

Direct Oxidation of Ethene to Acetic Acid

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Abstract: Direct oxidation of ethene to acetic acid over Pd-SiW₁₂/SiO₂ catalysts prepared by several methods was studied. A better method for reducing palladium composition of the catalysts was found. Acetic acid was obtained with selectivity of 82.7% and once-through space time yield (STY) of 257.4 g/h·L.

Keywords: Pd-SiW₁₂/SiO₂ catalyst, acetic acid production, ethene oxidation.

Compared with the chemical processes of naphtha oxidation, n-butane oxidation, methanol carbonylation and acetaldehyde oxidation currently used in the manufacture of acetic acid, direct selective oxidation of ethene to acetic acid is a very attractive process^{1,2}. Uchida *et al.*^{3,5} and Denko⁴ have reported a highly active catalyst system which produces acetic acid with 240 g/h·L of the STY and 86.4% of selectivity. The catalyst system consisted of 2% of Pd by weight, 0.02 of the mole ratio of Se to Pd and 30% tungstosilic acid (SiW₁₂) by weight on silica.

In order to further improve the activity of the catalyst system, we have studied on the effects of catalyst preparation method, especially on the effect of the methods for reducing different Pd precursors on the activity (**Table 1**).

The Pd-SiW₁₂/SiO₂ catalysts were prepared by incipient wetness impregnation method. The catalytic reaction was conducted under the same conditions as in the literatures^{3,4,5}. The selectivities were fractions of the sum of the products and calculated on the ethene-basis.

Table 1 The activity of Pd-SiW₁₂/SiO₂ catalysts prepared by different methods

Precursor	Reducant	AcOH STY.(g/h.L)	AcOH selec. %	AcH selec. %	CO ₂ selec. %
Pd(NH ₃) ₄ Cl ₂	NH ₂ -NH ₂	21.6	58.0	10.2	31.8
	H ₂	41.0	68.9	5.7	25.4
H ₂ PdCl ₄	NH ₂ -NH ₂	88.9	64.6	10.4	25.0
	H ₂	257.4	82.7	5.7	11.6
	HCHO	32.6	56.1	16.0	27.9

Reaction conditions: N₂:O₂:C₂H₄:H₂O(g) = 13:7:50:30 vol%; P = 0.5MPa; T = 423K;
GHSV = 3000 /hr.

Table 1 showed that the palladium precursors and reduction methods strongly

affected the activity of the catalyst. The activities of the catalysts using $\text{Pd}(\text{NH}_3)_4\text{Cl}_2$ as the precursor were lower than those using H_2PdCl_4 as the precursor. Compared with the hydrazine reduction method, the catalyst reduced by H_2 gave the higher acetic acid STY of 41.0 g/h·L, which is about twice of that on catalyst reduced by hydrazine. When H_2PdCl_4 used as the precursor, the reduction method becomes more important.

The catalyst obtained from H_2PdCl_4 precursor and H_2 reduction showed 257.4 g/h·L of acetic acid STY with 82.7% of the selectivity, whereas the catalyst reducing by formaldehyde and hydrazine showed only 32.6 and 89.0 g/h·L STY of acetic acid, respectively. The latter was very close to the best results, 93.1 g/h·L of acetic acid STY with 78.5% of selectivity, reported by Showa Denko⁴. From these results, it seemed that the reduction of Pd (II) to Pd in liquid phase leads to worse catalytic performance, of which the reason is still not clear since without characterizing the dispersion of the Pd on SiO_2 reduced by different methods.

Table 2 The activity of catalysts with different components

Catalyst	AcOH STY(g/L)	AcOH selec. %	AcH selec. %	CO ₂ selec. %
Pd/SiO ₂	50.9	30.8	1.5	67.7
SiW ₁₂ /SiO ₂	0	0	0	0
Pd-SiW ₁₂ /SiO ₂	257.4	82.7	5.7	11.6

Reaction conditions: $\text{N}_2:\text{O}_2:\text{C}_2\text{H}_4:\text{H}_2\text{O}(\text{g}) = 13:7:50:30$ vol%; $P = 0.5\text{MPa}$; $T = 423\text{ K}$; $\text{GHSV} = 3000/\text{hr}$.

Over the Pd/SiO₂ catalyst, as shown in **Table 2**, ethene combustion occurred predominately. However, SiW₁₂/SiO₂ catalyst was inactive for both the ethene combustion and acetic acid production. These results indicate that the acetic acid production occurs mainly at the sites where Pd and SiW₁₂ are well combined. Probably the reduction of Pd (II) by H_2 is favorable to the universal dispersion of tiny Pd particles and SiW₁₂ on SiO₂. Therefore, the catalyst showed higher activity and better selectivity to acetic acid. Based on the study, we envision that the Pd-Se-SiW₁₂/SiO₂ catalyst reduced by H_2 would also perform better than the catalyst with the same composition reported by Showa Denko⁴.

The study of Pd-Se-SiW₁₂/SiO₂ catalysts is under way.

References

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