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Ethane interaction with Pt-Cr/H-ZSM-5 catalysts, studied by EXAFS

Richard W. Joyner [1], Efim S. Shpiro [2], Peter Johnston [1], Khabib M. Minachev [2]
and Gulia G. Tuleouva [2]

[1] *Leverhulme Centre for Innovative Catalysis, University of Liverpool, PO Box 147, Grove St., Liverpool, L69 3BX, UK*
[2] *Zelinsky Institute of Organic Chemistry, USSR Academy of Sciences, 47 Leninsky Prospect, Moscow, USSR*

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The effect of high temperature ethane treatment on the dispersion and structure of a Pt-Cr/H-ZSM-5 catalyst has been studied by EXAFS and XPS. At the temperature where ethane aromatisation occurs, ($T = 820$ K), redispersion of platinum-chromium particles has been found, reducing the average particle diameter from 12 ± 2 Å to 8 ± 1 Å. The redispersion explains earlier observations that the aromatisation activity of these catalysts increases during initial use.

Keywords: Aromatization; dispersed catalysts; ethane; X-ray absorption

1. Introduction

The effect of reaction mixtures on the structure of supported metal catalysts remains a topic of considerable interest and importance. The application of X-ray diffraction is restricted to relatively large particle size, ($d >$ ca 20–30 Å) while electron microscopy cannot be applied in situ, and the image may be complicated by the presence of coke or other deposits. Extended X-ray absorption fine structure, (EXAFS) is well adapted to study small metal particles, (1), as has been demonstrated by studies of the interaction between rhodium catalysts and synthesis gas [2–5]. These results have indicated that small metal particles can demonstrate great structural flexibility. Much less is known of the way in which hydrocarbons can influence the structure of supported metallic particles. Gallezot et al. [4], reported that low temperature interaction between benzene and platinum particles of diameter ca 10 Å in zeolite Y leads only to a very subtle perturbation of the metallic structure.

To improve catalyst performance, however, it is necessary to follow metal dispersion and structure in the course of high temperature hydrocarbon reactions accompanied by coke deposition. Transmission electron microscopy shows that metal particles behaviour depends on treatment conditions and the original size range [6,7]. For model Pt/Al_2O_3 catalysts treated with acetylene, redispersion of bigger (90 Å) particles was observed, while smaller Pt particles (around 10 Å diameter) underwent sintering after use in reforming.

This letter presents EXAFS data on the structure and dispersion of metal alloy particles in a Pt-Cr/H-ZSM-5 catalyst after treatment with ethane at aromatisation conditions. We have previously shown that, after reduction in hydrogen the catalysts contained small Pt-Cr alloy particles within the zeolite structure [8]. Also, the ethane aromatisation activity of these catalysts increases during the first hour of use in a flow experiment, or for the first few pulses, in ethane pulsing experiments [9–11]. It is important to see if these changes in activity can be related to catalyst structure.

2. Experimental

The 0.5% Pt-0.75% Cr/H-ZSM-5 catalyst was prepared and calcined as described previously [9]; the Si/Al ratio of the zeolite was 22.5/1. EXAFS measurements were performed at the Daresbury Synchrotron radiation source using an in situ cell which has also been described [12]. Samples were reduced at 620 K for 1 h and subsequently at 820 K for 1 h in flowing hydrogen at 1 bar pressure, and then evacuated. To study the effect of reaction environment, the reduced sample was treated with 1:4 mixture of C_2H_6/Ar at 820 K, cooled in flowing gas to 300 K, and then exposed to the synchrotron beam. EXAFS spectra were recorded both in flowing gas and also after evacuation. Data were collected for the Pt L_{III} edge up to 600 eV above the absorption edge ($k = 12$ Å^{-1}) and analysed by standard methods [13]. Some measurements of the chromium K edge, energy 5989 eV, were also performed.

XPS measurements were made on reduced samples and also after treatment with ethane under analogous conditions to the EXAFS measurements, using a Kratos ES 200B spectrometer. The sample was transferred to the XPS spectrometer using a glove box filled with dry argon.

3. Results and discussion

XP spectra, (table 1), show that some Cr(O) is formed during H_2 treatment and that its fraction remains approximately the same after interaction with ethane 820 K. The only difference observed after treatment with ethane is an increase in the Pt $4f_{7/2}$ binding energy, which has also been observed for a

Table 1
XPS analysis of Pt/Cr/H-ZSM-5 catalyst

Treatment	Pt(O)		$Pt^{\delta+}$		Cr(O) [a] *BE*/eV	Cr(111) *BE*/eV
	BE/eV	%	*BE*/eV	%		
H_2, 820 K	72.3	100	–	–	577.2	573.4
Ethane/He, 820 K						
5 pulses of C_2H_6	71.8	51	73.0	49	577.6	573.6
Ethane/He, 820 K						
10 pulses of C_2H_6	71.8	66	73.2	34	577.4	573.3

[a] The Cr(O) peak area is 10–15% of the total for chromium and it does not change markedly during hydrocarbon treatment.

series of Pt/H-ZSM-5 catalysts [10,11]. Fig. 1 shows the experimental and calculated EXAFS spectra and table 2 gives the best fit parameters obtained from the EXAFS analysis. In agreement with our earlier studies, the best fit

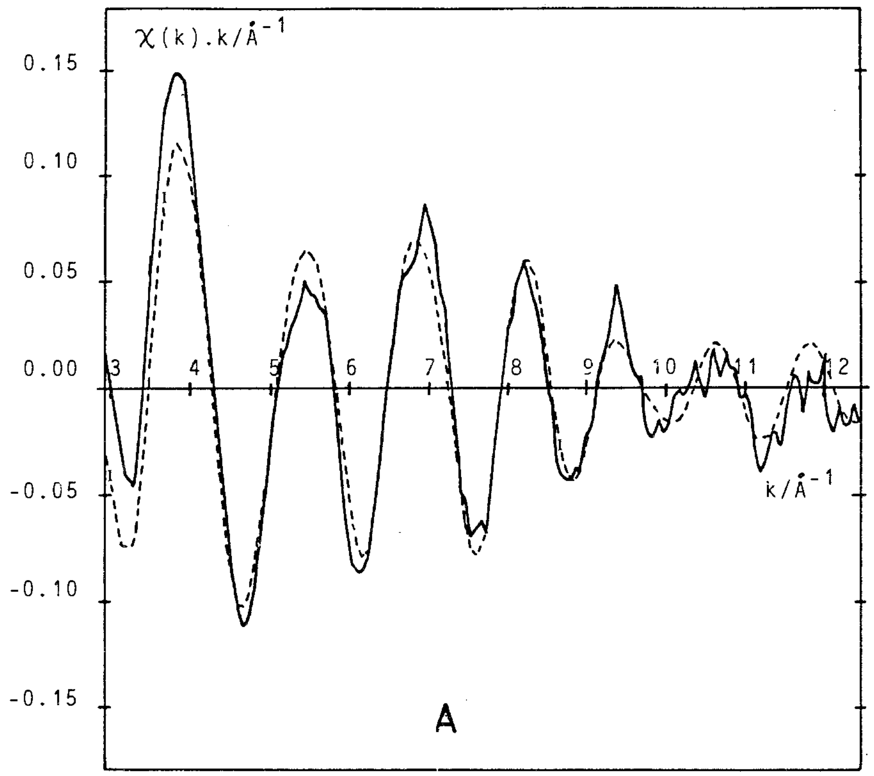

Fig. 1. Platinum L_{III} EXAFS for the Pt/Cr/H-ZSM-5 catalyst, solid line, experiment; dashed line, calculated using the parameters in table 2. (a) after reduction in hydrogen at 823 K, the sample was cooled to room temperature in hydrogen, which was then evacuated; (b) after exposure to ethane at 823 K and cooling to room temperature, the fit includes Pt-O coordination; (c) as (b), but replacing Pt-O with Pt-C coordination in the calculation.

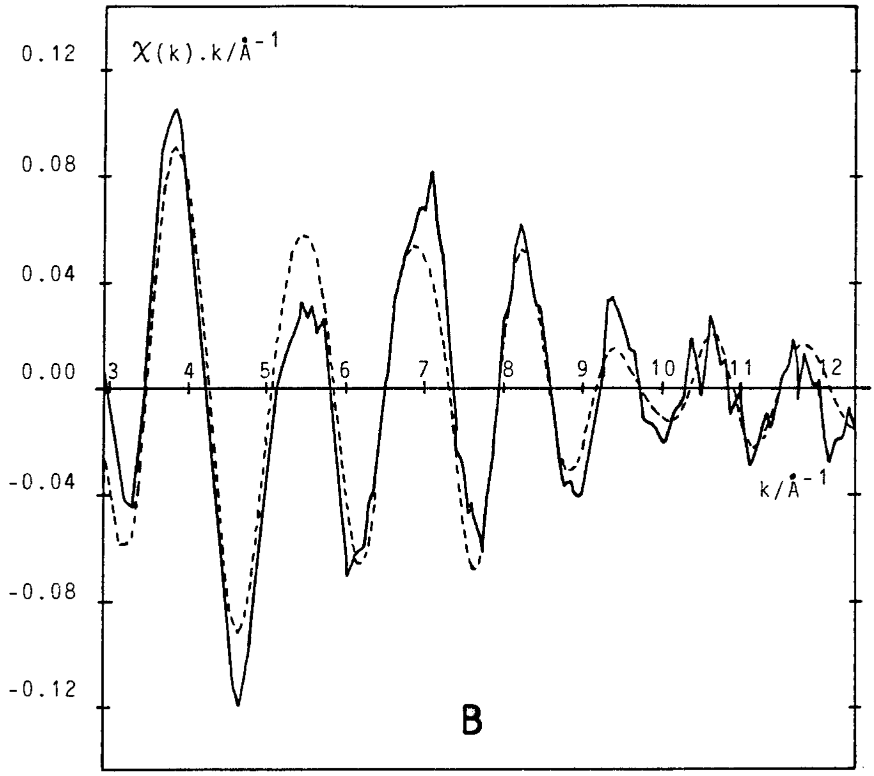

Fig. 1. (continued).

included three platinum–platinum distances, as well as platinum chromium and platinum–oxygen shells [7]. Each shell of neighbours was statistically significant at a level of $< 5\%$ [14]. These results confirmed formation of platinum-chromium particles which seem to be located within the zeolite structure. The metal particles appear slightly bigger than in our earlier study [8] with the nearest neighbour metal coordination number, (Pt-Pt plus Pt-Cr), increasing from 6.2 ± 1.5 to 8.2 ± 1.5. This may reflect a change in the Si/Al ratio of the zeolite support used, or small variations in preparation procedures. The main structural features, however, remain similar for both samples. The Pt-Cr particles are coordinated to oxygen, which reflects either their location inside the channels or occlusion by framework fragments [15].

The treatment of the pre-reduced catalyst with ethane at 820 K led to a decrease of the coordination number for the nearest neighbour Pt-Pt distance. The change is outside experimental error, which was estimated using the procedure described in [14], accounting explicitly for correlation between the values obtained for the coordination numbers and the Debye-Waller factors. The absolute error in N_1(Pt-Pt) does not exceed ± 0.8 while relative errors are expected to be significantly smaller, probably ± 0.5. Unexpectedly, the results

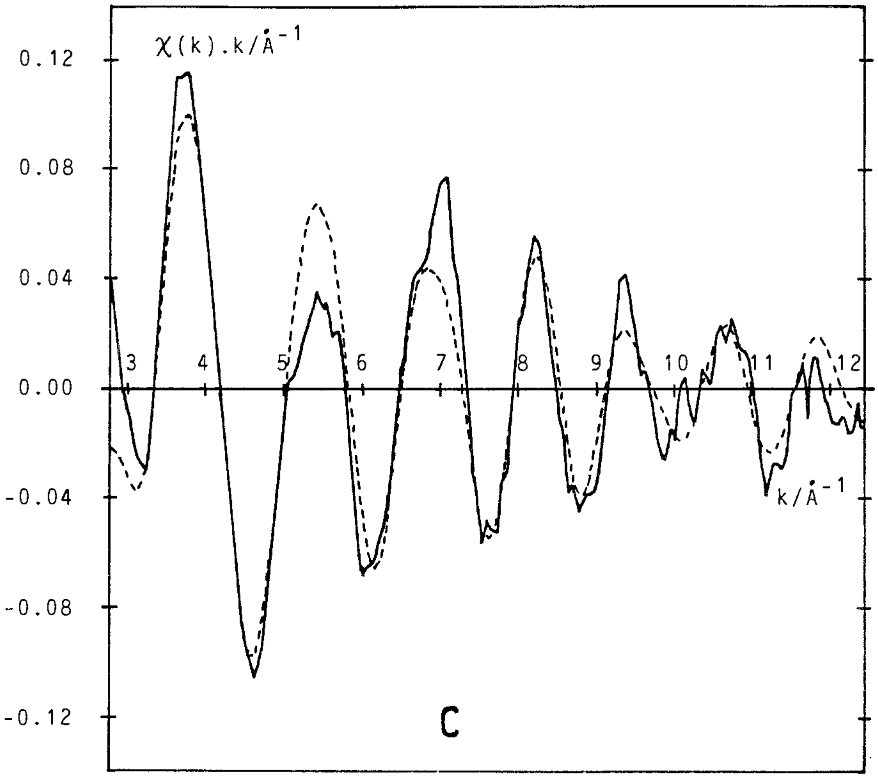

Fig. 1. (continued).

suggest that high temperature ethane treatment of Pt-Cr/ZSM-5 is accompanied by metallic particles redispersion, rather than sintering. The average particle size decreased from 12 ± 2 to 8 ± 1 Å and the number of atoms in the average cluster decreased from 60 ± 20 to 15–20 (±5), assuming spherical particles [15] (table 3).

The formation of complexes with reactant molecules is the most probable explanation for the disruption of metal particles. To probe whether metal-carbon bonds formed during ethane treatment, a platinum-carbon shell was included in the EXAFS fit, replacing the Pt-O shell. This led to a slight improvement in the fit and a further reduction of the Pt-Pt coordination number. The changes in fitting index are too small to allow definite conclusions, since phase shifts for carbon and oxygen are very similar.

Thus, EXAFS shows the structural flexibility of small metallic particles. Sintering, which might be expected by analogy with other supported metal catalysts of similar particles size [16], did not occur. In contrast, the particles became smaller. The redispersion or disruption is confined to relatively small particles, since it was not observed with a 1% Pt/H-ZSM-5 catalyst, which contained particles of 15–25 Å diameter. The driving force of this process is

Table 2
EXAFS results for Pt-Cr catalyst. All spectra were taken after cooling to 298 K

	Pt-Pt						Pt-O (Pt-C) [a]		Pt-Cr	
	N	*R*/A	*N*	*R*/A	*N*	*R*/A	*N*	*R*/A	*N*	*R*/A
Heating at 820 K in hydrogen	7.3±0.5	2.75±0.01	3.8±1	3.88±0.02	2.3±0.7	4.86±0.04	1.9±0.4	1.95±0.03	0.7±0.2	2.68±0.02
After reduction and heating ethane	5.6±0.5	2.75±0.01	2.7±1	3.90±0.02	2.2±0.7	4.82±0.04	1.2±0.4	1.97±0.03	0.6±0.2	2.65±0.02
/Ar at 820 K	5.0±0.5 [a]	2.76±0.01	2.8±1	3.91±0.02	2.8±0.7	4.88±0.04	0.7±0.3 [a]	1.92±0.03	0.6±0.2	2.67±0.02
Similar, but measured	6.0±0.5	2.76±0.01	3.0±1	3.88±0.02	1.9±0.6	4.82±0.06	1.1±0.2	1.97±0.03	0.5±0.2	2.68±0.02
in vacuo	5.2±0.5 [a]	2.75±0.01	3.3±1	3.88±0.02	2.1±0.6	4.88±0.06	0.8±0.3 [a]	1.96±0.03	0.6±0.2	2.70±0.02

[a] Fits including a Pt-C distance instead of a Pt-O distance.

Table 3
Average particle size of quasi-spherical shape particles

	N_{I} (Pt-Pt + Pt-Cr)	Average No. of atoms [a]	Average diameter/A [a]
823 K, H_2	8.0	60±20	12 ±2
823 K, H_2,	6.2	15±5	8.0±1
ethane/Ar	5.6 [b]	15±5	7.3±1
823 K, H_2,	6.5	15±5	8.5±1
ethane/Ar, vacuum	5.8 [b]	15±5	7.5±1

[a] Estimated as described in [15].

[b] With a Pt-C distance replacing Pt-O.

likely to be an interaction between metal and ethane or its reaction products, (aromatics, olefins or carbonaceous deposits). The mechanism is not the same as that observed previously for severely coked metal catalysts where carbon dissolution and particle movement occurred [16]. Indeed, samples treated in a similar way during catalytic studies gave high yields in the aromatisation of ethane [9,11]. The exposure of the catalysts to ethane in the present experiments corresponds to a period of increasing activity with time-on-stream in both continuous flow and ethane pulsing experiments [9,11]. This increasing activity of the metal/zeolite catalysts therefore results from redispersion of the metal particles. The activation is likely to be accompanied by carbon desposition at the metal, which is known to occur in the early stages reforming catalysis and has been reported in the recent EXAFS study by Guyot-Sionnet et al. [17]. In our study we cannot differentiate with certainty between Pt-C bonding and Pt coordination to oxygen of the zeolite framework (see table 2).

The EXAFS results allow us to understand the increase in platinum core level binding energies observed for both Pt/H-ZSM-5 and Pt-Cr/H-ZSM-5 catalysts in the course of ethane aromatisation [9,11]. The decrease of extra-atomic relaxation energy caused by a decrease of the particle size, and an increase of electron deficiency due to metal-carbon interaction will both cause XPS shifts to higher binding energy. Enhancement of the platinum-oxygen interaction is less probable, as no increase in the Pt-O coordination number was observed.

In conclusion, we emphasise that the redispersion of particles of ca. 12 Å diameter reflects the unique properties of the metal/pentasil system, where metallic particles are locked within the zeolite structure.

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