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Structural features and catalytic properties of Pt/CeO_2 catalysts prepared by modified reduction-deposition techniques

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The structural features and catalytic properties of Pt/CeO_2 catalysts prepared by liquid phase reduction-deposition techniques with formaldehyde and ethylene glycol as reducing agents, respectively, were investigated. TPR and CO pulse titration measurements revealed that smaller particle size and uniform dispersion of platinum were achieved by modified polyol preparation process, which is beneficial to generate appropriate Pt–O–Ce chemical bonding. XPS analysis further demonstrated the presence of strong metal-support interaction in above Pt/CeO_2 catalyst. It was observed that the reducing ability and the solvent effect play important roles in controlling the formation of nuclei as well as its growth rate. The sample prepared by modified polyol method exhibited higher catalytic activities and longer stability for the complete oxidation of dimethyl ether than Pt/CeO_2 catalyst prepared by HCHO liquid phase reduction.

KEY WORDS: complete oxidation; DME; HCHO liquid phase reduction; modified polyol method; Pt/CeO_2.

1. Introduction

CeO_2-supported precious metal catalysts have been the subjects of intensive researches because of their unique catalytic performances in various applications, such as the three-way catalysts for automobile exhaust emission control [1–5]. The significant promoting effect of ceria was generally attributed to its high oxygen storage capacity and facile Ce^{4+}/Ce^{3+} redox cycle. The easy generation of oxygen vacancies forms interfacial active centers, over which the reaction takes place. Most recently, Pt/CeO_2 was reported to be extremely active for the water–gas shift reaction [5,6], the oxidation of CO [1], the combustion of hydrocarbons [7] and the hydrogenation of olefins [8]. It was noted that the essential interaction between the noble metal and the ceria support could affect both the catalytic activity and the selectivity in various reactions [1–4]. From a principle point of view, the structural and electronic states of the perimeter interface could be determined by the preparation procedures, and be controlled through varying the preparation parameters, such as solvent, reducing agent, temperature and pH value of the mixed solution [1,2].

For instance, Pt/CeO_2 catalyst was reported to be more active than Pt/Al_2O_3 prepared by the same method for CO oxidation. High dispersion of Pt over ceria inhibited the sintering of Pt metal particles, resulting in rather high catalytic activity and stability [1]. The nature of this high catalytic activity was ascribed to the presence of$–Ce^{4+}–O^{2-}–Pt^{2+}–\square–$ linkages formed between ionic-dispersed Pt and ceria support by proper selecting of preparation processes and careful controlling of preparation parameters. There is no doubt that the dispersion of active metals, closely associated with the metal-support interaction, determines the catalytic performances. How to control and optimize the metal-support interaction manner is still a challenge due to the complexity of various preparation parameters involved. Moreover, metal agglomeration encountered in the preparation process is another significant problem to be solved.

Great efforts have been paid to explore improved preparation routes in the past decades [9–12]. The most attractive preparation route to load precious metals is still the liquid phase reduction process due to its simplicity. However, this conventional route often leads to the relatively large average metal particle size, broad size distribution and poor reproducibility. Colloidal route was found to produce well-homogenized ultrafine Pt catalysts, but the complexity of these synthesis methods hinders its wide utilization [10,11]. The traditional polyol process [13,14], as an effective method in controlling particle size and distribution, has been extensively used in the preparation of ultrafine and uniform metal powder. Whereas, reports about preparation of supported metal catalysts by polyol process are scarce. Recently it was reported that high dispersion of Pt on carbon could be obtained by a novel modified polyol method, which has both merits of liquid phase reduction and colloid procedures [15]. In this study, we modified the reduction-deposition process by using formaldehyde and ethylene

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glycol as reducing agents. Formaldehyde is a strong reducing agent, thus rapid nucleation could be realized by a fast reduction rate. By contrast, ethylene glycol is a weak reducing agent, but its high viscosity would control growth rate of metal particles.

Comparative study of Pt/CeO_2 catalysts prepared by the above reduction-deposition techniques i.e. HCHO liquid phase reduction and modified polyol method were performed to compare the structural features as well as the catalytic properties. The structure of the catalysts was investigated by XRD, TPR and XPS techniques. The complete oxidation of DME was selected as model reaction by considering its potential application in diesel engine and direct oxidation fuel as efficient mobile power source [16].

2. Experimental

2.1. Catalyst preparation

The CeO_2 support was prepared by precipitation of Ce $(NO_3)_3 \cdot 6H_2O$ aqueous solution with the addition of $NH_3 \cdot H_2O$ solution until the pH of the mixed solution was greater than 9.0 under vigorous stirring at 333 K. The precipitant was then aged in the mother liquid for 4 h, followed by filtration and washing with distilled water. The obtained solid was dried at 373 K for 10 h, and calcined at 723 K for 4 h in air.

Platinum of 3% by weight was then loaded on the CeO_2 support. 3 g of CeO_2 powder was first suspended in 120 mL aqueous solution of 246 mg chloroplatinic acid. Then, 1 M NaOH aqueous solution was gradually added to adjust the pH value of the mixed solution to 12, and excessive 37% HCHO solution with a mole ratio of HCHO : $PtCl_6^{2-} = 10 : 1$ was quickly added under vigorous stirring at 363 K. Thereafter, mixed solution was aged for 1 h under vigorous stirring at 363 K during which Pt^{4+} was exclusively reduced and deposited on the surface of CeO_2. The obtained solid was washed with hot distilled water until no Cl^- anion could be detected in the filtrate by $AgNO_3$ solution. After drying at 373 K for 10 h, the solid was calcined in air at 473 K for 4 h. The catalyst obtained was designed as Pt/CeO_2–HCHO.

Alternatively, the modified polyol method was used. The precursor, 246 mg chloroplatinic acid, was dissolved into 60 mL ethylene glycol (EG) and mixed with 3 g CeO_2 powder suspended in 20 mL distilled water. Similarly, the pH value of the solution was adjusted to 12 by the addition of NaOH. Then, the mixture was maintained at 403 K for 1 h to ensure the complete reduction of Pt. The resulting solid was treated following the same procedures as the Pt/CeO_2–HCHO sample. The catalyst thus obtained was referred as Pt/CeO_2–EG. For comparison, Pt/SiO_2–EG catalyst was prepared in the same way.

2.2. Characterization

The specific surface areas (S_{BET}) of the catalysts were calculated from a multipoint Braunauer–Emmett–Teller (BET) analysis of the nitrogen adsorption isotherms at 77 K recorded on a micrometrics ASAP 2000 instrument.

The powder X-ray diffraction (XRD) patterns were recorded using a Rigaku D/MAX-RB with CuK_α radiation operated at 40 kV and 100 mA.

The CO pulse titration measurements were carried out in a CHEMBET 3000 adsorption apparatus (QuantaChrome Inc. US) equipped with a TCD detector. Samples of 100 mg Pt/CeO_2 were loaded and pretreated in H_2 flow at 393 K for 1 h, and then purged with He at 423 K for 30 min to remove the adsorbed species. The CO pulse titrations were conducted after cooling down the samples to room temperature.

The temperature-programmed reduction (TPR) measurements were carried out in a conventional setup equipped with a TCD detector. Samples of 100 mg Pt/CeO_2 were loaded and pretreated in He flow at 473 K for 1 h to remove the adsorbed carbonates and hydrates. After cooling down to 140 K and introducing the reduction agent of 5% H_2/Ar, the temperature was then programmed to rise at 10 K/min.

X-ray Photoelectron Spectroscopy analyses were performed with an ESCALAB MK-II spectrometer (VG Scientific Ltd. UK) using AlK_α radiation (1486.6 eV) operated at an accelerating voltage of 12.5 kV. The powder samples were pressed into thin discs and mounted on a sample rod placed in a pretreatment chamber, in which the catalysts were *in situ* reduced with flowing hydrogen at desired temperature for 2 h. Then the samples were transferred into the analysis chamber where the spectra of Pt 4d, Ce 3d and O 1s levels were recorded. Charging effects were corrected by adjusting the binding energy of C 1s peak to a position of 284.6 eV.

2.3. Activity measurement

The catalytic activity was tested under atmospheric pressure in a continuous-flow fixed-bed reactor. Samples of 200 mg (40–60 mesh) were placed between two layers of quartz wool inside a quartz tube (i.d = 6 mm). Prior to catalytic reactions, the catalysts were reduced with 5% H_2/N_2 at 473 K for 2 h. The complete oxidation of DME was performed with a mixture feed of $CH_3OCH_3/O_2/He$ = 0.5/3/96.5 (vol%). The reaction temperature ranged from 298 to 403 K with a total feed gas flow rate of 43 mL/min, corresponding to a gas hourly space velocity (GHSV) of 10,000 h^{-1}. Effluents from the reactor were analyzed on-line by an HP 6890 gas chromatograph equipped with TCD and FID detectors. A Haysep D packing column was used to detect the CO, CO_2, O_2 and H_2, and an Innowax capillary column was employed to separate oxygenates and hydrocarbons.

3. Results and discussion

3.1. Surface area and structure

The BET surface area of the prepared CeO_2 powder was 103.5 m^2/g. The deposition of platinum caused a significant decrease in the specific surface area of CeO_2. The specific surface areas of Pt/CeO_2–EG and Pt/CeO_2–HCHO were measured to be 92.2 and 93.5 m^2/g, respectively. XRD showed the distinct fluorite oxide diffraction of CeO_2 in both of the Pt/CeO_2 samples, but no detectable diffraction peaks assigned to crystallines of platinum species can be detected. The average crystallite size of ceria was estimated to be 9.3 nm by using the Scherrer equation.

CO pulse titration measurements revealed that the average particle sizes of Pt in Pt/CeO_2–EG and Pt/CeO_2–HCHO were 1.9 and 2.5 nm, respectively. The corresponding Pt dispersions were then calculated to be 58.4% and 45.8%, accordingly. While the average Pt particle sizes in Pt/CeO_2–EG and Pt/CeO_2–HCHO increased to 3.0 and 3.7 nm after reduction with hydrogen at 773 K, indicating the occurrence of Pt sintering. However, it should be noted that the evaluated particle sizes and dispersions of Pt are relative values because CO can also be adsorbed on the ceria surface, especially in the presence of metals, giving rise to partial reduction of ceria [8]. Nevertheless, even if in a comparative way, the results of CO pulse titration still qualitatively suggested that modified polyol method is beneficial to obtain higher dispersion and smaller particle size of platinum over ceria support.

3.2 Temperature-programmed reduction

The TPR profiles of the Pt/CeO_2 catalysts are presented in figure 1. The reduction peaks related to platinum species in Pt/CeO_2–HCHO occurred at 256 and 430 K, respectively. By contrast, Pt/CeO_2–EG showed only one sharper reduction peak at 244 K, suggesting the presence of uniform Pt species. The difference in TPR profiles can be ascribed to the variation in Pt dispersion and Pt–CeO_2 interaction. The platinum species in Pt/CeO_2–EG exhibited sharp and single low-temperature reduction peak, indicating the presence of highly dispersed Pt particles with uniform particle size distribution. While the two reduction peaks of Pt/CeO_2–HCHO suggested the discrepancy in Pt/CeO_2 interaction. The reduction peak at 256 K may represent the reduction of smaller Pt particles closely interacting with CeO_2, and the reduction peak at 430 K corresponds to the reduction of segregated Pt particles, which need higher temperature to be reduced. Besides, a characteristic peak corresponding to the reduction of surface CeO_2 appeared at 653 K in both cases.

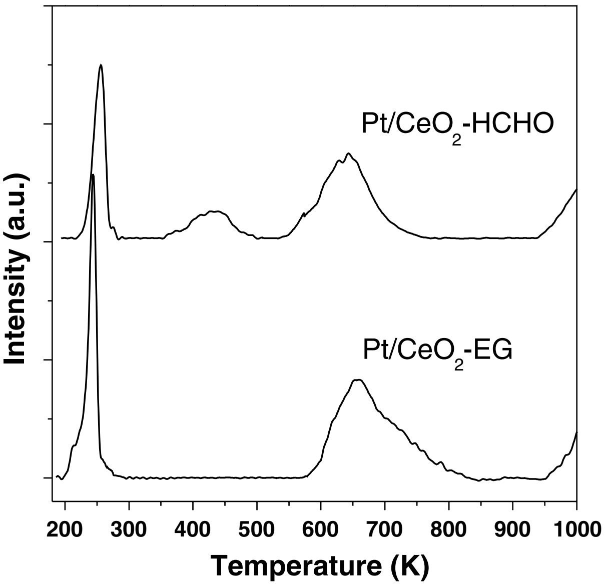

Figure 1. H_2-TPR profiles of Pt/CeO_2 catalysts prepared by different methods.

3.3. XPS measurement

In situ XPS measurements were conducted to explore the changes in the chemical states of platinum and cerium and in the atomic surface compositions of Pt/CeO_2 catalysts experienced reduction treatments with hydrogen, as summarized in table 1. Figure 2 compares the X-ray photoelectron spectra of Pt 4f, which can be resolved into three sets of spin-orbit doublets assigned to Pt^0, Pt^{2+} and Pt^{4+}. For the as-prepared Pt/CeO_2–HCHO, Pt species were mainly present as Pt^{2+} (56.8%) and Pt^{4+} (14.4%). After reduction with hydrogen at RT and 473 K, the percentages of Pt^0 increased to 68.2% and 75.3%, respectively. While total reduction of Pt species was achieved when the reduction temperature arrived at 773 K. Comparatively, the majority of the Pt species in as-prepared Pt/CeO_2–EG were Pt^0 (53.8%). Once reduced at RT, the proportion of reduced Pt species reached to 93.7%, and the Pt species were completely reduced to Pt^0 after reduction even at 473 K.

The XPS spectra of Ce 3d are shown in figure 3. The best curve-fitting of Ce 3d data was obtained to quantitatively determine the extent of ceria reduction. As shown in table 1, for the as-prepared Pt/CeO_2–HCHO, a certain amount of Ce^{3+} existed (about 26.8%), partly due to photoreduction of CeO_2. With the increase in the reduction temperature, the Ce (III) percentage increased to 39.7 at 473 K. Further increasing the reduction temperature, Ce (III) percentage slightly decreased to 37.0%. Similarly, the Ce (III) percentage decreased to 33.6% after reduction at 773 K, slightly lower than that of the Pt/CeO_2–HCHO after the same treatment.

The relative surface densities of Pt, Ce and O elements also changed after the sample was treated

Table 1
XPS data measured for the Pt/CeO_2 catalysts after different reduction pretreatments

Catalyst	Reduction temperature (K)	Species	BE of Pt 4f (eV)	Relative percentage (%)	Atomic ratios		Ce(III) (%)
					Pt/Ce	Ce/O	
Pt/CeO_2–HCHO	Fresh	Pt^0	71.6	28.8	0.8304	1.0549	26.8
		Pt^{2+}	73.2	56.8			
		Pt^{4+}	74.9	14.4			
	RT	Pt^0	71.3	68.2	0.5542	1.1588	28.9
		Pt^{2+}	73.0	31.8			
	473 K	Pt^0	71.4	75.3	0.4550	2.4592	39.7
		Pt^{2+}	72.8	24.7			
	773 K	Pt^0	71.7	100	0.3507	2.6248	37.0
Pt/CeO_2–EG	Fresh	Pt^0	71.6	53.9	0.7349	0.9886	30.9
		Pt^{2+}	73.1	31.3			
		Pt^{4+}	74.6	14.8			
	RT	Pt^0	71.7	93.7	0.4346	2.2827	28.3
		Pt^{2+}	73.4	6.3			
	473 K	Pt^0	71.7	100	0.2545	3.2721	39.2
	773 K	Pt^0	71.5	100	0.5817	2.4952	33.6

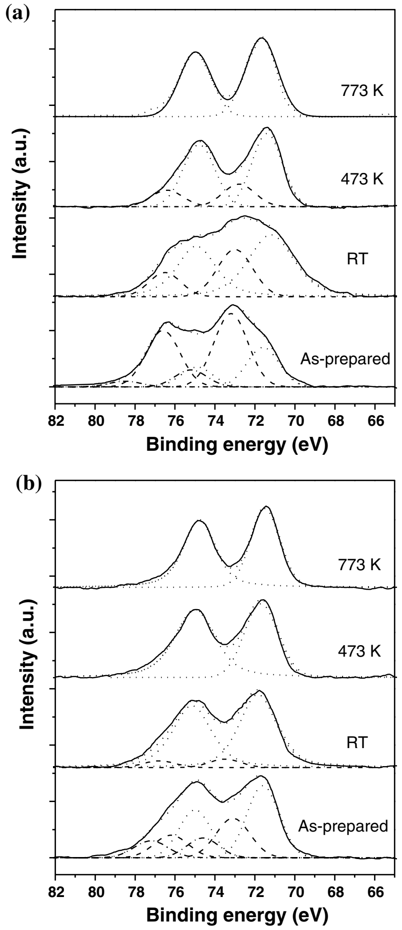

Figure 2. (a) XPS of Pt 4f for Pt/CeO_2–HCHO after different reduction pretreatments; (b) XPS of Pt 4f for Pt/CeO_2–EG after different reduction pretreatments.

under various reduction temperatures. This represented a quantitative evolution of the distribution of the Pt species on the ceria surface. For the as-prepared Pt/CeO_2–HCHO catalyst, an apparent platinum enrichment on the surface was observed. When the reduction temperature increased from RT to 773 K, the atomic ratio of Pt/Ce decreased from 0.55 to 0.35, accompanied by a simultaneously increase in the Ce/O ratio from 1.2 to 2.6. The increase in Ce concentration and the decrease in Pt concentration can be attributed to the highly possible Pt particle sintering, especially at higher reduction temperatures. Meanwhile, the coverage of ceria (or partially reduced ceria) on platinum surface and the simultaneously migration of platinum into the bulk of ceria which is often observed in CeO_2-supported metal catalysts may be another reason [4]. When the as-prepared Pt/CeO_2–EG is concerned, it can be found that the Pt/Ce atomic ratio decreased initially, while increased by further increasing the reduction temperature. This also might imply the occurrence of platinum sintering with increasing the reduction temperature, by considering the fact that the Pt particle was increased to 3.0 nm after reduction with H_2 at 773 K.

The results of TPR and XPS identically demonstrated the discrepancies in redox ability of platinum species in the Pt/CeO_2 catalysts prepared by different preparation routes, which determined the Pt dispersion as well as the consequent Pt-ceria interaction. The Pt/CeO_2–EG presented larger CO adsorption capacity, indicating smaller Pt particles dispersed on the ceria. Its TPR behavior further indicated the uniform distribution of Pt species. While the TPR profile of Pt/CeO_2–HCHO displayed two reduction peaks, suggesting a wide range of Pt particle size distribution. As shown in figure 2, the Pt

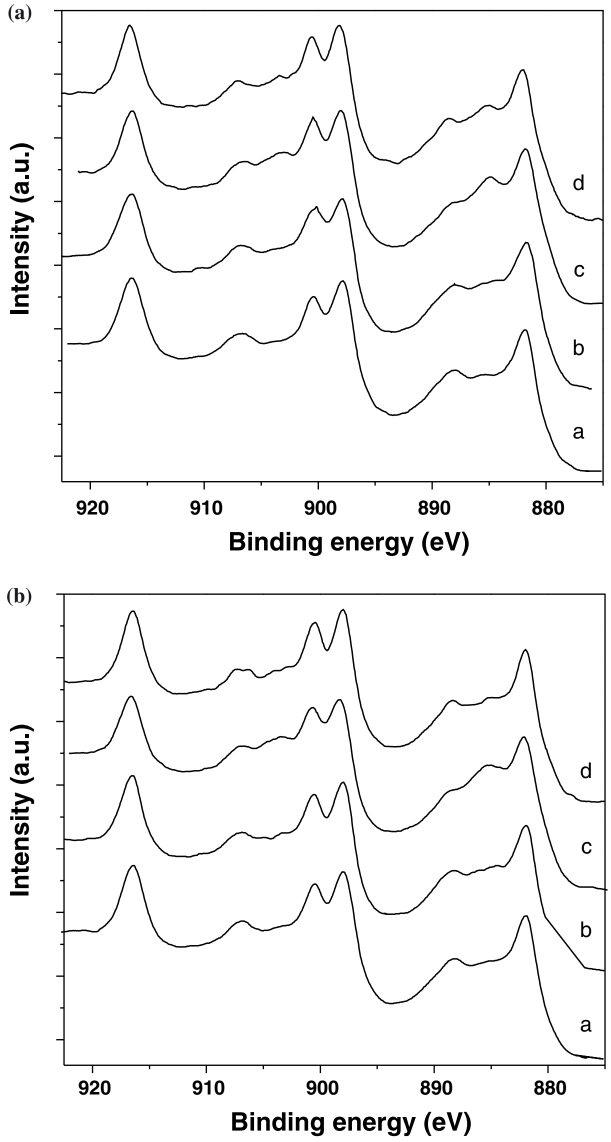

Figure 3. (a) XPS of Ce 3d for Pt/CeO$_2$–HCHO after different reduction pretreatments: a. as-prepared sample, and reduced with hydrogen at b. RT, c. 473 K, d. 773 K; (b) XPS of Ce 3d for Pt/CeO$_2$–EG after different reduction pretreatments: a. as-prepared sample, and reduced with hydrogen at b. RT, c. 473 K, d. 773 K.

species in the Pt/CeO$_2$–EG were reduced to Pt^0 even below RT, whereas Pt/CeO$_2$–HCHO only contained 68.2% of Pt^0 after the same treatment, and the remainings were reduced only at higher temperatures. Therefore, it is convincingly evidenced that the Pt species of Pt/CeO$_2$–EG had higher redox ability, based on its uniform dispersion.

3.4. DME oxidation

Recently, the potential application of DME in diesel engines and direct oxidation fuel cell process leads to the development of efficient catalysts for complete oxidation of DME at relatively low temperatures [17]. Here, the complete oxidation of DME was tested over the Pt/CeO$_2$ catalysts to establish the correlations between catalyst dispersion and catalytic performance.

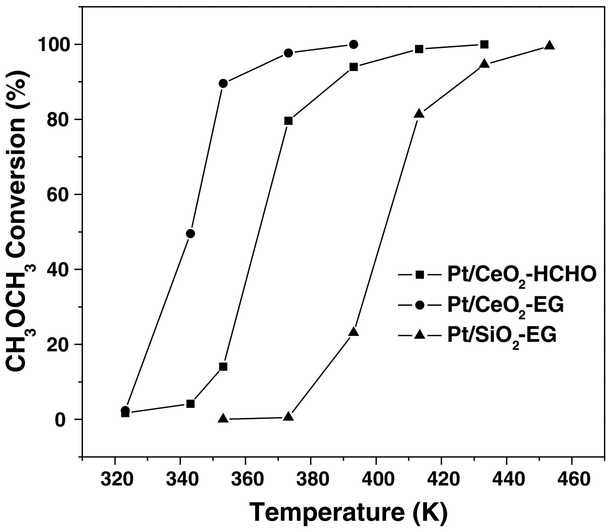

Figure 4. Comparison of DME oxidation over Pt/CeO$_2$ and Pt/SiO$_2$ catalysts.

The conversion of DME over Pt/CeO$_2$ catalysts as a function of temperature is presented in figure 4. It is obvious that the Pt/CeO$_2$–EG displayed the highest catalytic activity, achieving 100% conversion even at 348 K. Whereas the Pt/CeO$_2$–HCHO attained 100% conversion only at 393 K, 45 K higher than the previous catalyst. To confirm the Pt-ceria interaction on the Pt/CeO$_2$, the oxidation of DME was performed on Pt/SiO$_2$–EG. The catalytic activity of Pt/SiO$_2$–EG was obviously lower than Pt/CeO$_2$ catalysts, and proceeded to 100% conversion at 453 K. For clarity, the calculated TOF was roughly compared. For instance, the TOF value was 8.09×10^{-3} s^{-1} for the Pt/CeO$_2$–EG and 1.63×10 $^{-3}s^{-1}$ for the Pt/CeO$_2$–HCHO at 353 K. The activity of the Pt/CeO$_2$–EG at 353 K was attained only at 370 K by the Pt/CeO$_2$–HCHO, while the TOF of Pt/SiO$_2$–EG only reached $1.98 \times 10^{-3}s^{-1}$at 393 K.

Arrhenius plots of the rates are shown in figure 5. It can be seen that the Pt/CeO$_2$ catalysts had the almost same apparent activation energy of 77 kJ/mol, which was much less than that of 126 kJ/mol over the Pt/SiO$_2$–EG. This result suggests that the Pt-ceria interaction can reduce apparent activation energy for the oxidation of DME, and then enhances the catalytic activity.

The complete oxidation of DME was also tested at 373 K for 30 h, as shown in figure 6. It can be seen that the conversion of DME over Pt/CeO$_2$–EG was around 86% during 30 h, and only slightly decreased at the end of operation. Comparatively, the catalytic activity of the Pt/CeO$_2$–HCHO decreased quickly with time on stream, the conversion of DME decreased rapidly from 93% to 42% within 14.5 h, and the DME conversion even reduced to 6% after 30 h. Clearly, the catalytic activity

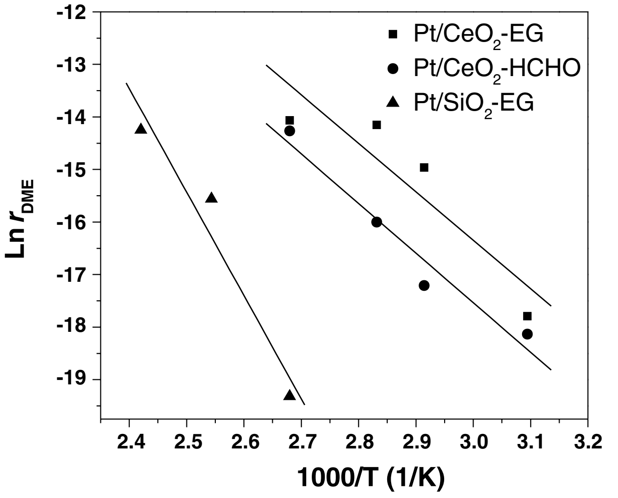

Figure 5. Arrhenius diagram of the rates for DME oxidation over Pt/CeO_2 and Pt/SiO_2 catalysts.

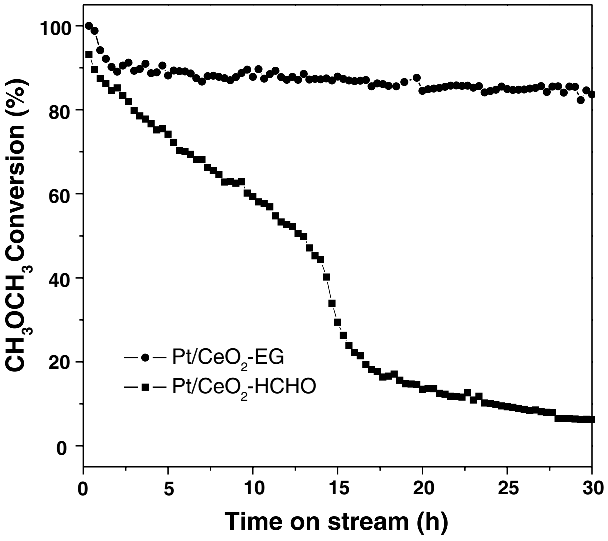

Figure 6. TOS behaviors of Pt/CeO_2 catalysts for DME oxidation at 373 K.

and stability of Pt/CeO_2–EG were significantly higher than that of Pt/CeO_2–HCHO over the entire temperature range investigated.

It was previously revealed that the high activity of Pt/CeO_2 catalyst for CO oxidation is related to the reduction of ceria in the vicinity of Pt particles, and the reduced ceria may in turn influence the activity of interfacial Pt sites [18]. Solymosi *et al.*, investigated the oxidation of DME over Rh catalysts with the conclusion that the activation of DME consists of formation of methoxy species, decomposition of CH_3O at the metal/support interface and the oxidation of its decomposition products [16]. Combining the reaction data of the complete oxidation of DME with the structural features of the Pt/CeO_2 catalysts, it is reasonable to say that the enhanced catalytic activity is due to the presence of Pt-ceria interaction, which provides the active sites for the adsorption and dissociation of O_2 as well as CH_3O. Apparently, higher dispersion of platinum on ceria in Pt/CeO_2–EG favors the easier CH_3O dissociation and the O_2 activation induced by the strong Pt-ceria interaction, and consequently better catalytic activity for the complete oxidation of DME was observed. Although the discrepancy of the average Pt particle size in both Pt/CeO_2 catalysts is small, this marginal difference may lead to significant difference in the Pt–O–Ce chemical bonding, which enhances the oxygen activation and inhibits the mobility of Pt particles. Meanwhile, the severe strong contact between Pt and ceria made the Pt particles difficult to aggregate, and thus its catalytic activity can be maintained.

It is clear that the metal-support interaction is critically dependent on the preparation method, which determines the catalytic activity and stability. The catalyst prepared by modified polyol method showed better activity and higher stability compared to the catalyst prepared by HCHO liquid phase reduction. This can be explained by the very narrow pore size distribution and more homogeneous metal distribution on ceria in Pt/CeO_2–EG. This result also suggested that the reducing ability and the solvent effect of different agents play important roles in determining the fine structures of the catalyst during the preparation process. Formaldehyde is a relatively stronger reducing agent, thus, a few Pt nuclei may be formed quickly in the suspension at mild temperature (343 K). Since the diffusion of Pt particles is relatively fast in water solution, the particle collision, adhesion and agglomeration through autocatalytic pathway will result in the formation of large Pt particles deposited on ceria surface. In this case, the nucleation and the growth steps of Pt nuclei proceeded simultaneously. Comparatively, ethylene glycol is weaker reducing agent, and higher temperature is needed to achieve complete reduction of Pt species. Meanwhile, the high viscosity of ethylene glycol limits the growth rate of small platinum nuclei. Once the diffusion of oxidized platinum becomes rate-limiting step (i.e., the reduction on the Pt^0 surface is relatively fast), all nuclei will grow at an equal rate resulting in uniform distribution and small particle sizes of Pt [19]. Therefore, the modified polyol method can effectively control the particles size and distribution of Pt particles even at relatively higher temperature through quick nucleation and complete separation of the nucleation and growth steps [18]. It seems clear that this preparation process is beneficial to obtain small and uniform Pt particles, and then produces strong Pt-ceria interaction.

5. Conclusions

The particle size of Pt as well as the Pt-ceria interaction during the preparation process was controlled by the nucleation and the growth rates which depend on the reducing ability and solvent effect of different agents.

Highly dispersed Pt/CeO_2 catalysts were prepared by HCHO liquid phase reduction and modified polyol method. The Pt/CeO_2–EG presented more uniform and narrow particle size distribution of Pt species than that of Pt/CeO_2–HCHO.

The Pt/CeO_2 catalysts showed excellent catalytic activity for the complete oxidation of DME. The activity and stability of the Pt/CeO_2 prepared by modified polyol method was superior to that of the Pt/CeO_2 prepared by HCHO liquid phase reduction, suggesting the different metal-support interaction and distribution of Pt species play crucial roles in governing the catalytic performance.

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