1) as a model reaction. A remarkable enhancement of the performance of acid mordenite was observed compared to reactions carried out in conventional organic solvents like toluene. Friedel–Crafts hydroxylation of electron-rich arenes by carbonyl compounds is of great industrial importance for the synthesis of compounds like polymeric Bakelite resins and bisphenol-A [11]. In industry, these reactions are normally carried out using strong liquid acid as catalysts.



Scheme 1. Friedel–Crafts hydroxyalkylation of anisole with paraformaldehyde.

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Such liquid acids are not only corrosive in nature but also hazardous to the environment and, therefore, disposal of the used catalyst is a major problem.

## 2. Experimental methods

Four different medium- and large-pore zeolites, i.e., Y, mordenite,  $\beta$  and ZSM-5, were obtained from PQ Corporation in either their protonic or their ammonium form. Friedel–Crafts condensation of anisole with paraformaldehyde was carried out under supercritical conditions at 60 °C and 100 atm in a Büchi autoclave with continuous mechanical stirring (500 rpm). Reactions using toluene as the solvent were carried out at atmospheric pressure at the desired temperatures. The reaction products were analyzed by gas chromatography (HP 5890) and products were identified by GC-MAS (HP 6890) analysis.

Carbon content of the used catalysts was determined by combustion analysis in a Fisons EA 1108 elemental analyzer. The nature of the adsorbed species on the used catalysts was identified by diffuse reflectance UV–visible spectroscopy on a Shimadzu spectrophotometer (UV-2101PC) using an integrating sphere accessory and BaSO<sub>4</sub> as standard. Regeneration of the used catalysts was done by burning the carbonaceous deposits in air flow at 450 °C for 4 h.

## 3. Results and discussion

Until now not much work has been reported on the use of acid zeolites in supercritical CO<sub>2</sub> [12], reactions being limited to alkylation on Y zeolites [13–17], disproportionation reactions [18–21], cracking of linear alkanes [22,23], and isomerization of linear alkanes over Y zeolites [24]. These precedents, however, have mostly focused on the deactiva-

tion of the zeolite catalysts that was found to be much slower in supercritical CO<sub>2</sub>. The slower deactivation has been attributed to an enhanced diffusivity and solubility of the poisons in the supercritical CO<sub>2</sub>. In the present work we clearly demonstrate that the positive influence of supercritical CO<sub>2</sub> in zeolite-catalyzed Friedel–Crafts reactions depends primarily on the size of the zeolite pores with respect to the substrate and product dimensions.

Table 1 lists the physical parameters of the zeolites used as catalysts in this study. The selection of the zeolites was done to include uni-, bi-, and tridirectional channel structures with similar Si/Al ratios. The results of Friedel–Crafts hydroxyalkylation of anisole with paraformaldehyde are also given in Table 1. It can be seen that, except in the case of ZSM-5, the conversion of anisole to the condensation product was much higher under supercritical conditions than that using toluene as solvent. Given the known high solubility of aromatic compounds in supercritical CO<sub>2</sub> [12], it is reasonable to assume that during the reaction anisole and dimethoxydiphenylmethane were dissolved in supercritical CO<sub>2</sub>, while the catalyst and polymeric formaldehyde remained in a separate phase.

The influence of catalyst/substrate ratio on the conversion under supercritical conditions is shown in Fig. 1. It can be seen that in supercritical CO<sub>2</sub>  $\beta$ , Y, and mordenite zeolites exhibit the same type of behavior, the anisole conversion increasing significantly with the increase in catalyst loading. On the other hand, the activity of HZSM-5 in supercritical CO<sub>2</sub> was considerably lower than that of other zeolites. The above results can be interpreted assuming that the pore size of ZSM-5 (5.4 × 5.6 Å) is the main factor responsible for the observed low conversion given that the kinetic diameter of anisole is close to the pore size. Even under supercritical conditions, in which diffusion of the reactants is less hindered, the restricted pore geometry of ZSM-5 impedes formation of the bulkier condensation products.

Table 1

Textural properties of the zeolite catalysts and the reaction results for Friedel–Crafts hydroxyalkylation of anisole with paraformaldehyde

Catalyst (Si/Al)	Pore structure	$S_{\text{BET}}$ (m <sup>2</sup> /g)	Reaction		Conv. <sup>a</sup> (%)	Selectivity (%)		
			Medium	$T$ (°C)		<i>o, o'</i>	<i>o, p'</i>	<i>p, p'</i>
H- $\beta$ (12.5)	3D; 7.5 × 5.7 Å Cavities 11 Å	590	scCO <sub>2</sub>	60	54	0.3	10.5	89.1
			Toluene	110	32	0.9	13.5	85.6
HY (15)	3D; 7.4 Å pores Cavities 13 Å	640	scCO <sub>2</sub>	60	55	1.3	18.6	80.1
			Toluene	110	31	2.2	20.5	77.3
ZSM-5 (17.5)	2D; 5.4 × 5.6 Å	380	scCO <sub>2</sub>	60	9	0.8	15.6	83.5
			Toluene	110	6	3.0	26.3	70.6
H-mord (10)	1D; 7.4 Å pores	420	scCO <sub>2</sub>	60	57	1.9	14.7	83.4
			Toluene	110	20	3.0	21.3	75.6
			Toluene	60	9	1.9	17.8	80.3
			Cyclohexane	60	6	2.2	20.2	77.6
H-mord regenerated	–	–	scCO <sub>2</sub>	60	47	1.4	14.8	83.8
			Toluene	110	15	4.0	26.8	69.2

Catalyst 0.2 g, anisole 3.0 g, paraformaldehyde 0.2 g, reaction time 6 h.

<sup>a</sup> Conversion defined as ((initial moles of anisole – remaining moles of anisole)/initial moles of anisole × 100).

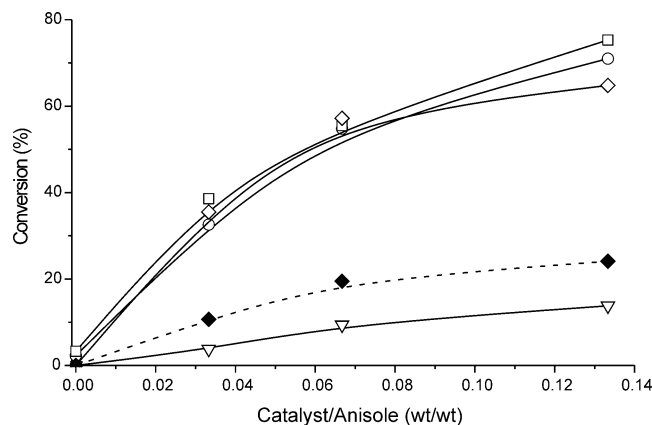
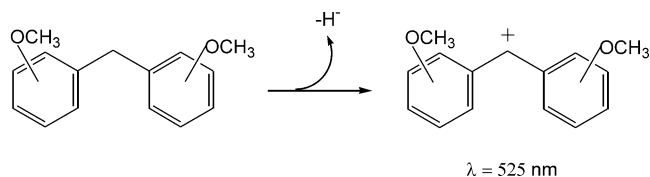


Fig. 1. Conversion of anisole in supercritical  $\text{CO}_2$  for four catalysts after 6 h reaction time for hydroxyalkylation reactions at various catalyst to anisole ratios used in this work (O, H $\beta$ ; □, HY; ◇, H-mord; ▽, HZSM-5; ◆, H-mord in toluene).

Concerning the product distribution, the major isomer of the condensation in all circumstances was found to be the *p*, *p'* isomer followed by much lesser amounts of the *o*, *p'* isomer. Trace quantities of the *o*, *o'* isomer were also detected. Selectivity of the different isomers of the condensation product was found to be very similar with all the zeolite catalysts except that under supercritical conditions a small enhancement of the *p*, *p'* isomer was noticed. No other by-products were formed.

A few differentiating points between the supercritical conditions and toluene deserve a comment. Conversions obtained with supercritical  $\text{CO}_2$  were almost double those observed in a conventional organic solvent, despite the fact that the reaction temperature in the latter case was almost twofold. It must be mentioned here that reactions in toluene under atmospheric conditions were carried out at 110 °C corresponding to the reflux temperature of toluene. The conversion was found to be considerably lower when the reaction was carried out at 60 °C. Toluene has been frequently used as a solvent for related hydroxyalkylation reactions [25]. Other organic solvents such as cyclohexane showed even lower conversion (Table 1).

Particularly interesting is the case of unidirectional mordenite zeolite, for which the difference in conversion between supercritical  $\text{CO}_2$  and toluene was about threefold. The pore openings of mordenite (7.4 Å) correspond to a large-pore zeolite like those of Y (7.4 Å) and  $\beta$  (7.5 × 5.7 Å; 6.5 × 5.6 Å). However, due to the unidirectional channel structure of mordenite, the restricted diffusion of the reactants makes this zeolite behave frequently as a medium-pore zeolite like ZSM-5 and quite different from a typical tridirectional large-pore zeolite, such as  $\beta$  or Y [10]. Indeed, this similarity between mordenite and ZSM-5 is also observed for the hydroxyalkylation reaction of anisole in toluene (see Fig. 1 for results in toluene). It can be seen from Table 1 that under atmospheric reaction conditions, the activity of mordenite was in between that for medium-pore ZSM-5 and that for large-pore Y or  $\beta$  zeolites. In contrast, in supercritical



Scheme 2. Diarylcarbenium ion generation during the reaction.

$\text{CO}_2$ , as a consequence of much favorable diffusion of reactants in this fluid, the activity of mordenite was found to be very similar to that for tridirectional large-pore zeolite, e.g.,  $\beta$  or Y. The change in regime for mordenite from ZSM-5-like behavior in toluene to that typical for tridirectional large-pore zeolites in supercritical  $\text{CO}_2$  clearly shows the advantages of easier diffusion of the reactants and products under supercritical conditions. It is well known that diffusion is a major problem in the liquid-phase reactions of unidirectional zeolites due to blockage of the pore mouths, causing complete deactivation of the catalysts.

A second point of interest is the nature of the organic material adsorbed in the catalysts during the course of the reaction. It has been reported that under supercritical conditions deactivation of the catalysts was less rapid due to easier dissolution of coke in supercritical liquid. During *n*-heptane cracking on Y zeolites [22,23] and disproportionation of ethylbenzene [21,26] partial regeneration of moderately deactivated catalysts has been reported under supercritical conditions. In this regard, we have reported earlier that the major poisons formed in the liquid phase hydroxyalkylation reactions are the diarylcarbenium ions generated from the products by hydrogen abstraction [25,27]. This carbenium ion compensates the negative charge of the zeolite framework and remains strongly adsorbed inside the solid, causing the deactivation of the catalysts (Scheme 2). It is expected that this carbenium ion species will be hardly soluble in supercritical  $\text{CO}_2$ . In fact, at the end of the reaction the acidic zeolites are completely deactivated, indicating that the catalyst was highly poisoned by deposition of the carbenium ions. Carbon analysis of the used catalysts showed that for reactions under supercritical fluid conditions zeolite mordenite contained about 10.7 wt% carbon, while for reactions under atmospheric conditions in toluene at 110 °C the amount of carbon was 8.6 wt%. This indicates that in reactions under supercritical fluid conditions poisoning of the catalysts was disfavored to some extent compared to reactions in toluene. It can be seen that for threefold higher conversion and hence much higher product concentration, the amount of poison deposited on the catalysts under supercritical fluid conditions was not very much different from that observed in the case of reactions in toluene. Given that poisoning is related to hydride transfer from the products (Scheme 2), enhanced diffusion will decrease the residence time on the active sites and will thereby reduce the chances for catalyst deactivation.

The diarylcarbenium ion exhibits a strong absorption band in the visible range at around 525 nm accompanied by a

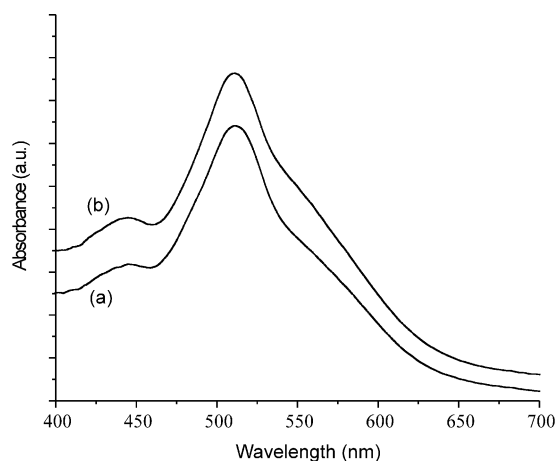


Fig. 2. Diffuse reflectance UV-visible spectra of the H-mord catalysts after being used for the Friedel-Crafts hydroxyalkylation of anisole with paraformaldehyde in (a) supercritical CO<sub>2</sub> and (b) toluene.

shoulder at longer wavelengths. We have observed this band in all the catalysts regardless of the reaction conditions, indicating that the same type carbenium ion was formed in all cases. Fig. 2 shows typical diffuse reflectance UV-visible spectra of H-mord catalysts used in supercritical and atmospheric liquid-phase reactions. In other words, it appears that the reaction mechanism remains the same for both conventional organic solvents and supercritical fluid conditions, the only differentiating feature being the relative diffusion of the reactants and products inside the pores.

After being used in the hydroxyalkylation reactions the catalysts became completely deactivated. Partial regeneration of mordenite can be achieved by burning off the carbonaceous deposits in air flow at 450 °C. It can be seen from Table 1 that the regenerated catalysts showed almost 80% of the initial activity of the fresh catalysts with almost similar product distributions. When the activities of the regenerated mordenite catalysts in supercritical CO<sub>2</sub> and toluene were compared, the same type of enhanced activity under supercritical fluid conditions as in the case of fresh mordenite was observed.

The isomer distribution observed for the regenerated mordenite in supercritical CO<sub>2</sub> remained identical to that of fresh zeolites, but when the reaction was carried out in toluene a significant increase in *o*, *o'* and *o*, *p'* isomers was noticed. The actual isomer distribution for regenerated mordenite was very similar to that of ZSM-5. This suggests that probably small amounts of carbonaceous deposits remaining inside the channels hindered free diffusion through the pores during reactions in toluene. This impeded diffusion is again more pronounced in toluene than in supercritical CO<sub>2</sub>. As a result, a larger contribution of the external surface to the catalytic activity is observed for the reaction in toluene catalyzed by regenerated mordenite, the distribution being identical to the case of ZSM-5.

In conclusion, enhanced diffusion coefficient of the reactants in supercritical fluids is an advantageous feature for re-

action utilizing microporous zeolites as catalysts. Given that frequently the major drawback of zeolites is their limited internal diffusion, supercritical fluids are suitable to overcome these limitations. We have found that this effect is general for all zeolites but it is particularly remarkable for unidirectional mordenite. In this case, the pore size allows the mass transfer inside the particle (pore size higher than the reactants or products) but its activity in the conventional organic solvents is still severely limited by the restricted diffusion associated with the unidirectional geometry of the pores. The use of supercritical CO<sub>2</sub> dramatically enhances the diffusion thereby increasing the catalytic activity.

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