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Effect of hydrogen spillover on the hydrogenation of 1-hexene over diluted carbon molecular sieve supported Pt catalyst

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Abstract

Pt supported on a carbon molecular sieve (Pt/CMS) was prepared by pyrolysis of polyfurfuryl alcohol containing pre-reduced Pt particles. The catalysts were characterized by hydrogen chemisorption, XRD, N_2 adsorption/desorption and TEM. Hydrogen chemisorption showed that not all the Pt particles were exposed to H_2 molecules. Oxidation treatment made Pt particles more accessible to H_2. Catalyst activity was evaluated by hydrogenation of 1-hexene. Hydrogen spillover was demonstrated by diluting Pt/CMS with activated carbon or hydrogen type zeolite Y. The initial conversion of 1-hexene was increased from 86.5% to 98.5% and to 100% when Pt/CMS was diluted with activated carbon and hydrogen type zeolite, respectively. The high initial conversion was sustained for 6 h in the presence of diluents while the conversion decreased quickly for Pt/CMS alone.

Keywords: Pt; Carbon molecular sieve; Hydrogenation of 1-hexene; Hydrogen spillover

1. Introduction

A polyfurfuryl alcohol (PFA)-derived carbon molecular sieve has a typical pore size of 0.4–0.5 nm. Pt supported on a carbon molecular sieve (Pt/CMS) prepared by direct reduction of Pt precursor PFA/furfuryl alcohol has shown shape selectivity in olefin hydrogenation reactions [1–4]. In the work of Trimm and Cooper, Pt/CMS was prepared by direct reduction of chloroplatinic acid in PFA during the carbonization process. The results showed that small, linear olefins (propylene and 1-butene) were hydrogenated more efficiently over Pt/CMS than branched olefins such as isobutene [2]. Similar results were reported by Schmitt and Walker from experiments with Pt/CMS catalysts prepared by essentially the same methods as Trimm et al. except that activated carbon was added to the mixture of chloroplatinic acid and PFA prior to carbonization [3]. Shape selectivity was demonstrated for the competitive hydrogenation of 3-methyl-1-butene with 1-butene or cyclopentene. When 1-butene was reacted competitively with 3-methyl-1-butene, the results showed a good selective catalysis: high selectivity to 1-butene and no conversion to 3-methyl-1-butene. Rajagopalan et al. [4] reported a novel synthesis method for the creation of highly active and thermally stable Pt supported on carbon catalyst. Their synthetic method was similar to that of Trimm and Cooper, but furfuryl alcohol was used as a reducing agent and also monomer, and surfactants were added to disperse Pt particles in furfuryl alcohol. Well-dispersed Pt nanoparticles ranging from 2 to 4 nm were obtained. The results showed that the Pt particles were clearly embedded in the carbon material and thus were accessible only through the pores of the nanoporous carbon. The pore size of the microporous carbon was centered at 0.4–0.5 nm. The hydrogenation activities of alkenes such as ethene, propylene, butene and isobutene are strongly dependent upon the molecular size and the pore opening of catalyst support. The molecular sieving effect arises from restricted or configurational diffusion in the nanopores.

Hydrogen spillover refers to surface diffusion of surface hydrogen species from the metal sites, where they are produced by the dissociation of hydrogen molecules to the oxide support

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(diluent) that has no activity for dissociative hydrogen adsorption [5]. Hydrogen spillover plays an important role in heterogeneous catalysis [6]. Hydrogen spillover on Pt-loaded carbon materials such as activated carbon or carbon black was investigated [7] and proved by inelastic neutron scattering (INS) spectroscopy at 223 °C [8]. The contribution of hydrogen spillover was also observed by hydrogen chemisorption and benzene hydrogenation at 25 °C [9]. If the shape selective and hydrogen spillover concepts were combined, large molecules could be hydrogenated on the surrounding support by spillover hydrogen generated from active metal sites located inside of CMS. In the present work, Pt/CMS was prepared by pyrolysis of PFA containing pre-reduced Pt particles. Its hydrogenation activity was tested by gas phase hydrogenation of 1-hexene. The contribution of hydrogen spillover was investigated by diluting Pt/CMS with two kinds of diluents—activated carbon (AC) and hydrogen type zeolite Y (HY).

2. Experimental

2.1. Materials

1-Hexene (99+%), hexane (≥99.0%), Triton X-100, furfuryl alcohol (FA, 99%), *p*-toluenesulphonic acid monohydrate (PTSA, 98.5%) and oxalic acid (99+%) were obtained from Sigma–Aldrich (Oakville, ON) and used as received. Solvents *n*-hexadecane (Aldrich) and acetone (EMD Chemicals Inc.) were analytical grade. Platinum (II) acetylacetonate ($Pt(acac)_2$, Pt 49.48%), and Pt 1 wt% on activated carbon powder (reduced, nominally 50% water, Pt/AC) were purchased from Alfa Aesar (Ward Hill, MA). CBV720 (zeolite H-SDUSY, $SiO_2/Al_2O_3 = 30$, BET surface area 780 m^2/g) was supplied by Zeolyst International (Valley Forge, PA). Pelletized form of activated carbon (Shirasagi C2X4/6-2), obtained from Japan EnviroChemicals Ltd., AC (C2X4/6-2), was ground to less than 100 mesh prior to use.

2.2. Preparation of Pt/CMS catalysts

Pt/CMSs were prepared by polymerization of furfuryl alcohol (FA) with in situ reduction of Pt precursor and calcination at high temperature under He atmosphere. The typical procedure with pre-reduction of Pt precursor ($Pt(acac)_2$) was as follows: 12.5 g of furfuryl alcohol was first added to a flask, then 12. 50 g of Triton-X 100 (used for dispersion of Pt particles) and 1.0 g of platinum (II) acetylacetonate ($Pt(acac)_2$) were added to furfuryl alcohol while stirring. The mixture was refluxed for 24 h under nitrogen. An additional amount of furfuryl alcohol (13.75 g) was then added to the solution. After stirring for 30 min, 16.10 g of *p*-toluenesulphonic acid monohydrate (PTSA) aqueous solution (6.83 wt%) or 21.00 g of oxalic acid aqueous solution of (28.6 wt%) was added dropwise to the mixture. The polymerization of furfuryl alcohol was carried out at 20 °C for 24 h.

After polymerization, the polymer mixture was dissolved in acetone and ultrasonicated for 1 h. The composite was left at room temperature overnight before it was cured at 110 °C for 16 h and at 200 °C for 6 h under nitrogen. The cured composite was ground to less than 20 mesh particles and pyrolyzed at 800 °C for 4 h (or as specified in the text) in a tube furnace under a helium atmosphere. The final materials were further ground to less than 100 mesh for catalysis use. Pt/CMSs were named as Pt/CMS-PTSA and Pt/CMS-OA, respectively, for *p*-toluenesulphonic acid or oxalic acid as polymerization catalyst. A blank sample (CMS) was prepared at the same conditions as Pt/CMS-PTSA, except that PTSA was not added.

2.3. Analytical methods

Surface areas and pore size distributions of Pt/CMSs were determined using a Micromeritics ASAP 2010 unit. Nitrogen adsorption/desorption was used for total surface area and pore size determination. The *t*-plot method was used to calculate micropore areas and volumes. The pore areas and volumes for mesopores (>2 nm) and macropores (>50 nm) were calculated by the BJH method. Average pore diameter was calculated by using the BET method. Median pore diameter was determined by the Horvath–Kawazoe method.

Pt dispersion of the catalyst was determined by H_2 and CO chemisorption using a Micromeritics ASAP 2010C unit. Pt-loaded catalyst samples were degassed at 35 °C for 1 h. Then the reduction was carried out by flowing hydrogen at 110 °C for 0.5 h, at 200 °C for 0.5 h and finally at 400 °C for 6 h (5 °C/min ramp rate). The system was evacuated at 35 °C for 60 min before an initial chemisorption analysis was performed at 35 °C to determine the percentage of Pt dispersion. The system was then evacuated for another 60 min at the same temperature to remove the weakly adsorbed hydrogen. A repeat analysis was done at the same temperature after reintroducing the active gases. CO chemisorption was also conducted at 35 °C. The method published by Prado-Burguete et al. was used to calculate the hydrogen and CO uptakes as well as metal dispersion [10]. Therefore, the linear portion of the isotherm in the pressure range from 300 to 600 mmHg was extrapolated to zero pressure to determine the hydrogen uptake and metal dispersion. For CO chemisorption the difference between the first analysis and the repeat analysis were used. The average Pt particle size, d, was calculated from $d\ (\text{nm}) = 1.08/D$ (dispersion of Pt = H/Pt) according to the same method [10].

Diffraction patterns were collected with a Bruker D8 Advance, equipped with twin Co X-ray monochromating parabolic mirrors on the incident and diffracted beam sides. Diffraction data was collected between 40° and 100° 2θ. Average particle size of Pt was calculated by Scherrer equation.

Pt particle size was also characterized by transmission electron microscopy (TEM) on a JEOL 2010 STEM, operated at 200 keV. Samples were prepared by drop method. A small amount of powder was sonicated in 100% ethanol. One drop was removed with a micropipette and dropped onto a copper (or nickel) support grid. The sample was then lightly coated with carbon to reduce charging in the TEM.

Sulphur content in Pt/CMS-PTSA was determined by energy-dispersive X-ray fluorescence spectroscopy (ASTM

4239M). Pt content of Pt/CMS was determined by ICP-MS the same way as reported by Yang et al. [11].

2.4. Hydrogenation reaction system and product analysis

A stainless steel U-tubular reactor (1.0 cm i.d. with one arm of 10.0 cm length) was used in the gas phase hydrogenation experiments. Hydrogenation of 1-hexene was carried out using three different catalyst configurations:

1. Pt/CMS alone: in this case, 0.20 g of catalyst (100 mesh) was mixed with glass beads (60–80 mesh).
2. Pt/CMS diluted with activated carbon: 0.20 g of Pt/CMS was first mixed with 0.20 g of activated carbon; they were then mixed with glass beads.
3. Pt/CMS diluted with CBV720: 0.20 g of catalyst was mixed with 0.20 g of CBV720. Hydrogenations of 1-hexene were also conducted with blank activated carbon and CBV720, non-activity was observed.

Finally, a commercial catalyst Pt/AC (dried in a vacuum oven at 80 °C overnight) was tested for hydrogenation of 1-hexene as the same as Pt/CMS's configuration and conditions. The total volume of catalyst mixtures was 2.0 mL. The catalyst mixture was loaded in the middle of one arm of the U-tubular reactor. The other arm was full of glass beads with diameter of 2 mm. Pt/CMS-OA was used in hydrogenation as prepared without pre-treatment. The reactor was heated in a water bath maintained at 50 ± 1 °C. Hydrogen gas (20 cm^3 min^{-1}, NTP) was used as a carrier and simultaneously as a reactant. The feed (1-hexene) was held in a bubbler kept at 20 °C and introduced into the reactor via continuous hydrogen flow. Prior to the hydrogenation test, the quantity of 1-hexene condensed between saturator and reactor was measured and this value was used in calculating the actual weight of 1-hexene flowing through the catalyst bed during the reaction. The gaseous reaction effluent was passed through a cold trap filled with acetone and dry ice at about −78 °C to condense the liquid product. The liquid products were accumulated hourly, collected and diluted with hexadecane before analysis by GC–FIMS.

A 30 m × 250 μm × 0.25 μm HP1-MS non-bonded column was used for GC–FIMS analysis. The injection (0.2 μl; 19:1 split) was made with the oven at 45 °C. The oven was heated at 10 °C/min to 300 °C. After the completion of the run, the masses for hexane (86) and hexene (84) were extracted. The peaks of these compounds were integrated and the concentrations of the corresponding compounds were calculated using the response factors obtained from analyzing the standards of hexane and hexene at the identical conditions.

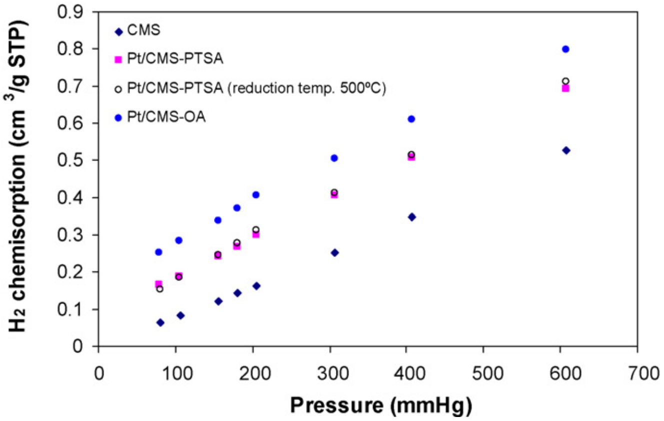

Fig. 1. H_2 chemisorption isotherms of Pt/CMS under different characterization conditions. The reduction temperature of samples was 400 °C other than specified in figure. The pyrolyzation temperature was 800 °C.

3. Results and discussion

3.1. Synthesis of Pt/CMS

Lafyatis et al. [12] measured the surface area of CMS by CO_2 isotherm and found that the surface area of CMS depended on the final pyrolysis temperature; it displayed a maximum between 800 and 900 °C. The micropore diameter declined at higher pyrolyzation temperatures, resulting in decreasing effective diffusivities for CO_2 and *n*-butane. Longer final pyrolyzation time also decreased the pore-mouth diameter. According to their results, a pyrolyzation temperature of 800 °C and length of 4 h were used in the present study.

Table 1 presents the results of H_2 chemisorption and dispersion of Pt/CMSs. Fig. 1 gives the hydrogen adsorption isotherms of Pt/CMS prepared at different conditions. It shows that the H_2 and CO uptakes of Pt/CMSs are much lower than the results obtained over carbon-supported Pt pre-treated with He, however, they are similar to that pre-treated with H_2 [13].

Table 1
H_2 and CO uptake and Pt dispersion of Pt/CMS

Sample	Pt content (wt%)	H_2 uptake (cm^3/g)	CO uptake (cm^3/g)	H/Pt (×100)	CO/Pt (×100)	*d* (nm, H_2)	*d* (nm, CO)	*d* (nm, XRD)	*d* (nm, TEM)
CMS	0								
Pt/CMS-PTSA	4.6	0.1191	0.188	4.5	3.6	24.0	30.4	9.5	5.5
Pt/CMS-PTSA[a]	4.6	0.1094		4.1		26.1			
Pt/CMS-OA	–[b]	0.2112		8.0		13.5		8.4	6.5
Pt/CMS-OA-1[b,c]	4.6	0.2095		7.9		13.6			

[a] Reduction at 500 °C.
[b] Pt content not available, should be similar with Pt/CMS-PTSA since it was synthesized using the same initial composition other than polymerization catalyst.
[c] Pyrolyzation at 600 °C, the other catalysts were pyrolyzed at 800 °C.

Table 2
The effect of oxidation treatment on hydrogen uptake

Samples	Conditions of burn-off temperature (°C)/time (min)	Burn-off degree (wt%)	H_2 uptake (cm^3/g)	H/Pt[a] (×100)	d[a] (nm)
CMS	350/30	2.2	–	–	–
Pt/CMS-OA	–	–	0.2112	8.0	13.5
Pt/CMS-OA-2	200/15	0.36	0.3023	8.8	12.3
Pt/CMS-OA-3	250/15	6.8	0.3615	9.8	11.1
Pt/CMS-OA-4	350/30	62	0.1737	1.9	56.4

[a] Pt contents in the burn-off samples are corrected and used to calculate H_2 uptake and average Pt particle size.

Nevertheless, dispersion of Pt in Pt/CMS-PTSA determined by CO had almost the same value (Table 2) as compared with that determined by H_2, which confirms the molecular size of H_2 is not a limiting factor for its chemisorption.

Rajagopalan et al. [14] reported that for Pt supported on nanoporous carbon derived from PFA resin, the amount of hydrogen uptake depended on the reduction temperature. Fig. 1 shows the hydrogen adsorption isotherms of Pt/CMS-PTSA analyzed under different conditions. The hydrogen uptake remained constant when the reduction temperature increased from 400 to 500 °C. Pyrolyzation temperature might be a factor here. In Rajagopalan's work, the Pt/CMS was pyrolyzed at 600 °C, while in our case, the pyrolyzation temperature was 800 °C. According to the conceptual model for structure evolution in PFA-derived CMS proposed by Mariwala and Foley [15], pyrolyzation at lower temperature produced larger pore opening. Therefore, one Pt/CMS (Pt/CMS-OA-1) was pyrolyzed at 600 °C. Compared to Pt/CMS-OA, which was pyrolyzed at 800 °C, the sample pyrolyzed at 600 °C has similar Pt dispersion and Pt particle size as indicated in Table 1 (calculated from H_2 uptake).

p-Toluenesulphonic acid (PTSA), the catalyst used for the polymerization of furfuryl alcohol, contained sulphur, which could cause poisoning of noble metals. Moreno-Castilla et al. [16] reported a sulphur-poisoning effect over Fe/carbon catalyst prepared with PTSA. The sulphur content of Pt/CMS-PTSA was 0.05 wt%. To eliminate this poisoning effect, another polymerization catalyst, oxalic acid (OA), was introduced. Fig. 1 compares the hydrogen adsorption isotherm of P/CMS synthesized with PTSA and OA. It shows that Pt/CMS-OA, which was synthesized with OA, has much higher hydrogen uptake and Pt dispersion than those prepared with PTSA. This result confirmed the poisoning effect of sulphur in PTSA.

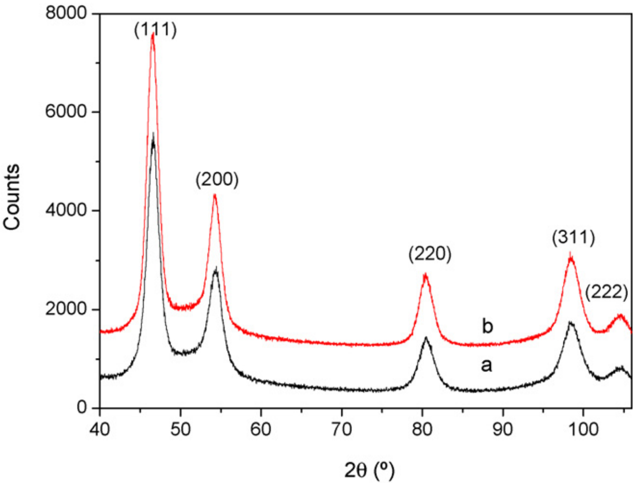

Fig. 2. XRD pattern of Pt/CMS-PTSA (a) and Pt/CMS-OA (b).

Pt/CMSs were characterized by XRD to calculate the average diameter of Pt particles (Fig. 2). TEM images were also used to study the size and distribution of Pt particles (Figs. 3–6). TEM micrograph showed that Pt particles were well dispersed in CMS support. The average Pt particle sizes estimated from TEM are 5.5 nm for Pt/CMS-PTSA and 6.5 nm for Pt/CMS-OA (Table 1). The average Pt particle sizes calculated by XRD using the Scherrer equation were 9.5 and 8.4 nm, respectively, for Pt/CMS-PTSA and Pt/CMS-OA, which were closer to that determined by TEM. Average particle size of Pt in Pt/CMS-PTSA determined by XRD and TEM were much smaller than those calculated from hydrogen uptake, 35.1 nm (Table 1). A similar trend was observed for Pt/CMS-OA. This result suggests that part of the Pt particles were not exposed to probe molecules. Those Pt particles, which cannot be reached by H_2 molecules, are probably situated in the channels with very small pore openings, or wrapped by carbon.

The assumption that part of Pt particles was covered by carbon was supported by the results of Aldag [17]. He found that the catalytic activity for the reactions of neopentane increased 100-fold when the carbon contamination on the Pt

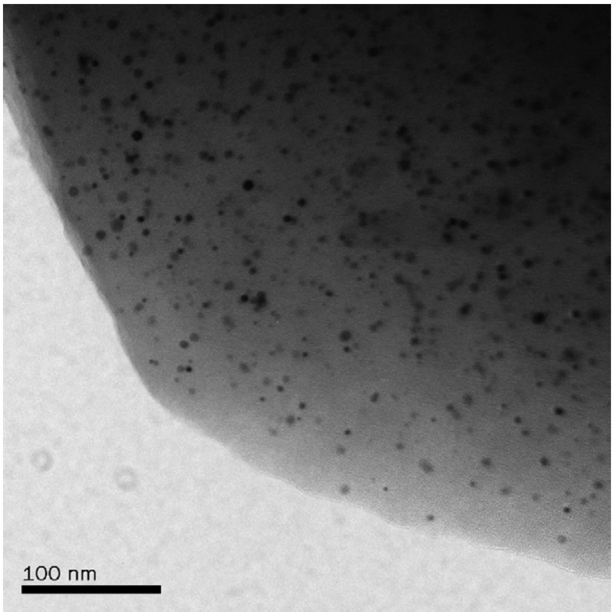

Fig. 3. TEM micrograph of Pt/CMS-PTSA.

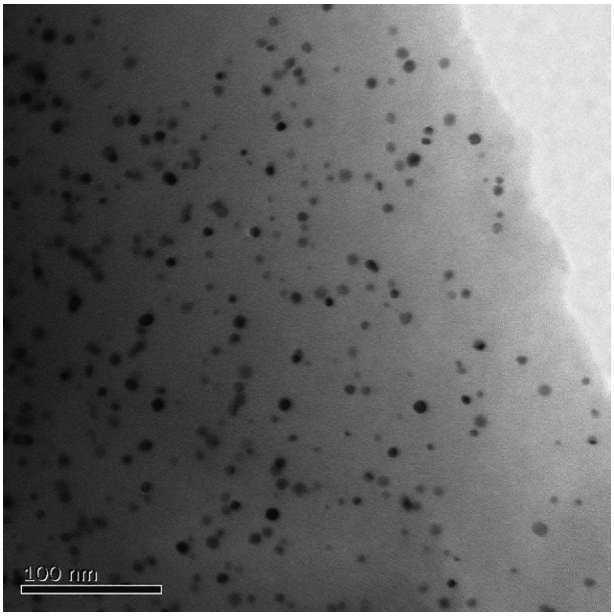

Fig. 4. TEM micrograph of Pt/CMS-OA.

surface was removed by treatment in oxygen. Therefore, oxidation treatment was introduced in our work to investigate its effect on hydrogen uptake. The oxidation treatments were performed in a muffle furnace with temperature programming at a ramp rate of 2 °C/min. The results are listed in Table 2. This shows that hydrogen uptake increased with the burn-off degree of Pt/CMS up to 7%. When the burn-off degree was relatively low (0.36% and 6.8%), the carbon on the catalyst surface, in the channel or in the pore mouth could be burned, which exposed more Pt particles to hydrogen. At the same time, the pore size could be enlarged due to the removal of carbon in the channel or pore mouth. This was beneficial. However, when the burn-off degree was higher (62%), the structure of Pt/CMS was destroyed and Pt particles agglomerated. These results further confirm the assumption that some Pt particles were not exposed to probe molecules.

It seems that Pt promoted the oxidation of carbon. Compared to the blank sample (CMS), the burn-off degree of Pt/CMS-OA-4 was much higher at 350 °C. It was reported that the spillover oxygen migrated from Pt/Al_2O_3 onto the coke and oxidized it into carbon dioxide more efficiently than gaseous oxygen [18]. Baumgarten and Schuck [19], and Baumgarten and Dedek [20] also observed that the oxidation rate of benzoic acid was increased when oxygen was activated on Pt, although there was no direct contact between the benzoic acid adsorbed on alumina and the Pt/Al_2O_3. This increase was explained by oxygen spillover, the transfer of activated oxygen from the catalyst to the benzoate ions bound on the alumina surface. In our case, the enhanced burn-off degree can also be explained by oxygen spillover from Pt onto carbon support. Spillover oxygen can also decrease the treating temperature and time in order to reach the same burn-off degree (Table 2).

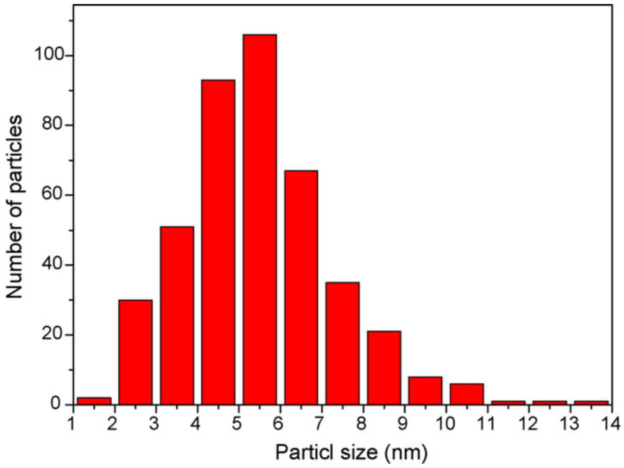

Fig. 5. Particle size distribution of Pt in Pt/CMS-PTSA.

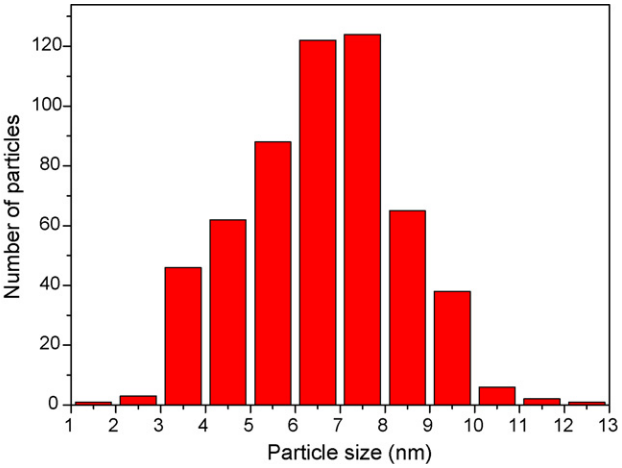

Fig. 6. Particle size distribution of Pt in Pt/CMS-OA.

Finally, the BET surface area determined with N_2 for Pt/CMS-OA was 28 m^2/g and micropore volume was 0.02 cm^3/g, which were much lower than that determined for a similar catalyst with methyl chloride [4]. Nitrogen adsorption has limitations when dealing with materials such as carbon molecular sieve with a high degree of ultramicroporosity [21]. One of the problems encountered in attempting to determine the pore size distribution of CMS with nitrogen is probably due to the very low adsorption rate at 77 K [1]. Similar problems were also observed for zeolite A when using N_2 adsorption and desorption isotherm to measure the surface area [22].

3.2. Hydrogenation of 1-hexene

The hydrogenation of 1-hexene was tested to measure the catalytic activity of Pt/CMS-OA. At the same time, in order to investigate the contribution of hydrogen spillover, Pt/CMS-OA was diluted with two diluents—activated carbon (AC) and hydrogen type ultrastable zeolite Y (CBV720), respectively. Hydrogenation of 1-hexene was also conducted over a commercial Pt/AC catalyst (Pt/AC) for comparison.

Fig. 7 compares the gas phase hydrogenation results for Pt/CMS-OA and Pt/CMS-OA diluted with AC or CBV720. An initial 1-hexene conversion of 87% was observed for Pt/CMS-OA in the absence of diluent. The conversion decreased with

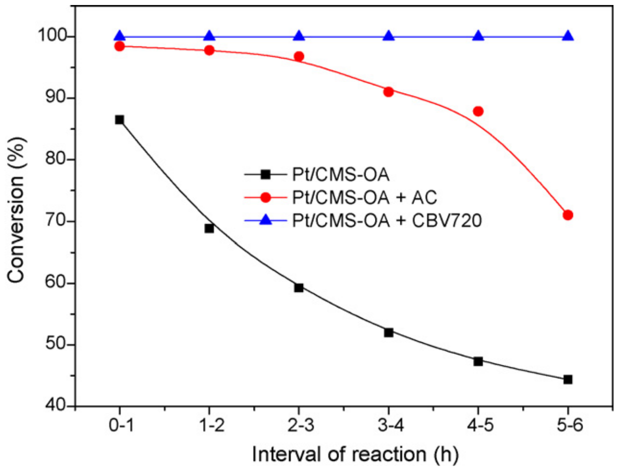

Fig. 7. Catalytic activity of Pt/CMS-OA, and diluted with AC and HY for hydrogenation of 1-hexene.

catalyst hours indicating deactivation of catalyst during first 5 h reaction. At 6 h reaction time, the conversion of 1-hexene reached to 44.4%. The conversions of 1-hexene over Pt/CMS-OA after 6 h diluted with AC (71.0%) and CBV720 (100%) were significantly higher than that of Pt/CMS-OA without dilution. Since diluents activated carbon (AC) and HY zeolite (CBV720) have no activity for 1-hexene hydrogenation under the reaction conditions used, the results clearly demonstrate the contribution of hydrogen spillover in the hydrogenation of 1-hexene. 1-Hexene could be adsorbed on AC or CBV720, and hydrogenated by spillover hydrogen species from Pt/CMS-OA, and thus contribute to the overall activity.

Our results also show that different diluents, AC and CBV720, had different effects on the conversion of 1-hexene. CBV720, a zeolite HY, had a more positive effect on the conversion than that of activated carbon (AC). The conversion decreased with reaction time for Pt/CMS-OA diluted with AC, while for that diluted with CBV720 the conversion remained constant. It was found that both the number of acid sites and acid strengths of diluents influenced the conversion of toluene on Rh/γ-Al_2O_3 [23]. The number of acidic sites increased in order: HY $\gg$ AC $>$ Al_2O_3 $>$ SiO_2, while the strengths of the acidic sites increased in order: HY $\cong$ AC $>$ Al_2O_3 $>$ SiO_2. The turnover frequencies of Rh increased with increasing number of acid sites of the diluents, although the diluent was inactive without any metal. It is proposed that the aromatic molecule, adsorbed on acid sites as carbonium ion, could be hydrogenated by the spillover hydrogen originating from the metal [23]. The high contribution to hydrogen spilt-over over Pt/CMS-OA diluted with CBV720 is probably due to higher number of acid sites of CBV720 over AC.

Finally, it can be seen from Table 3, that Pt/AC was much more active for 1-hexene hydrogenation than Pt/CMS-OA, although Pt/CMS-OA has higher Pt content. It was obvious that pore size played an important role in the gas phase hydrogenation of 1-hexene at these conditions. The large pore size catalysts with mesopore, such as Pt/AC (BET surface area 820 m^2/g, medium pore size by H–K method 1.09 nm, mesopore volume 0.44 cm^3/g, and micropore volume 0.25 cm^3/g), had 100% hydrogenation conversion of 1-hexene. The advantage of the small pore catalyst such as Pt/CMS was its use in shape selectivity. It may also be used to selectively exclude the contact of organic sulphur molecules with Pt particles located in the pore of CMS to reduce the sulphur-poisoning effect.

Table 3
The results of gas phase hydrogenation of 1-hexene

Catalyst	Average conversion every hour (%)						
	Diluents	0–1	1–2	2–3	3–4	4–5	5–6
AC	None	0	0	0	0	0	–
CBV720	None	1.4	0	0	0	0	0
Pt/CMS-OA	None	86.5	68.8	59.3	52.0	47.3	44.4
	AC	98.5	97.8	96.8	91.0	87.9	71.0
	CBV720	100	100	100	100	100	100
Pt/AC	None	99.4	99.0	99.3	98.8	99.2	98.8
	AC	86.5	77.3	69.8	65.6	67.3	60.9
	CBV720	99.6	99.7	99.8	99.8	99.9	99.5

4. Conclusions

Pt particles encapsulated in a carbon molecular sieve were prepared by pyrolysis of polyfurfuryl alcohol containing pre-reduced Pt particles or platinum acetylacetonate. For the preparation of Pt/CMS, the polymerization catalyst, oxalic acid, is better than *p*-toluenesulphonic acid monohydrate. Some Pt particles in the Pt/CMS derived from polyfurfuryl alcohol and $Pt(acac)_2$ are inaccessible. Oxidation treatment (<250 °C) can make more Pt particles available to hydrogen. Gas phase hydrogenation of 1-hexene was conducted at 50 °C and at atmospheric pressure. An average conversion in the sixth hour of reaction of 44.4% was obtained over Pt/CMS catalyst. At the same reaction condition, the conversions of 1-hexene were increased to 71.0% and 100% when Pt/CMS was diluted with activated carbon and zeolite HY, respectively, clearly indicating the role of hydrogen spillover in these reactions.

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