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Effect of preparation procedures on the activity of supported palladium/lanthanum methanol decomposition catalysts

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Abstract

A series of palladium catalysts promoted with lanthanum were prepared on a silica support and the activities of these catalysts examined for the decomposition of methanol into CO and H_2. The preparation procedure and the La_2O_3/Pd weight ratio of these Pd/La_2O_3/SiO_2 catalysts (5 wt.% Pd) was found to be important for high catalytic activities. If Pd is deposited after La_2O_3 using a precipitation procedure, the methanol decomposition activity increases up to a La_2O_3/Pd weight ratio of 1.0. The optimized weight ratio for the methods of co-precipitation and co-impregnation were found to be 0.8 and 0.5, respectively. Relatively low activities are obtained if a sequential procedure with La_2O_3 deposition in the final step is applied. The effect of the preparation procedure and La_2O_3/Pd weight ratio on activity of the resulting catalysts can be explained by: (i) the amount of Pd particles in contact with La_2O_3 moieties, positively affecting the activity, and (ii) the extent of coverage of Pd particles by La_2O_3 patches, negatively affecting the activity.

Keywords: Methanol; Decomposition; Palladium; Lanthanum oxide; Precipitation; Impregnation

1. Introduction

The methanol decomposition to CO and H_2 is a highly endothermic reaction and has gained interest as a method of increasing fuel efficiency for methanol powered vehicles and as a convenient medium for long distance heat transportation [1]. For the development of heat recovery systems, however, new catalysts for methanol decomposition are needed, which are active at relatively low temperatures (200–250°C) [1]. The objective of the present work is to maximize the methanol conversion as a function of catalyst weight at a given flow rate. Cu based catalysts [2–4], Pt-catalysts [5], Ni-catalysts [1], and Pd-catalysts [6–8] have been reported to be active in the decomposition of methanol. Catalysts containing both La_2O_3 and Pd were found very active in the synthesis of methanol, as described e.g. in [6,7,9–15], but have not been systematically tested for the reverse reaction. Furthermore, these methanol synthesis catalysts were only prepared by impregnation, and the activity was not specifically related to the preparation procedure or the La_2O_3/Pd ratio. In this paper we describe the effect of the preparation procedure on the activity of SiO_2 supported La_2O_3/Pd catalysts for the decomposition of methanol into CO and H_2. We used both impregnation and precipitation techniques to prepare the catalysts, and varied the La_2O_3/Pd ratio. Differences in methanol decomposition activity are discussed in relation to the morphology of the catalysts, which is largely affected by the preparation procedure.

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2. Experimental

2.1. Catalyst preparation: precipitation

SiO_2 supported La_2O_3 was prepared by a homogeneous deposition precipitation (HDP) method. The La_2O_3 was precipitated by injecting a 0.05 M ammonia solution at a rate of $2\,ml\,min^{-1}$ into an aqueous SiO_2 suspension ($2\,g\,l^{-1}$) containing $La(NO_3)_3{\cdot}6H_2O$. The precipitate was filtered, washed and dried at 400 K to prepare SiO_2 supports containing 1–12 wt.% La_2O_3. Precipitation of $Pd(OH)_2$ was conducted using an apparatus as described by Geus [16]. The prepared La_2O_3/SiO_2 support was re-suspended in a NaOH solution of pH 10, and precipitation of $Pd(OH)_2$ was achieved by injecting a HCl acidified solution of $PdCl_2$ ($1\,g\,l^{-1}$). The pH was kept constant by simultaneous injection of a computer-controlled amount of a NaOH solution into the La_2O_3/SiO_2 suspension. After precipitation, the catalyst was filtered, thoroughly washed to remove remaining NaOH, and dried at 400 K for 1 h to prepare catalysts containing 5 wt.% Pd.

Co-precipitation of Pd and La was achieved by injecting a HCl acidified solution of $PdCl_2$ ($1\,g\,l^{-1}$) and $La(NO_3)_3{\cdot}6H_2O$ in an aqueous SiO_2 suspension ($2\,g\,l^{-1}$) at pH 10, using the procedure and equipment described above. The resulting catalyst was filtered, thoroughly washed, and dried at 400 K for 1 h, before activity testing. For comparison, several precipitated catalyst samples were also calcined at 673 K for 1 h, before catalytic testing and were found to perform similarly in the methanol decomposition reaction to catalysts without this oxidative pretreatment.

2.2. Catalyst preparation: impregnation

Incipient wetness co-impregnation of fumed silica (Alpha Aesar, BET surface area $400\,m^2/g$) was performed using a solution of $(NH_3)_4Pd(NO_3)_2$ (to yield 5 wt.% Pd in catalyst) and variable amounts of $La(NO_3)_3{\cdot}6H_2O$ (approximately 3 ml solution was used for 1 g of SiO_2). The catalysts were dried overnight at 400 K followed by calcination at 673 K for 1 h in static air. Sequential procedures for catalyst preparation were performed by incipient wetness impregnation of the SiO_2 support with $La(NO_3)_3{\cdot}6H_2O$ or $(NH_3)_4Pd(NO_3)_2$, respectively, followed by drying and calcination in static air at 673 K for 1 h. Subsequently, the catalysts were impregnated, using the same incipient wetness method, with a solution of the second component of the catalyst (either $(NH_3)_4Pd(NO_3)_2$ or $La(NO_3)_3{\cdot}6H_2O$).

2.3. Catalyst characterization

The N_2-BET surface area of the various La_2O_3/SiO_2 mixed oxides and catalysts was determined after calcination at 675 K for 2 h. Selected catalysts were analyzed after reduction and methanol decomposition experiments by transmission electron microscopy. Samples were thoroughly mortared, dispersed in ethanol and introduced on a carbon grid. Magnifications of 85,000–140,000 were used to distinguish the individual Pd particles. Particle sizes were determined by averaging the diameter of at least 15 particles on every TEM micrograph.

2.4. Determination of methanol decomposition activity

Reduction of the catalysts was performed in a flow of $100\,ml\,min^{-1}$ 6% H_2 in Ar at 473 K (ramp: $3\,K\,min^{-1}$) for 2 h, before catalytic testing. A conventional quartz plug-flow reactor was used for the activity measurements, which was connected to a GC, equipped with an Alltech Hayesep D 100/120 column and a 10 feet HP 13X molecular sieve column. Column switching was applied to optimize the separation of H_2, CO, methane and methanol. A TCD detector was used for CO and methanol determination, and a FID for the detection of traces of methane. Generally, a sample size of 250 mg of catalyst was exposed at 500 K to a He flow of $85\,ml\,min^{-1}$, containing a (saturated) concentration of 15% methanol. The GC calibration was adjusted for the volumetric changes caused by the reaction. Applying the necessary volumetric corrections, the carbon balance was always closed within 1%. For many precipitated Pd catalysts, the catalytic methanol decomposition activity was found to decrease during the first hours of operation. After 3 h on stream, the activity stabilized. The activity determined after 3 h on stream was therefore used to compare various catalysts in the decomposition of methanol.

3. Results

3.1. Characterization of La_2O_3/SiO_2 supports

The precipitation curve of $La(OH)_3$ in the presence and absence of SiO_2 is presented in Fig. 1. The pH shows a maximum as a function of time in the absence of SiO_2, whereas a continuous increase is observed in the presence of SiO_2. This difference in the curves is indicative for a good interaction between the hydroxyl groups of SiO_2 and La_2O_3. Precipitation of $La(OH)_3$ occurs at a continuous rate at pH 8 and is completed after 200 min, as witnessed by the rapid increase in pH at this time.

The development of the surface area of precipitated and calcined La_2O_3/SiO_2 mixed oxides as a function of La_2O_3 content is presented in Fig. 2. Based on Fig. 2, the surface area appears to decrease from an extrapolated value of 250 $m^2\,g^{-1}$ for bare silica to 150 $m^2\,g^{-1}$ for the sample containing 12 wt.% La_2O_3. The discrepancy between the initial values of 400 $m^2\,g^{-1}$ reported for the untreated silica and the 250 $m^2\,g^{-1}$ value is most likely related to densification of the silica support upon catalyst preparation. The La_2O_3/SiO_2 mixed oxides prepared by impregnation showed a similar trend in surface area, decreasing from 267 $m^2\,g^{-1}$ for a sample containing 4 wt.% La_2O_3, to 228 $m^2\,g^{-1}$ for a sample with a La_2O_3 loading of 10 wt.%. XRD analysis did not reveal any

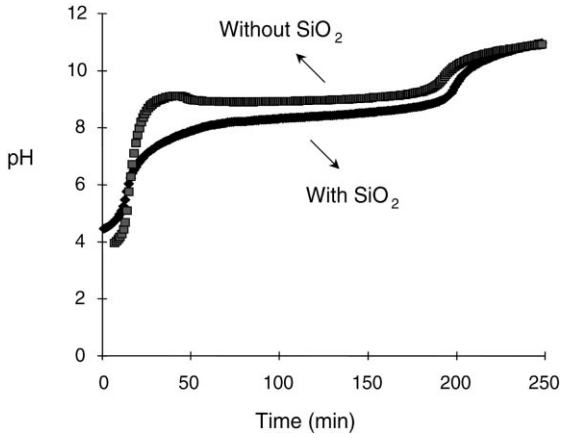

Fig. 1. Precipitation curves of $La(OH)_3$, with, and without silica in suspension. The absence of a maximum in the pH as a function of time indicates a strong interaction between silica and precipitating $La(OH)_3$.

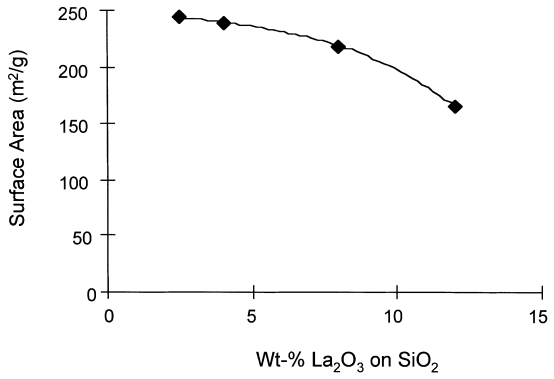

Fig. 2. Development of the N_2-BET surface area of precipitated La_2O_3/SiO_2 samples as a function of La_2O_3 loading. The samples were calcined at 673 K before BET measurements were performed.

features of lanthanum oxides in the samples prepared by impregnation or precipitation, suggesting that an amorphous La-phase was formed. TEM micrographs of the La_2O_3/SiO_2 mixed oxides were similar in appearance to the ones presented by Vidal et al. [17]. Particle sizes of approximately 5 nm were estimated using the difference in contrast between the La_2O_3 particles and the SiO_2 support.

3.2. Characterization of $Pd/La_2O_3/SiO_2$ catalysts

The La_2O_3/SiO_2 supported Pd catalysts were also characterized by surface area measurements, XRD, and TEM. Only a minor change in the N_2-BET surface area of the La_2O_3/SiO_2 mixed oxides was observed upon incorporation of Pd. Besides the diffraction pattern of Pd particles in some of the impregnated catalysts, the XRD analysis did not reveal the formation of any new phases after deposition of Pd by impregnation or precipitation procedures.

Significant differences in catalyst morphology were observed in TEM micrographs. The effect of the preparation method and La_2O_3 content on the Pd particle size is summarized for catalysts containing 5 wt.% Pd in Fig. 3. The Pd particle size was found to decrease as a function of La-loading when the co-precipitation or co-impregnation methods were used, whereas the particle size was invariant to La-loading when sequential precipitation was applied. A minimum Pd particle size of about 2–3 nm was obtained at a La_2O_3/Pd ratio of 1 using the co-precipitation method, and

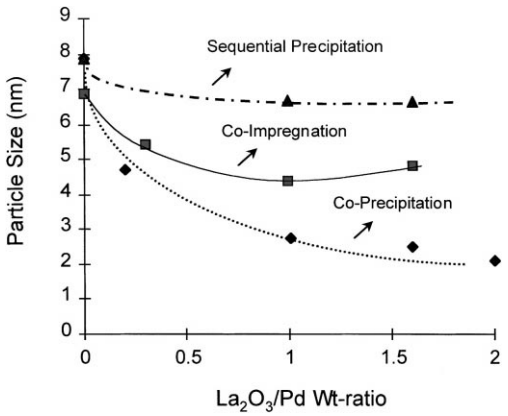

Fig. 3. Development of the Pd particle size as a function of the La_2O_3 content in the catalyst. Solid line: co-impregnation; dashed: co-precipitation; alternating dash: sequential precipitation (Pd on La_2O_3/SiO_2). The particle sizes were determined by TEM, averaging the diameter of at least 15 particles. The catalysts contained 5 wt.% Pd.

particle sizes of approximately 5 nm were obtained for catalysts prepared by impregnation methods.

3.3. Activity tests

Fig. 4 illustrates the relative activities of the impregnated and precipitated catalysts for methanol decomposition. The carbon selectivity towards CO was higher than 99% for all the catalysts tested, and only minor amounts of co-products, CH_4 and CO_2 were observed. The co-impregnation method provided the best catalytic performance at a relatively low La_2O_3/Pd weight ratio of 0.5. For catalysts prepared by the co-precipitation procedure a somewhat higher La_2O_3/Pd weight ratio of 0.8 was determined. An even higher La_2O_3/Pd wt. ratio of at least 1.0 is required to optimize the activity of catalysts prepared by sequential precipitation, while the maximum in the activity curve is less prominent than for the other preparation methods. At the respective optimized La_2O_3/Pd weight ratio, the obtained methanol decomposition activity is quite similar for these preparation methods. The activity for impregnated as well as precipitated catalysts is significantly reduced if the catalysts are prepared by adding La_2O_3 in the final step.

4. Discussion

Promotion of Pd/SiO_2 by La_2O_3 has already been extensively discussed in literature dealing with the synthesis of methanol. Hicks and Bell [10,18] and Rieck and Bell [19] recognized that the activity and selectivity of Pd catalysts depends on Pd dispersion, crystallite morphology, and support composition. An electronic effect (strong metal support interaction

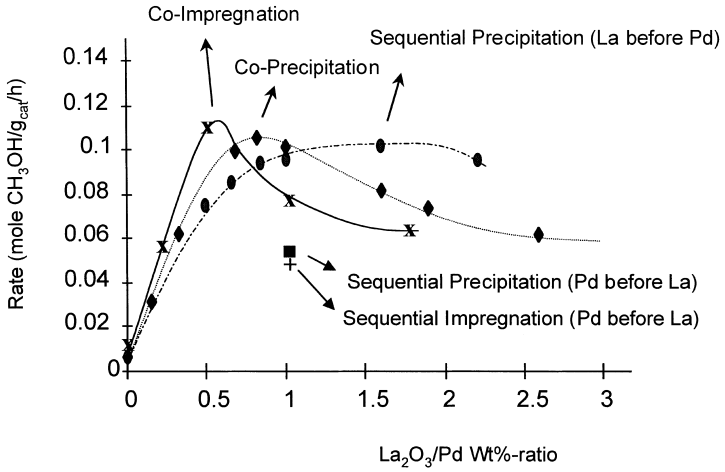

Fig. 4. Activity of $Pd/La_2O_3/SiO_2$ catalysts in the decomposition of MeOH as a function of the La_2O_3/Pd weight ratio and the preparation method. A residence time of 0.32 h g cat(dm MeOH)$^{-3}$ was used to determine the MeOH conversion at 500 K after 3 h on stream. The catalysts contained 5 wt.% Pd.

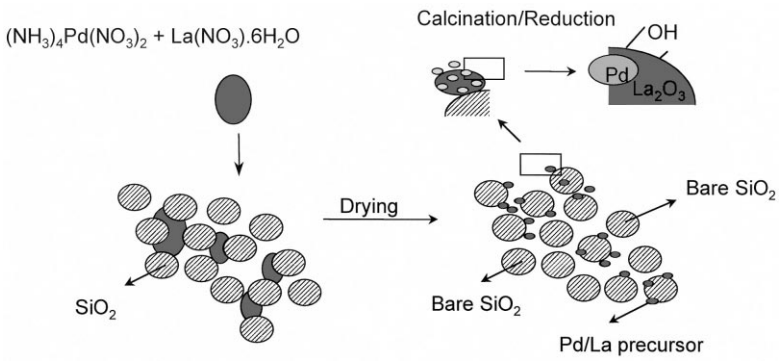

Fig. 5. Representation of the synthesis pathway for impregnated catalysts.

(SMSI)) is claimed to effect the activity [9], as well as decoration of the metal particles by reduced LaO_x patches [19]. Hydrogenation of CO and CO_2 using noble metals (Pd, Rh) has also been extensively studied in the group of Prins [13,14,20,21]. Borer and Prins [21] showed that Rh particles were covered by La_2O_3 if La impregnation was the final step of a sequential preparation procedure, and indicated that well dispersed Rh particles were formed if the impregnation procedure was reversed or when co-impregnation was applied. Gotti and Prins [14] show that basic metal oxide additives must be in contact with the Pd particles to be effective in methanol synthesis. More recently, Seone et al. [22] studied the effect of the La precursor ($LaCl_3$ or $La(NO_3)_3$) on the resulting activity of La promoted Pd catalysts in the synthesis of methanol. The authors claim that the decoration of Pd by La_2O_3 patches is a result of the preparation procedure, rather than an effect of the reduction of La_2O_3 and migration of LaO_x species [19,22]. In agreement with these studies, we found that the preparation procedure and La_2O_3/Pd ratio largely affects the activity of La promoted Pd catalysts in the decomposition of methanol. We propose that the activity is determined by (i) the extent of direct contact between La_2O_3 and Pd moieties (i.e. Pd deposited on La_2O_3 or adjacent to these moieties), and (ii) the amount of Pd particles covered by La_2O_3 patches. The effect of the preparation procedure on these two parameters is illustrated in Figs. 5 and 6.

The processes occurring during the co-impregnation procedure are schematically presented in Fig. 5. The mixed solution of the nitrates of Pd and La is introduced in the pores of the SiO_2 support. The TEM results and surface area measurements indicate that the solution was not entirely homogeneously 'wetting' the silica, resulting in areas of bare silica after drying. Calcination and reduction converts $La(NO_3)_3$ into La_2O_3, and the Pd precursor into metallic Pd. At low La_2O_3 loadings the Pd population of the catalyst will only be partly promoted. Increasing the La_2O_3/Pd ratio results in localized clusters with an intimate contact between Pd and La_2O_3 and a high catalytic activity. Further increasing the La_2O_3/Pd ratio results in covering of Pd by La_2O_3 and decreases activity (Fig. 4). Deposition of La_2O_3 patches on Pd is very likely to occur when a sequential preparation procedure is applied in which La_2O_3 is deposited on SiO_2 after Pd and is consistent with the relatively low activities of catalyst prepared by this method. Both Prins [14] and Bell [19] used this preparation procedure when studying the methanol synthesis reaction. However, for our objectives of optimizing the activity of the catalysts, the methods of adding the Pd and La simultaneously at low La_2O_3/Pd ratios or adding the Pd after La_2O_3 addition appears to be preferred.

The chemical processes occurring in the precipitation solution are schematically illustrated in Fig. 6. Upon injection of the acidic precursor solution three co-precipitating species can be formed: $La(OH)_3$, $Pd(OH)_2$ and a mixed $PdLa(OH)_5$. If La is omitted from the precursor solution, only $Pd(OH)_2$ entities will be generated which react with Si–OH to form structure A (Fig. 6). Upon drying and reduction, SiO_2 supported Pd particles are formed with an average size of 7–8 nm (Fig. 3). If Pd is omitted from the precursor solution, only $La(OH)_3$ will be formed, which

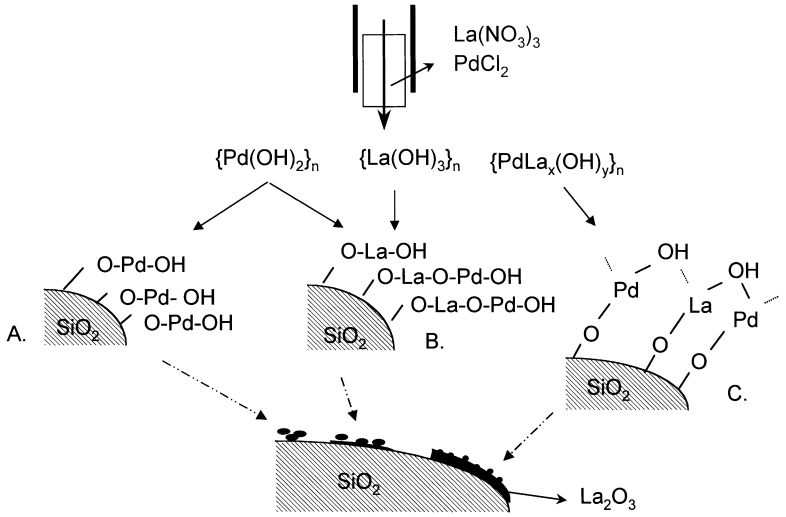

Fig. 6. Representation of the synthesis pathway for precipitated catalysts.

interacts with Si–OH groups of silica and forms a well-dispersed La_2O_3 phase upon drying and calcination [17]. The precipitation curve of $La(OH)_3$ in the presence of SiO_2 (Fig. 1) clearly shows a strong interaction between the $La(OH)_3$ and Si–OH. If a La_2O_3/SiO_2 mixed oxide is used as the support material, the $Pd(OH)_2$ species generated by injection of a La free $PdCl_2$ solution will interact with La–OH groups and form structure B (Fig. 6). The individual Pd particle size is determined by the cluster size of the $Pd(OH)_2$ precursor in the precipitation solution. This size is apparently independent of the presence of La_2O_3 on SiO_2. If the La_2O_3 content of the La_2O_3/SiO_2 support is sufficient to provide enough La–OH groups for interaction with $Pd(OH)_2$ (around a La_2O_3/Pd ratio of 0.8–1.0), the activity of the resulting catalyst in methanol decomposition is optimized. The maximum in the curve is not very distinctive, and the activity is only slightly decreased at higher La_2O_3 loading. Covering of Pd particles by La_2O_3 moieties apparently is not significant during this preparation procedure.

Depending on the molar La/Pd ratio in the precursor solution, all three species ($La(OH)_3$, $Pd(OH)_2$ and mixed $PdLa(OH)_5$) can be formed if the co-precipitation procedure is applied. Under these conditions, the Pd particle size is significantly reduced as a function of increasing La content (Fig. 5). A decrease in particle size to about 3 nm was observed. It is hypothesized that $PdLa(OH)_5$ moieties interact with silica in structure C (Fig. 6), resulting in intimately mixed La_2O_3/Pd clusters. The presence of a La atom next to a Pd atom, prevents the formation of (relatively) large Pd clusters, and thus reduces the particle size. Above a certain La/Pd ratio, however, coverage of the small Pd particles starts to negatively effect the performance of the catalyst, explaining the decreasing activity at La_2O_3/Pd ratios above 0.8. The somewhat higher optimized La_2O_3/Pd ratio found for co-precipitation (0.8) than co-impregnation (0.5) (Fig. 5) is likely caused by formation of separated $La(OH)_3$ and $Pd(OH)_2$ clusters in the precipitation procedure, resulting in Pd particles not interacting with La_2O_3 (or $La(OH)_3$) moieties. The somewhat higher surface area of the impregnated samples could be indicative of a higher fraction of unused silica, suggesting that localized structures with the La_2O_3/Pd ratio are formed at the particular composition of the impregnation solution.

A direct relationship between the Pd particle size and the activity in methanol decomposition is not apparent (see Figs. 3 and 4). The Pd particle size of the co-precipitated samples is significantly smaller than sequentially prepared catalysts, while similar decomposition activities were observed. The relative small effect of the particle size, i.e. dispersion on the

catalytic activity is in agreement with results presented in the literature [10], suggesting other factors, such as those discussed above have a stronger effect on the methanol decomposition activity.

5. Conclusions

La_2O_3 promoted Pd/SiO_2 catalysts are very active in the decomposition of methanol. The preparation procedure and the La_2O_3/Pd ratio strongly affect the methanol decomposition activity. The explanation for these differences can be related to (i) the quantity of Pd particles in contact with La_2O_3 moieties, positively affecting the activity, and (ii) the extent of coverage of Pd particles by La_2O_3 moieties, negatively affecting activity. For procedures where La_2O_3 and Pd are simultaneously added to silica, an optimized La_2O_3/Pd ratio exists for co-impregnation (0.5), as well as co-precipitation (0.8). A minimum La_2O_3/Pd weight-ratio of about 1.0 is required to obtain high methanol decomposition activities if Pd is deposited after La_2O_3. The coverage of Pd particles by La_2O_3 patches is very likely when La_2O_3 is incorporated in the final step, yielding a relatively low methanol decomposition activity.

The La_2O_3/Pd ratio also affects the Pd particle size if co-deposition of La_2O_3 and Pd is applied. Pd particles as small as 3 nm can be prepared by co-precipitation. However, a general correlation between the activity and Pd particle size was not found. For our purposes of maximizing catalyst activities, the preparation methods of choice are either simultaneous additions of La and Pd at low La_2O_3/Pd ratios or sequential addition of the Pd upon the La_2O_3 deposited on SiO_2.

Acknowledgements

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References

[1] Y. Matsumura, N. Tode, T. Yazawa, M. Haruta, J. Mol. Catal. A: Chem. 99 (1995) 183.
[2] W.-H. Cheng, Appl. Catal. B: Environ. 7 (1995) 127.
[3] I.A. Fisher, A.T. Bell, J. Catal. 184 (1999) 357.
[4] R. Kieffer, M. Fujiwara, L. Udron, Y. Suma, Catal. Today 36 (1997) 15.
[5] S. Imamura, T. Higashihara, Y. Saito, H. Aritani, H. Kanai, Y. Matsumura, N. Tsuda, Catal. Today 50 (1999) 369.
[6] Y. Saitoh, S. Othsu, Y. Makie, T. Okada, K. Satoh, N. Tsuruta, Y. Terunuma, Bull. Chem. Soc. Jpn. 63 (1990) 108.
[7] M. Rebholz, N. Kruse, J. Chem. Phys. 95 (1991) 7745.
[8] Y. Matsumura, M. Okumura, Y. Usami, K. Kagawa, H. Yamashita, M. Anpo, M. Haruta, Catal. Lett. 1997.
[9] T.H. Fleisch, R.F. Hicks, A.T. Bell, J. Catal. 87 (1984) 398.
[10] R.F. Hicks, A.T. Bell, J. Catal. 90 (1984) 205.
[11] J.M. Driessen, E.K. Poels, J.P. Hindermann, V. Ponec, J. Catal. 82 (1983) 26.
[12] H.S. Hahm, W.Y. Lee, Appl. Catal. 65 (1990) 1.
[13] C. Sellmer, R. Prins, N. Kruse, Catal. Lett. 47 (1997) 83.
[14] A. Gotti, R. Prins, J. Catal. 175 (1998) 302.
[15] Y. Usami, K. Kagawa, Y. Matsumura, H. Sakurai, M. Haruta, Appl. Catal. 171 (1998) 123.
[16] J.W. Geus, Stud. Surf. Sci. Catal. 16 (1983) 1.
[17] H. Vidal, S. Bernal, T. Baker, D. Finol, J.A. Perez-Omil, J.M. Pintado, J.M. Rodriguez-Izquierdo, J. Catal. 183 (1999) 53.
[18] R.F. Hicks, Q.-J. Yen, A.T. Bell, J. Catal. 89 (1984) 498.
[19] J.S. Rieck, A.T. Bell, J. Catal. 99 (1986) 278.
[20] A. Gotti, R. Prins, Catal. Lett. 37 (1996) 143.
[21] A.L. Borer, R. Prins, J. Catal. 144 (1993) 439.
[22] X.L. Seoane, N.S. Figoli, P.C. L'Argentiere, J.A. Gonzalez, A. Arcoya, Catal. Lett. 47 (1997) 213.