Comments on the use of buckminsterfullerene encapsulated in zeolite Y as a potential catalyst

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Buckminsterfullerene encapsulated within zeolite Y is found not to be a reactive radical initiator for the formation of dimethoxyethane from dimethyl ether below 200°C. Above this temperature the expected acid catalysed conversion of dimethyl ether to hydrocarbons is observed. Dimethoxyethane formation is observed when bibenzoyl peroxide is used as a radical initiator. These studies indicate that any radical formed by the encapsulated buckminsterfullerene is relatively unreactive.

Keywords: buckminsterfullerene; zeolite Y; dimethyl ether conversion; dimethoxyethane

1. Introduction

Considerable interest has followed the initial discovery of buckminsterfullerene as a stable soluble allotrope of carbon [1,2]. The initial research interest involved characterisation and theoretical studies [3,4] and subsequent work has mainly been concerned with functionalisation using standard organic techniques and reactivity studies [5,6]. It has been observed that buckminsterfullerene readily forms radical species when heated or photochemically activated [7–9] and these radicals have been characterised by electron spin resonance spectroscopy. More recently, buckminsterfullerene has been encapsulated in the aluminophosphate VPI-5 [10] and zeolite X [11] and, although characterised by advanced techniques, there have been no indications given as to the potential application to which encapsulation could lead.

Encapsulation of molecular species within microporous materials is a subject that is receiving considerable attention. For example, Corma et al. [11] used a platinum complex within ultrastabilised zeolite Y to demonstrate a novel asymmetric catalyst. Most recently, Parton et al. [12] synthesised a mimic of cytochrome P-450 by encapsulating an iron phthalocyanine within a zeolite. In this way, encapsulation can induce novel reactivity patterns as well as aiding the stabilisation of reactive species. Since buckminsterfullerene can form radicals and these have been demonstrated to be formed with buckminsterfullerene encapsulated in zeolite X [9] it was considered to be of interest to investigate the use of these systems as an initiator for a simple radical reaction. In this paper we present the results of our attempts to use buckminsterfullerene in this way.

2. Experimental

Buckminsterfullerene was prepared and purified to give only the C_{60} using standard literature procedure [1]. Encapsulation was investigated using a number of techniques. A solution of C_{60} (0.01 g) in benzene (30 ml) was used for all impregnation methods and zeolite H-Y (0.1 g) was used corresponding to one C_{60} molecule per four supercages. To aid dissolution of the C_{60} in benzene CS_2 (0.05 ml) was added to the solution. Following this time the material was recovered by filtration and dried in vacuo at 100°C and was then pelleted and sieved to give particles 600 μm in size. This solution was added to zeolite H-Y and stirred at 50°C for 24 h, a method used by Anderson et al. [10]. The mixture was filtered hot, however it was found that the C_{60} was quantitatively recovered in the filtrate and so this method was unsuccessful in this case. A similar result was obtained if the mixture was refluxed for 24 h. To achieve impregnation of the C_{60} the following method was adopted, the C_{60} solution was heated with zeolite H-Y in a teflon lined autoclave at 200°C for 96 h. The C_{60} impregnated zeolite was investigated for the conversion of dimethyl ether in a standard fixed bed laboratory glass microreactor (i.d. = 6 mm). In a typical experiment dimethyl ether (2.5 ml min^{-1}) and nitrogen diluent (7.5 ml min^{-1}) were passed over the zeolite and the reactor effluent was analysed using on-line gas chromatography.

3. Results and discussion

It was decided to investigate the activation of dimethyl ether since previous studies [13] have indicated that dimethyl ether can react with radical centres to form the methoxy methylene radical which could dimerise to form dimethoxyethane:

$$CH_3OCH_3 + R\cdot \rightarrow CH_3OCH_2\cdot$$

$$2CH_3OCH_2\cdot \rightarrow CH_3OCH_2CH_2OCH_3$$

This reaction has been studied in view of its importance to the mechanism of the conversion of methanol and dimethyl ether to hydrocarbons. The conversion of dimethyl ether over C_{60} impregnated zeolite H-Y was investigated in the temperature range 80–200°C and the results, shown in table 1, indicate that no significant reaction was observed. Above this temperature conversion of the dimethyl ether to

Table 1
Reaction of dimethyl ether

Catalyst	Temperature (°C)	MeOMe conversion (%)	$MeO[CH_2]_2OMe$ selectivity (%)
C_{60}/H-Y	80	0	–
	100	0	–
	160	0	–
	200	0	–
DBP[a]	25	0.5	100
	80	5.5	100
	160	3.5	100
	200	2.5	100

[a] Dibenzoyl peroxide (10%) impregnated onto silica, similar results were obtained for dibenzoyl peroxide impregnated into zeolite H-Y.

hydrocarbons was observed and would be expected from the acid catalysed reaction and this was further confirmed by the observation of similar results for zeolite H-Y in the absence of the C_{60}. To confirm that a radical initiated reaction could be observed with dimethyl ether under these conditions similar reactions were carried out using dibenzoyl peroxide impregnated on silica and zeolite H-Y. Under these conditions the dibenzoyl peroxide was relatively unstable and the duration of the experiments was restricted to only 5 min, however conversion of dimethyl ether to dimethoxyethane was observed for temperatures from 25 to 200°C confirming that radical formation from dimethyl ether had occurred.

The previous studies with buckminsterfullerene [9] indicate that radicals would be formed under these experimental conditions. The results of this study therefore indicate such radicals are probably stabilised by the zeolite and, as such, are unreactive to molecules that can readily react with radicals. This may be due to the radical being delocalised over the symmetrical C_{60} structure and, if this is the case, then some improvement in reactivity may be achieved if the C_{60} is functionalised to remove the symmetry and hence restrict delocalisation.

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