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Metathesis probes of Re promoters on reforming catalysts

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Propene metathesis results show conclusively that a significant fraction of the Re is in a positive oxidation state in EUROCAT-4 (0.3% Re/0.3% Pt/alumina) pre-treated in H_2 to 673 K, and, since some of the product (and reactant) alkenes are self-hydrogenated the zero-valent Pt component is not entirely encapsulated in this Re_xO_y.

Keywords: Rhenia promoters; reforming catalysts

1. Introduction

Work on bimetallic catalysts for the reforming of naphtha and alkanes to aromatic feedstocks and high octane fuels [1] started in the 1960s and has produced alumina-supported Pt–Ir, Pt–Re [2], and Pt–Sn [3] phases.

Despite continued developments [4] the precise active sites and the state of promoters are not yet understood with certainty; this is certainly the case for Pt–Re reforming catalysts despite EXAFS analysis [5].

In these Re^0 could be the promoter. This could deposit on Pt [6] and inhibit the sintering of Pt in part by alloy formation [7]. Certainly if Re_xO_y were initially present in such catalysts after calcination, Pt would enhance its reduction [8] possibly via spilt-over hydrogen [9] (although the surface of the bimetallic crystallites so produced would be expected [10] to be Pt-enriched). The metal dispersion may be increased [11] by the Pt–Re interaction. The hydrogenolysis activity of Pt–Re certainly appears to be higher than for either the Pt or the Re alone and this is true for single crystal or supported metal samples [12,13]. Interestingly, Cunningham [13] found that in *n*-butane hydrogenolysis 0.3% Pt/alumina (CK303; EUROPT-3) showed much higher selectivity to propane (S_3) while 0.3% Pt/0.3% Re/alumina (CK433; EUROPT-4) showed much higher selectivity to ethane (S_2), 0.3% Pt/alumina $S_2 = 0.581$, $S_3 = 0.703$;

0.3% Pt/0.3% Re/alumina $S_2 = 0.795$, $S_3 = 0.456$.

However, since hydrogenolysis activity is retained in the bimetallic catalyst zero-valent Pt must remain the predominant state of the group VIII metal. With Pt/alumina the addition of Re enhances the formation of Pt–O–Al bonds at low temperature and hence stabilises the Pt [14] in a high area state.

In practice the Pt–Re/alumina catalysts are pre-sulphided [15] to reduce the hydrogenolysis activity enhanced by Re addition, possibly by reducing the size of Pt ensembles. Kim and Somorjai [12,13] found that Re^0 condensed onto Pt(111) under UHV conditions increased the rate of hydrogenolysis by a factor of 64, but this increase was reduced to a mere 7 when S was added. It may also be that such ReS_x suppresses conversion of carbonaceous material to graphitic carbon [16]; certainly Pt–Re/Al_2O_3 has lower rates of built up carbonaceous deposits than Pt/Al_2O_3 alone [17]. Others believe that Re in a positive oxidation state (e.g. Re_xO_y [18]) is the promoter [19]. A lower oxide Re_xO_y could be produced by spillover of hydrogen from the Pt centres [9]. Once produced it could then migrate back to the Pt in the reverse direction to the spilt-over hydrogen [20].

The uncertainty concerning the nature of the Pt–Re interaction in such catalysts may be one reason why attempts [21] have been made to try to prepare Pt/ReO_2 colloidal particles in which the two phases are known to be in contact.

Catalysis is often the most sensitive probe for the surface state of heterogeneous catalysts and here metathesis has been used to probe alumina-supported catalysts containing Pt and Re for the first time. Since metathesis of propene to butenes and ethene is catalysed by Re^{x+} (or W) on alumina, this reaction is therefore very sensitive to the presence of Re in a positive oxidation state.

2. Experimental

0.3% Re_xO_y/alumina (AP/Al_2O_3) was derived by impregnation with NH_4ReO_4 and then pretreatment by

(i) calcination at 973 K for 3 h in air,

(ii) cooling to 298 K and flushing with N_2 for 30 min,
and then undertaking metathesis at 428 K.

0.3% Re_xO_y/alumina (PA/Al_2O_3) was derived by impregnation with $HReO_4$ and then pretreatment by

(i) calcination at 973 K for 3 h in air,

(ii) cooling to 298 K and flushing with N_2 for 30 min,
and then undertaking metathesis at 428 K.

EUROCAT-4 (0.3% Re/0.3% Pt/alumina (CK433)) was pretreated at

(i) 673 K for 2 h in air and cooled to room temperature and flushed with N_2 for 1 h,

(ii) 673 K for 2 h in 6% H_2/N_2 (99%) and cooled to room temperature and flushed with N_2 for 1 h, and

(iii) 428 K propene was introduced (at 20 cm^3/min) and the temperature was increased to 468 K,

after which, metathesis activity was measured under isothermal conditions. Then the activities of 0.3% Re_xO_y/alumina derived by impregnation of NH_4ReO_4 (AP/alumina) and $HReO_4$ (PA/alumina) at 428 K were also measured separately. Some characterisation was carried out by temperature-programmed reduction (TPR) and X-ray photoelectron spectroscopy (XPS; corrected to Al 2p at 74.7 eV for the Al_2O_3 support).

3. Results and discussion

The results in table 1 were obtained. *First*, it is clear that propene metathesis to ethene and butenes is seen on all catalysts and this appears to indicate unequivocally that a significant fraction of the Re is in a positive oxidation state in the Pt–Re/Al_2O_3 EUROCAT-4 pre-treated in this way (i.e. in hydrogen up to 673 K). *Second*, for all catalysts the trans : cis but-2-ene ratio (over 2) and the C_4/C_2 ratio (about 2) are higher than expected and the latter may suggest some parallel dimerisation of product ethene. *Third*, there is some hydrogenation of reactant and product alkenes on the probably zero-valent Pt component in EUROCAT-4 and therefore the Pt cannot be entirely encapsulated in the Re_xO_y already inferred to be present in this catalyst. It is not surprising to find the Pt catalysing ethene hydrogenation [22] since the rates of this will be fast and here we see:

21% hydrogenation for C_2H_4,
5% hydrogenation for propene,
1% hydrogenation for butenes.

It would be interesting to demonstrate for alumina-supported catalysts that Re^0 was inactive in metathesis (unlike Re^{x+}). There is a problem in this respect, however, in that Re_xO_y/alumina inevitably contains a variety of Re states simultaneously. Alumina can be thought of as a defective spinel or as a close packed array of O^{2-} ions in which Al^{3+} cations sit; in either case there will inevitably be sites on which Al^{3+} is missing and into which ReO_4^- tetrahedra can fit, especially since the sizes of these tetrahedra are defined by the anions rather than the cations (although the sizes of Re^{7+} and Al^{3+} are not so very different in any case). Furthermore, the interaction between ReO_4^- from solution and the alumina surface is likely to be enhanced by the solubility of the alumina in the impregnating solution which is at pHs (i.e. about 5 for PA and about 8 for AP) far removed from 7.

It seems therefore that at low concentration ReO_4^- (species I) will be adsorbed by and inserted into the alumina surface and will then be rather stabilised and difficult to reduce. However, Re_2O_7 rafts with ReO_4 tetrahedra and ReO_6 octahedra (species II) will subsequently be formed at higher Re uptakes and these will be more easily reduced.

Table 1
Products of propene metathesis activity for EUROCAT-4 and Re_xO_y/alumina catalysts for various reaction times

Product (%)	EUROCAT-4		AP/alumina		PA/alumina	
	26 min	54 min	37 min	58 min	28 min	52 min
methane	0.02	0.00	0.00	0.00	0.00	0.00
ethane	0.40	0.20	0.01	0.01	0.01	0.01
ethene	1.89	1.67	4.13	4.18	5.46	5.10
propane	4.27	4.01	0.25	0.26	0.24	0.30
propene	89.11	89.93	86.07	85.62	81.76	82.54
butane	0.06	0.06	0.00	0.00	0.00	0.00
but-1-ene	0.36	0.26	0.53	0.56	0.90	0.86
t-but-2-ene	2.60	2.47	6.17	6.38	7.78	7.55
c-but-2-ene	1.20	1.13	2.84	2.99	3.85	3.65
hex-1-ene	0.00	0.00	0.00	0.00	0.00	0.00
t/c C_4 ratio	2.17	2.19	2.17	2.13	2.02	2.07
C_4/C_2 ratio	1.84	2.10	2.30	2.37	2.29	2.36

After reduction and especially in the presence of Pt a significant fraction of species II may be reduced to a low or zero oxidation state. However, XPS results (see fig. 1) for the $Pt/Re_xO_y/Al_2O_3$ before and after TPR revealed a Re 4f 7/2 peak which was unchanged in position. This is consistent with TPR results mentioned in a moment suggesting that most of the Re in this catalyst remains in a positive and constant oxidation state. We expect Re^0 4f 7/2 to be at 40.46 eV and Re^{7+} 4f 7/2 to be at 46.7 eV. Clearly the peaks here correspond more closely to the latter. Therefore inevitably a real Re_xO_y/alumina catalyst will contain a range of species including I and II.

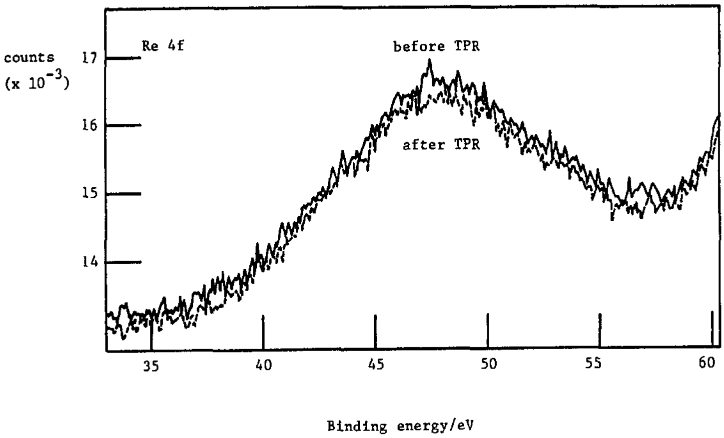

Fig. 1. X-ray photoelectron spectra of Re 4f 7/2 peaks in $Pt/Re_xO_y/Al_2O_3$ (EUROCAT-4) before and after temperature-programmed reduction (TPR).

Furthermore, metathesis catalysts are always pre-calcined to ensure maximum activity and this is consistent with a view of the poor metathesis activity of Re^0.

However, although we cannot consider a Re^0/alumina catalyst per se, we can consider whether an increased extent of reduction allows metathesis on lower oxidation state Re to be sustained as we see here for EUROCAT-4.

In TPR of 2.9% Re_xO_y/Al_2O_3 derived from AP ($T_{max} = 667$ K) the %reduction of Re is 81% (assuming Re_2O_7 is initially present); a catalyst derived from PA has a higher T_{max} and a higher %reduction (i.e. 678 K and 87%). However, fig. 2 shows that pre-reduction to this extent produces a rapidly deactivating metathesis activity. This is not the pattern seen for the $Pt/Re_xO_y/Al_2O_3$ reforming catalyst reduced under more standard conditions. Hence sustainable activity in metathesis is most likely to be attributable to Re in a positive oxidation state. It is this species which we believe we are specifically probing.

4. Conclusions

Should we be surprised at the presence of Re_xO_y in such reduced $Pt–Re/Al_2O_3$ catalysts? Probably not, given that Re_xO_y on Al_2O_3 (introduced as $HReO_4$ and then calcined) reduces at a maximum rate at temperatures above those used here (i.e. 700–900 K [23]).

That metathesis detects Re in a positive oxidation state in the present $Pt–Re/Al_2O_3$ catalyst after reduction, does not mean that none of the Re (including that in *contact* with Pt) is zero-valent. Clearly a range of Re states may be present in such catalysts. Other catalytic probes will clearly be needed to investigate the zero-

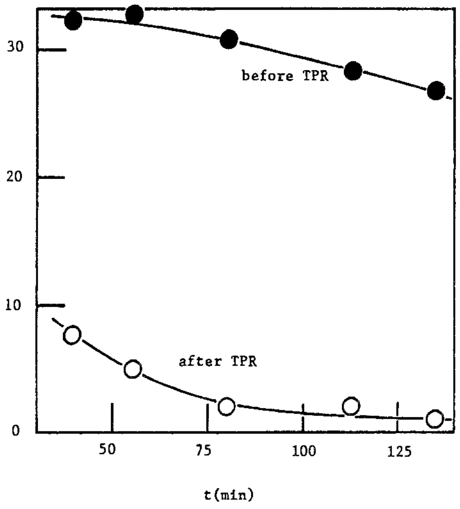

Fig. 2. Effect of temperature-programmed reduction (TPR) on 2.9% Re_xO_y/Al_2O_3 activity in propene metathesis.

valent Re undoubtedly present in contact with Pt (e.g. ammonia synthesis might be relevant etc). It is likely that rhenium ions in low concentrations can be inserted into cation vacancies in the defective alumina support, producing species which are very difficult to reduce. It may be these highly dispersed components of the Pt–Re and Re catalysts that are being detected by the metathesis reaction here.

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