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Coking and regeneration of palladium-doped $H_3PW_{12}O_{40}/SiO_2$ catalysts

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The coking during propene oligomerisation and subsequent regeneration of both silica-supported heteropoly acid $H_3PW_{12}O_{40}$ (PW) and its palladium-modified form (1.6–2.5 wt% Pd) have been studied. ^{31}P MAS NMR studies have revealed that the Keggin structure of the catalyst was unaffected by coke deposition in both unmodified PW/SiO_2 and Pd-modified form. As shown by ^{13}C MAS NMR and TGA/TPO, the Pd modification affects the nature of the coke formed: for the standard catalyst (PW/SiO_2) both soft coke, comprising mainly high molecular weight aliphatic oligomers, and hard coke, comprising polynuclear aromatics, are formed whilst on the Pd-modified catalyst only the soft coke is observed. Coke formation causes strong deactivation of the catalyst in the oligomerisation of propene. The aerobic burning of coke on the unmodified PW/SiO_2 occurs in the temperature range of 470–520 °C. Doping the catalyst with Pd significantly decreases this temperature to allow catalyst regeneration at temperatures as low as 350 °C without loss of catalytic activity.

Keywords: heteropoly acid, palladium modification, propene oligomerisation, coke formation, catalyst regeneration

1. Introduction

Heteropoly acids (HPAs) have been extensively studied as acid and oxidation catalysts for a wide range of reactions [1–4]. Industrially, they have found application in several processes such as the oxidation of methacrolein to methacrylic acid, oxidation of ethylene to acetic acid and the hydration of olefins [5]. HPA-based solid acid catalysts, especially those comprising the strongest Keggin-type HPAs such as $H_3PW_{12}O_{40}$ (PW) or $H_4SiW_{12}O_{40}$ (SiW), are more active than conventional solid acids such as SiO_2–Al_2O_3, H_3PO_4/SiO_2 and zeolites [1,4]. However, their use is restricted because of the difficulty of HPA regeneration [1]. Generally, in acid-catalysed organic conversions, especially in the gas phase, solid acid catalysts are deactivated by coke formation (coking). In the case of conventional catalysts, such as SiO_2–Al_2O_3 or zeolites, regeneration can be successfully achieved by a controlled burning of the deposited coke with oxygen at 450–550 °C [6,7]. In the case of HPA catalysts, this method is not applicable as they have relatively low thermal stability. Thus PW and SiW structures practically decompose above 465 and 445 °C, respectively [8]. Therefore, for HPAs to be more widely used for heterogeneous acid catalysis an efficient and reliable methodology of their regeneration would be beneficial. Supercritical extraction of coke with CO_2 or SO_2 as solvents has been reported [9]. Modification of conventional solid acid catalysts by platinum group metals, e.g., Pt or Pd, to enhance their regeneration is well known [6,7] and allows a significant reduction in the temperature of coke gasification with oxygen. Similar doping could facilitate the regeneration of HPA catalysts.

This work concerns an investigation into the deactivation and regeneration of silica-supported PW catalysts in the gas-phase conversion of hydrocarbons. The oligomerisation of propene, previously studied with HPA catalysts [10], was chosen as a model reaction. The effect of palladium doping on the coke formation and burning was studied. It was shown that the Pd modification allows the regeneration of PW/SiO_2 catalysts at temperatures as low as 350 °C without loss of activity.

2. Experimental

2.1. Materials

Tungstophosphoric acid, $H_3PW_{12}O_{40}\cdot nH_2O$, from Aldrich, palladium acetate from Johnson Matthey and silica Aerosil 300 from Degussa were used without further purification. All solvents were analytical grade and distilled before use.

2.2. Techniques

Magic-angle spinning (MAS) solid-state NMR studies were carried out on a Bruker Avance DSX400 NMR spectrometer. The ^{31}P NMR spectra were recorded at 161.99 MHz using a 7 mm rotor probe with 85% phosphoric acid as an external standard. The spinning rate was 4 kHz. The ^{1}H–^{13}C cross polarization MAS NMR spectra were recorded at a frequency of 100.6 MHz. The peaks

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were referenced to tetramethylsilane (TMS) as an external standard. The spinning rate was 3–4 kHz.

Thermogravimetric analysis (TGA) was performed using a Perkin–Elmer TGA7 analyser. The carrier gas was air and the samples were heated from 40 to 700 °C at a rate of 20 °C/min. The TGA was calibrated using iron, nickel and perkalloy curie point. The TGA/TPO analysis of "soft" and "hard" coke was carried out as described elsewhere [10].

2.3. Catalyst preparation

A 20 wt% PW/SiO_2 catalyst (PWI) was prepared by impregnating Aerosil 300 silica with an excess of a methanolic solution of $H_3PW_{12}O_{40}$ as described elsewhere [11]. The catalyst was dried overnight at 120 °C and then powdered.

Palladium-doped 20 wt% PW/SiO_2 catalysts, containing 1.6–2.5 wt% Pd, were prepared by impregnating the powdered 20 wt% PW/SiO_2 catalyst (1 g) with a toluene solution of $Pd(OAc)_2$ ($0.02\ mol\,l^{-1}$, ca. 10 ml) at room temperature for 30 min with stirring. A quick decolouration of the toluene solution was noted, indicating the quantitative adsorption of Pd(II) from solution to form a Pd(II) salt of PW on the silica surface, as represented by

$$\begin{aligned}&Pd(OAc)_2 + H_3PW_{12}O_{40}/SiO_2\\&\quad\rightarrow PdHPW_{12}O_{40}/SiO_2 + 2HOAc\end{aligned}\tag{1}$$

Then toluene was slowly evaporated using a rotary evaporator. During the evaporation Pd(II) was readily reduced to Pd(0) by toluene, regenerating the PW acid and turning the beige solid black:

$$\begin{aligned}&PdHPW_{12}O_{40}/SiO_2 + 2[H]\\&\quad\rightarrow (Pd^0 + H_3PW_{12}O_{40})/SiO_2\end{aligned}\tag{2}$$

The oxidation of arenes, e.g., toluene, by Pd(II) salts in solution is well known [12,13]. As seen, a similar reaction readily occurs on the silica surface. No reduction or leaching of PW was observed during the similar treatment of 20 wt% PW/SiO_2 with toluene in the absence of $Pd(OAc)_2$. The Pd-modified catalysts were finally dried overnight at 120 °C. The 2.5 wt% Pd sample will be represented hereafter as PWII.

Alternatively, to ensure the complete reduction of Pd(II) to Pd(0) and to avoid the formation of a Pd(II) salt of PW on the silica surface, the 2.5 wt% Pd-modified PW/SiO_2 catalyst was prepared by the following procedure. First, a 2.5 wt% Pd on silica was prepared by impregnating Aerosil 300 with a $Pd(OAc)_2$ solution in dichloromethane and reducing Pd(II) to Pd(0) under a flow of 25% H_2 in N_2 at 250 °C for 2 h. Next, 20 wt% PW was loaded on the solid as described for PWI. The catalyst thus prepared is coded PWIII.

2.4. Coking

Coking was performed in a fixed-bed flow reactor under propene at atmospheric pressure. Prior to coking, the catalyst (3.0 g) was pre-treated at 200 °C under a 20 $ml\,min^{-1}$ flow of dry nitrogen for a period of 2 h. Then the sample was treated with propene at 20 $ml\,min^{-1}$ and 200 °C for a certain period of time, typically 1 h for soft coke and 2 h or more for hard coke. (Hereafter "soft" and "hard" coke are referred to as mainly high molecular weight aliphatic oligomers and heavy polynuclear aromatics, respectively [6,10].) After that the volatile hydrocarbons were removed from the catalyst by purging with dry nitrogen at 20 $ml\,min^{-1}$ and 200 °C for 15 min.

2.5. Propene oligomerisation

The propene oligomerisation was carried out using a stainless-steel tubular fixed-bed flow reactor, housed in a three-zone SSL tubular furnace fitted with Eurotherm temperature controllers, with on-line GC analysis (a Varian 3800 gas chromatograph equipped with TCD and FID detectors and a 30 m VH1 megabore column). The gases were passed through the catalyst bed using mass flow controllers for propene and nitrogen. A typical experiment was carried out as follows. The catalyst (1 g) was activated by heating under a nitrogen flow (30 $ml\,min^{-1}$) for 2 h at 200 °C in a fixed-bed reactor. For the oligomerisation of propene a mixture of propene and nitrogen 1 and 49 $ml\,min^{-1}$, respectively, was fed to the catalyst bed. The reaction was carried out at 200 °C.

3. Results and discussion

3.1. ^{31}P MAS NMR studies

The ^{31}P NMR spectra of all the as-made samples showed a simple peak around −15 ppm which is associated with bulk Keggin-type PW [11]. The unmodified HPA sample (PWI) coked for 1 h showed a small additional shoulder around −14 ppm which may be explained by partial dehydration of the HPA [14]. The PWI sample coked for 3 h showed a single peak at −15.6 ppm but required longer recycle delay for acquiring the spectra. This indicates that the Keggin structure remains intact in the hard coked sample. The longer recycle delay needed for acquiring the spectra may be due to the interaction of HPA with hard coke or the segregation of HPA particles on SiO_2 (pure HPAs need a similar long recycle delay). The samples of the palladium-modified PWII coked for 1 and 3 h showed the typical peak around −15 ppm with a similar long delay needed for the PWI sample coked for 3 h. This indicates that the Keggin structure in the unmodified and Pd-modified HPA catalysts is not destroyed by the formation of coke in these samples.

3.2. ^{13}C CP MAS NMR studies

The ^{13}C CP MAS NMR spectra of the coked unmodified and Pd-modified samples were different. The unmodified PWI coked for 1 h and for 3 h showed a broad peak around 21 ppm which can be attributed to aliphatic hydrocarbons. Due to the unresolved nature of this broad peak a more

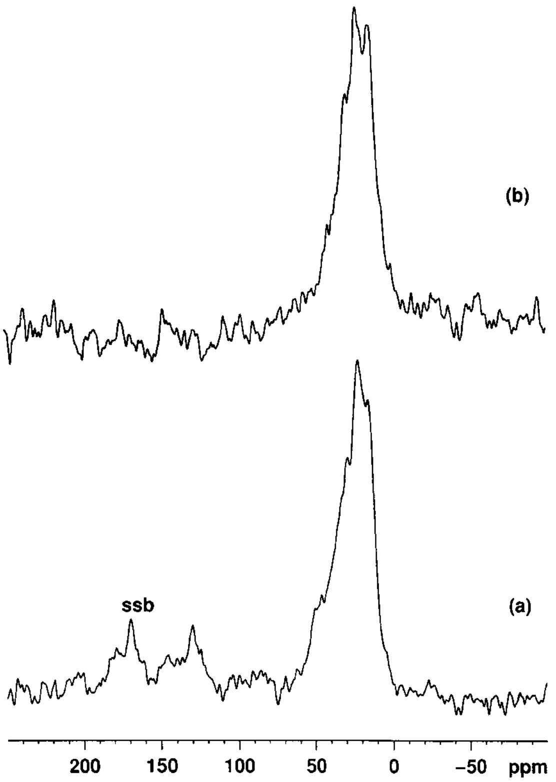

Figure 1. ^{13}C CP MAS NMR of catalysts coked for 3 h: (a) PWI and (b) PWII; ssb = spinning side band.

definitive assignment is not possible. There is also another peak around 129 ppm which can be assigned to aromatic hydrocarbons (figure 1). The relative intensity of the aromatic peaks is higher in the hard coked samples. As the spectra were recorded using cross polarization, a quantification of the aliphatic/aromatic ratio is possible. The PWII and PWIII samples coked for both 1 h and 3 h showed peaks which could only be assigned to aliphatic hydrocarbons. Thus both hard and soft coke form on the unmodified catalyst, while Pd-doping inhibits the formation of hard coke.

3.3. TPO/TGA measurements

TGA analysis for Pd-modified catalysts, PWII and PWIII, pretreated under a flow of nitrogen at 200 °C showed that these solids contained no carbonaceous materials and the TGA was similar to that of the unmodified HPA catalyst (figure 2). The weight losses around 100–140 °C can be attributed to the loss of water of hydration and a small weight loss above 450 °C is due to the decomposition of the Keggin structure and the evolution of the constitutional water ($1.5H_2O$) from $H_3PW_{12}O_{40}$.

The effect of palladium concentration in the range 1.6–2.5 wt% on the nature of coke formed was also studied. For the Pd-modified materials, a reduction in the temperature of coke removal with increasing Pd content was observed. It was noted that the weight loss in the temperature region 400–600 °C associated with the presence of hard coke on the surface decreased and a new region for coke removal centred around 350 °C became apparent (figure 3). This suggests that coke was forming not only on the PW/SiO_2 catalyst surface but also on (or near) the Pd(0) particles present, with the latter coke being removed at the lower temperature. For the 2.5 wt% Pd catalyst (PWII) a single peak in the temperature profile centred at 350 °C was noted (figure 3). Similar results were obtained for Pt/Al_2O_3 catalyst, assuming that either platinum catalyses the oxidation of coke or coke deposited on the metal is different from that on the alumina [6].

A more detailed TPD study of the coked samples for the unmodified PWI and 2.5 wt% Pd-modified PWII was carried out. The coked PWI catalyst showed a total weight loss of 9.7%. Out of this the weight loss of 1.4% and a further weight loss of 0.65% upto 143 °C can be attributed to the loss of water. In addition there is a weight loss of 2.05% around 246 °C which can be attributed to the aliphatic hydrocarbons (soft coke). A further weight loss of 5.6% around 518 °C can be attributed to polyaromatics (hard coke). The TGA of coked PWII on silica showed a similar pattern of weight loss (except for aromatics) to-

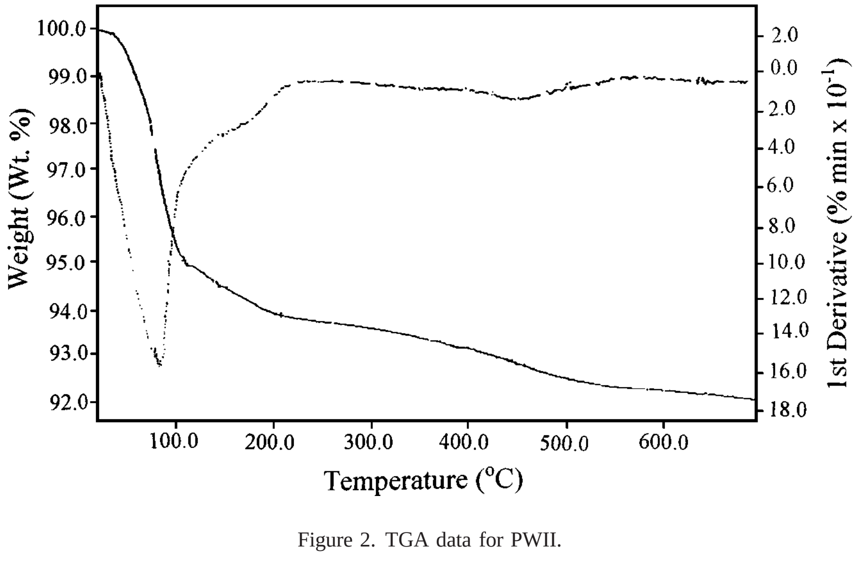

Figure 2. TGA data for PWII.

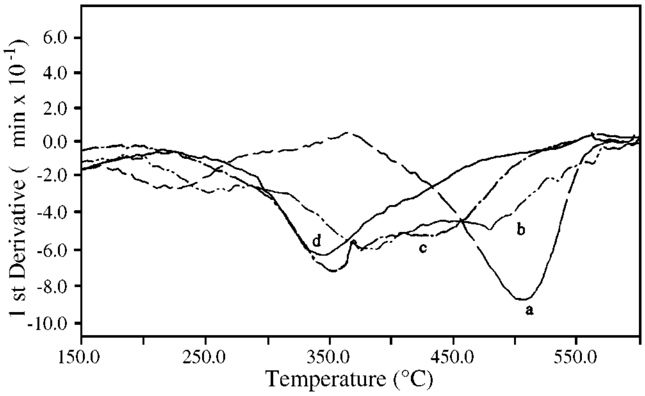

Figure 3. TGA data for coked catalysts: (a) PWI, (b) 1.6 wt% Pd-modified PWI, (c) 2.0 wt% Pd-modified PWI and (d) PWII (2.5 wt% Pd).

talling to about 7.7%. The weight loss of about 2.7% up to 137 °C could be due to the loss of water. Further weight losses at 238 °C (0.9%) and 353 °C (4.13%) could be due to aliphatic hydrocarbons (soft coke). No significant weight loss at higher temperatures, which could be attributed to aromatics, was observed.

3.4. Catalyst regeneration and reactor studies

Oligomerisation of propene was studied as a test reaction for the deactivation/regeneration of the Pd-modified catalysts. Product analysis using gas chromatography showed the major products to be in the range of C_{12} to C_{18} oligomers. Similar results for the oligomerisation of propene using heteropoly acids have been reported earlier [10].

The PWII catalyst showed a very high initial activity, with a rapid deactivation (figure 4). The reaction was continued for a period of about 3 h by which time the conversion dropped to about 17%. The reaction was stopped at this point and the catalyst was cooled down in a nitrogen stream (49 ml min^{-1}) and was regenerated at 350 °C in air (50 ml min^{-1}) for a period of 2 h. Then the second run with the regenerated catalyst was carried out. Again, a very high initial activity was observed, followed by rapid deactivation. In the second cycle the conversion was virtually the same as that in the first cycle. It should be noted that under the conditions studied the Pd-modified PWII deactivated a bit faster than the unmodified PWI. However, the PWI catalyst did not regain its activity after regeneration under the above conditions. No attempt has been made to optimise the performance of the catalysts.

Similar results were obtained with the PWIII catalyst prepared by loading PW on 2.5% Pd/SiO_2 (figure 5). In this case, after the first oligomerisation run the catalyst was regenerated by air treatment as above, followed by the reduction under a flow of 25% H_2 in N_2 at 225 °C for 2 h. These results indicate that the PWII and PWIII catalysts are quite similar, both containing palladium mainly as Pd(0). Apparently, the Pd(II), even when present in a small amount in PWII (in the form of $PdHPW_{12}O_{40}$), does not significantly affect catalyst performance.

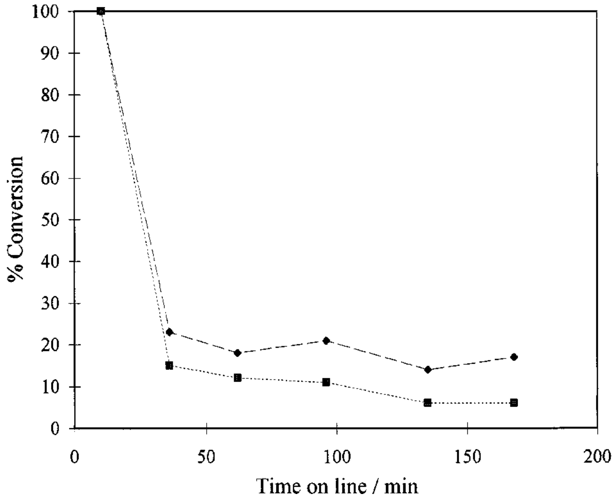

Figure 4. Catalyst performance of (♦) fresh and (■) regenerated PWII for propene oligomerisation.

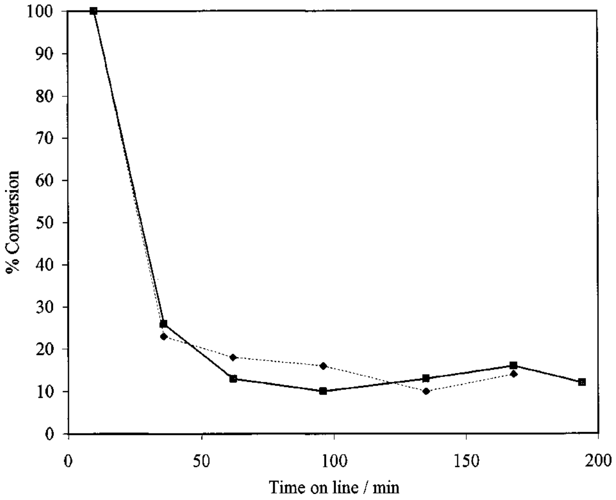

Figure 5. Catalyst performance of (♦) fresh and (■) regenerated PWIII for propene oligomerisation.

4. Conclusions

Solid-state NMR studies show that the formation of coke during the oligomerisation of propene, although deactivating the catalyst, does not affect the Keggin structure of silica-supported PW. Palladium modification of a PW/SiO_2 catalyst hindered the formation of hard coke, i.e., only soft coke was detected. The undoped catalyst, however, forms a mixture of hard and soft coke. On the other hand, and most importantly, the aerobic gasification of coke on Pd-modified PW occurs at a significantly lower temperature than on the undoped PW, which allows regeneration of the catalyst without destroying the Keggin structure of PW, hence without loss of its catalytic activity.

Acknowledgement

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