

CHARACTERISTICS AND CATALYTIC ACTIVITY OF Pd-Cu/SiO₂ SYNTHESIZED BY SOL-GEL METHOD FOR THE HYDRODECHLORINATION OF TETRACHLOROETHYLENE

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ABSTRACT

The double metallic catalyst Pd-Cu/SiO₂ was synthesized using sol-gel method with various ratios of Pd/Cu and characterized for their physico-chemical properties. Their catalytic activities were also tested for the hydrodechlorination of tetrachloroethylene, one of the most popular solvents used in different industries. Better tetrachloroethylene conversion over double metallic samples compared to the single ones indicated the advantage of these materials in keeping the active sites out of deactivation.

I - INTRODUCTION

Tetrachloroethylene (TTCE) as well as other chlorinated organic compounds are popular solvents used for metal cleaning, drying washing, textile industries, and also chemical intermediates for organic synthesis thanks to their specific advantaged properties. However, due to their toxicity, it is impossible to discharge them directly into environment. Of all treatment methods, hydrodechlorination (HDC) can be considered one of the most effective since it allows recovering of the hydrocarbons as feedstock for other industries [1].

To accelerate this reaction, a Pd or Pt containing catalyst should be used. However, two major disadvantages of these catalysts are high price and rapid deactivation, preventing them to be applied in larger scale. To resolve these problems, a second metal will be added and partly replaced for the precious active Pd or Pt [2 - 5].

In this research, Cu was selected as a second metal. The Pd-Cu/SiO₂ catalyst was synthesized

using sol-gel method, expecting nano particle size samples could be resulted in. Different ratios of Pd/Cu samples were prepared for better evaluation of Cu replacement effect on characteristics and catalytic activity of the catalyst in hydrodechlorination of TTCE.

II - EXPERIMENTAL

1. Synthesis of Pd-Cu/SiO₂ catalyst

The Pd-Cu/SiO₂ samples with different Pd/Cu ratios were synthesized using sol-gel method described as the following [6]:

Preparation of gel: Palladium acetyl acetate, copper acetate, ethanol and EDAS ([3-(2-ethylamine) propylamine] trimethoxy silane) were mixed at different ratios depending on the desired catalyst compositions (table 1). The solution was stirred until a clear blue could be observed. Then, TEOS (tetraethoxysilane), ammoniac solution and ethanol were gradually added. After 10 minutes of vigorous stirring, the mixture was sealed and heated to 80°C for 3 days.

Gel drying: Finishing the gelling and aging gel, drying gel under the vacuum condition of 1.2 kPa, at 80°C for one day. The drying period was ended after another 3 days heating at 150°C.

Calcination: In the final step, samples were calcinated at 400°C in airflow for 12 hours.

Compositions of gel mixtures for preparation of catalysts containing 1% metal in total were given in the Table 1.

Table 1: Composition of Pd-Cu/SiO₂ samples

Sample	Pd/Cu (%wt)	EDAS, ml	Ethanol, ml	TEOS, ml	NH ₃ , ml
SC-0	100% Pd	0.12	29	10.9	0.08
SC-25	75/25	0.19	29	10.8	0.25
SC-50	50/50	0.27	29	10.7	0.25
SC-75	25/75	0.34	29	10.7	0.25
SC-100	100% Cu	0.41	29	10.6	0.08

2. Characterization of catalyst samples

Synthesized samples were characterized for specific area, pore structure and pore distribution, using physical adsorption of N₂ at 77K on an ASAP 2010 Micromeritics, USA. Metal particle distribution was determined by TEM images (JEM 1010/JEOL, Japan). Metal particle dispersion over the support was measured by CO chemical adsorption performed on an Autochem II 2920 Micromeritics, USA.

3. Study on catalytic activity of Pd-Cu/SiO₂ samples for hydrodechlorination of TTCE

Catalytic activities of Pd-Cu/SiO₂ samples for hydrodechlorination of TTCE were studied on a micro-flow reaction setup. The reaction was carried out in gas phase with fix bed catalyst. Composition of feedstock and products were analyzed using a GC-FID (column TR5) on-line connected to the reaction system. The TTCE saturated vapor was carried to the reactor using Ar gas. The typical reaction conditions were as follows: 50 mg catalyst, H₂ (10%H₂/Ar) flow of 80 ml/min, Ar (99,99% Ar) flow of 120 ml/min, and reaction temperature of 200 - 300°C. Before the reaction, all catalyst samples were activated at 300°C for 3 hrs under hydrogen flow.

III - RESULTS AND DISCUSSION

1. Physico-chemical characteristics of the Pd-Cu/SiO₂ catalyst samples

a) Specific surface area and pore structure distribution of the Pd-Cu/SiO₂

In order to determine specific surface area and pore structure of the Pd-Cu/SiO₂ catalyst synthesized by sol-gel method, sample SC-50 was analyzed. Measurements showed that this sample had a specific surface area of 252.3 m²/g, with typical adsorption and desorption isotherms of porous materials, meaning type 4 as classified by Brunauer [7] as being observed in figure 1.

Concerning the pore size, average pore width of this material mostly concentrated in the range of 30 - 35 Å, indicating a medium pore structure. With these characteristics, Pd-Cu/SiO₂ synthesized by sol-gel method was expected to be an appropriate catalyst for the hydrodechlorination of tetrachloroethylene since it might allow feedstock molecules to diffuse easily through the pore structure and contact with active sites for the reaction to occur.

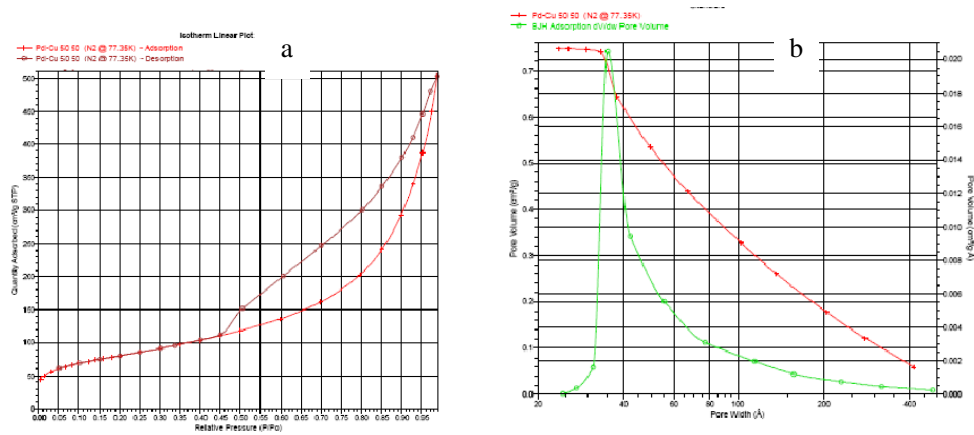


Figure 1: Adsorption and desorption isotherms of Pd-Cu/SiO₂ sample (a) and its pore distribution (b)

b) Metals distribution in Pd-Cu/SiO₂ samples

The distribution of Pd and Cu particles in catalyst samples could be observed by TEM

images. Figure 2 showed different distribution types of Pd and Cu in Pd-Cu/SiO₂ samples, depending on the ratio of Pd/Cu.

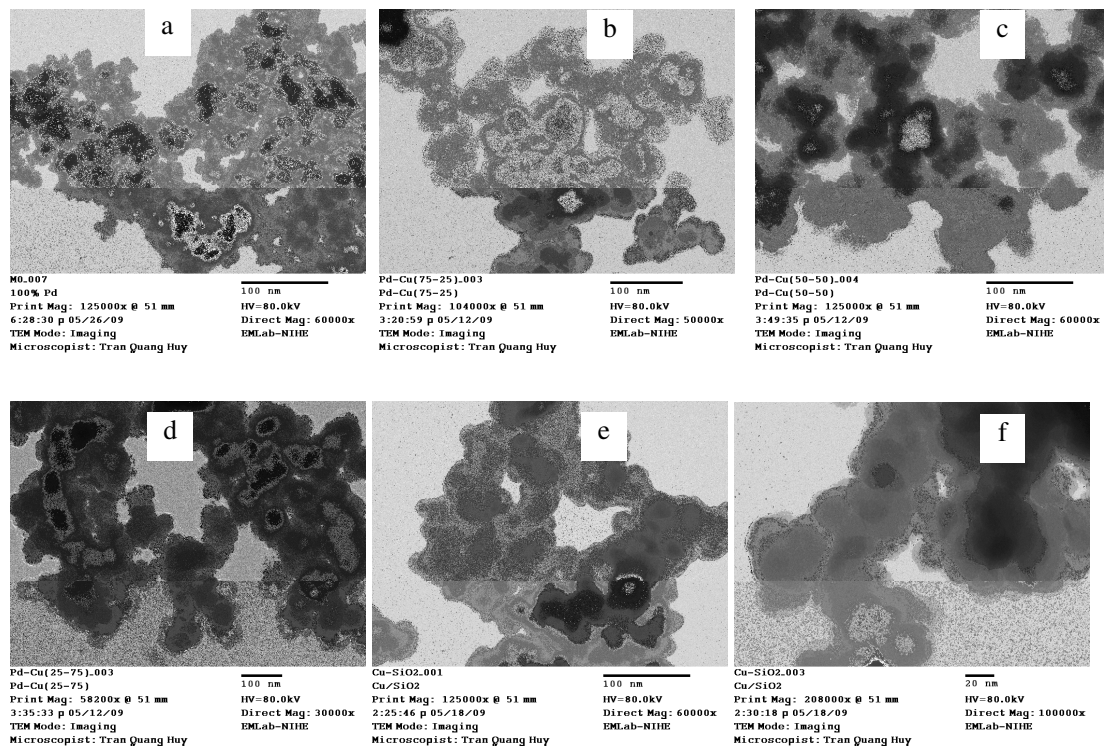


Figure 2: TEM images of Pd-Cu/SiO₂ samples at different Pd/Cu ratios: SC-0(a), SC-25(b), SC-50 (c), SC-75 (d), SC-100 – Mag. 60 K(e), SC-100 – Mag. 100K (f)

Observing figure 2, it was easily to recognize that, a common point among these samples was the spherical shape of catalyst crystals. The diameters of these crystals were in the range of 10-50 nm. In these crystals, metal particles appeared as black dots, whose distribution became gradually scattered as the amount of Pd decreased, and almost disappeared when no Pd was present in the catalyst (sample SC-100). This indicated that those black dots were mostly presented for Pd particles and not for Cu ones. An explanation for this observation was might be due to the smaller size of Cu presented in the sample synthesized using sol-gel method, so that no Cu particle could be seen in a TEM with magnification of 60 thousands (Figure 2e), or even with magnification of 100 thousands (Figure 2f). Therefore, with this TEM technique, no Cu particles distribution could be observed. To observe Cu atoms, other techniques or a TEM with higher magnification must be used.

c) Metal sites dispersion over the support

For the determination metal particles dispersion over the support using CO chemical adsorption, three samples SC-0, SC-50 and SC-75 were selected. The results were presented in table 2.

Table 2: Metal particles dispersion over the support in Pd-Cu/SiO₂ samples

Sample	Metal Dispersion, %	Metal particle size, nm
SC-0	29.73	3.8
SC-50	7.31	11.2
SC-75	5.69	33.8

From table 2, it could be seen that when a part of Pd was replaced by Cu, the metal dispersion over the SiO₂ was significantly decreased, and the metal particle size was considerably increased. These observations were similar to the notices of other research [6] and could be explained as the following. During the CO adsorption, only Pd particles

participated, and no Cu particles joined. As the result, for the double metallic catalyst Pd-Cu/SiO₂, the measurement of metal dispersion over the support was true only for Pd. Then, from the SC-0 to SC-75, the amount of Pd was decreased, leading to a lower dispersion of metal over the SiO₂.

Besides, the presence of Cu particles might result in an strong effect on CO adsorption of Pd particles. Cu atoms could associate with Pd ones to form alloy, which prevented Pd particles to participate in the CO adsorption. This effect became more significant as the amount of Cu increased. Consequently, the amount of CO adsorbed on Pd was considerably decreased, resulting in lower metal dispersion. This explained why the metal dispersion decrease was not in proportion with the amount of Pd removal.

Concerning metal particle size, an increasing in metal diameter was observed. This was also originated from the association of Cu with Pd particles, leading to a formation of larger metal particles in double metallic catalysts (SC-50 and SC-75) compared to the ones found in pure Pd sample (SC-0).

From these observations, it should be noted that, although CO adsorption measurements revealed low metal dispersion in double metallic catalysts, it did not mean the total metal dispersion over the SiO₂ was decreased at all.

2. Catalytic activity of the Pd-Cu/SiO₂ catalysts

a) Catalytic capability of the Pd-Cu/SiO₂ for the Hydrodechlorination

Catalytic activity of the five Pd-Cu/SiO₂ samples was tested for the hydrodechlorination of Tetrachloroethylene (TTCE) in gas phase at 300°C, under the same conditions described in the Experimental section. The results were shown in figure 3.

Observing figure 3, it was noted that the TTCE conversion was decreased in the order of SC-50 > SC-75 > SC-25 > SC-100 > SC-0, corresponding to average conversions of 75% >

38% > 23% > 22% > 12%. Of the five tested catalysts, SC-50 revealed the highest activity for this reaction compared to others, and the SC-0 was the worst.

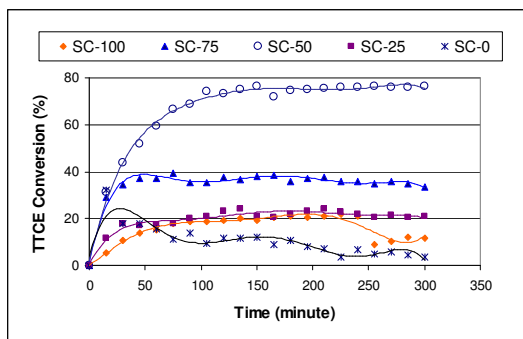


Figure 3: Catalytic activity of the Pd-Cu/SiO₂ samples for hydrodechlorination of TTCE

Looking back the TEM image of Pd-Cu/SiO₂ samples (figure 2), it can be found that Pd particles were more evenly distributed in higher Pd ratio samples (SC-0, SC-25, SC-50). These explained why these samples showing higher catalytic activity compared to high Cu ratio ones (SC-75 and SC-100). However, SC-0 containing 100% of Pd was not the one with highest catalytic activity, although Pd was proved to be very active for hydrodechlorination [2, 3, 4, 5]. This might be a consequence of clustering of very small Pd particles which were densely distributed over the support. Clusters of metal particles might be sintered at the reaction temperature, then decreasing number of active sites for the catalysis. Another reason was that Pd could be easily poisoned by chlorine or polymer formed during the reaction. Those made the pure Pd catalyst deactivate quickly [4 - 6, 8].

The presence of Cu particles may increase the distance between active sites (Pd), preventing them of clustering and melting at high temperature, maintaining their catalytic activity for the whole reaction period. It seemed that, the ratio of Pd/Cu = 50/50 was the best of all five tested compositions. Lower Cu might not be enough for isolating of Pd sites (SC-25),

but higher Cu might also lead to short of Pd active sites for the reaction. In addition, in the TTCE hydrodechlorination mechanism [4, 5, 6, 8], Cu adsorbed chlorinated organic compound and Pd adsorbed hydrogen for the generation of active hydrogen atom, which in turn would be used for the regeneration of Cu sites. This mechanism made catalytic activity of the double metallic catalysts higher and more stable. However, further study should be made for confirmation of this finding.

b) Effect of temperature on catalytic activity of the Pd-Cu/SiO₂

To investigate the effect of temperature on the hydrodechlorination of TTCE over Pd-Cu/SiO₂ catalyst, the SC-50 was selected for testing at 300°C and 200°C. The results were shown in figure 4.

Figure 4 showed that TTCE conversions decreased (from 75% to 55%) at lower temperature of hydrodechlorination (from 300°C to 200°C). In addition, the conversion of TTCE was also more stable at higher temperature and no deactivation of the catalyst could be noted during 300 minutes of reaction. The reason for this difference was that since hydrodechlorination was a slightly endothermic reaction, then increasing temperature might speed up the reaction. As a result, higher TTCE conversion could be observed. Moreover, low temperature might not facilitate the hydrogen molecule dissociate into hydrogen atoms for the regeneration of deactivated sites. Consequently, catalytic activity was unstable and decreased after a short period of reaction (80 minutes) as being observed at 200°C.

IV - CONCLUSION

The Pd-Cu/SiO₂ samples synthesized using sol-gel method had a relatively large specific surface area and medium pore structure. The catalyst crystals appeared in spherical shape of nano size (50 nm) as being expected for the sol-gel method. The presence of Cu in the catalyst composition resulted in larger metal sites due to association of Cu with Pd. For the

determination of metal dispersion over the support in a double metals catalyst, CO adsorption was good only for Pd sites, but not for Cu ones.

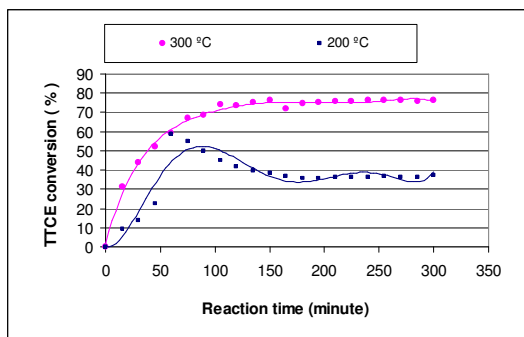


Figure 4: Hydrodechlorination of TTCE over SC-50 at different temperatures

Concerning catalytic activity, the double metallic catalysts were more effective than the single ones, with the best of SC-50 (75% TTCE was converted). Stability for long working period of this sample revealed a good effect of the second metal (Cu) for the remaining Pd activity during hydrodechlorination. Temperature significantly affected the hydrodechlorination of TTCE over Pd-Cu/SiO₂ catalyst as well. Better conversion of TTCE could be obtained if the reaction was carried out at higher temperature.

Those are our preliminary research results on Pd-Cu catalyst for the hydrodechlorination. The role of the second metal, optimization of

reaction conditions and catalyst composition for better hydrodechlorination of chlorinated organic compounds, both in the scientific and in the economic aspects will be focused in our further studies.

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