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Oxidation of formaldehyde over Pd/Beta catalyst

Sang Jun Park [a], Inkwon Bae [a], In-Sik Nam [a,*], Byong K. Cho [a], Seong Moon Jung [b], Ju-Hyung Lee [b]

[a] School of Environmental Science and Engineering/Department of Chemical Engineering, Pohang University of Science and Technology (POSTECH), Pohang, Republic of Korea
[b] Hausys R&D, LG Hausys Ltd., Research Park, Daejeon, Republic of Korea

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ABSTRACT

The role of catalyst support in the complete oxidation of HCHO has been investigated over the metal oxide- and zeolite-supported Pd catalysts. The 0.25Pd/Beta catalyst exhibited the highest intrinsic activity for the complete oxidation of HCHO among other monometallic catalysts, mainly due to the high HCHO adsorption capacity of Beta zeolite support and the fast surface reaction for HCHO oxidation on Pd as determined by TPD and TPSR studies, respectively. Formate and dioxymethylene have been identified as major reaction intermediates by an in situ FTIR study. These reaction intermediates are the most abundant surface species on the Pd/Beta catalyst during HCHO oxidation, so their oxidation is the rate determining step of the complete oxidation of HCHO. When Mn was incorporated into the 0.25Pd/Beta catalyst, the HCHO oxidation activity was further improved, especially in the low temperature region; HCHO was completely oxidized to CO_2 over the 0.25Pd/20Mn/Beta catalyst at 40 °C and 50,000 h^{-1}. The enhanced oxidation activity of the 0.25Pd/20Mn/Beta catalyst could be understood by a kinetic synergism between MnO_x and Pd for the oxidation of HCHO. Oxygen adsorbs on and diffuses through MnO_x along an oxygen concentration gradient to Pd, while Pd consumes oxygen via HCHO oxidation to create the oxygen concentration gradient in MnO_x on the surface of the Beta zeolite. A possible reaction pathway has been proposed that could elucidate the enhanced HCHO oxidation activity over the bimetallic 0.25Pd/20Mn/Beta catalyst by the extended Mars–van Krevelen mechanism involving direct and indirect surface reactions over the bimetallic Pd–MnO_x catalyst system.

1. Introduction

The sick house syndrome has become a critical issue in finishing a new house due to the increasing public health concern on hazardous indoor pollutants [1–4]. Volatile organic compounds (VOCs) emitted from finishing paints, building materials and new furniture for the interior design of a house are the main contributors to indoor air pollutants, particularly in newly-built houses and apartments [5–7]. Among the VOCs, formaldehyde (HCHO) has been recognized as one of the most harmful VOCs in a new house, as it has been used widely by the construction industry to manufacture composite wood products and other household items. Harmful health effects of HCHO include eye, nose and throat irritation, skin rash and severe allergic reactions, and it may also cause cancer [8]. Recently, the indoor air quality standard was established to regulate the emission of HCHO, even in a new house during a certain period of time after the completion of construction [9]. Over the past decade, the removal of HCHO has been investigated in three ways [10–14]: by adsorption, photocatalysis and catalytic oxidation. The most effective method of removing HCHO is the catalytic oxidation of HCHO to CO_2 and H_2O even at room temperature [1,12–15].

Supported noble metal catalysts show high removal activity of HCHO even at room temperature, and their activity strongly depends on the catalyst supports and noble metals employed [1,7,14]. It has been reported that Pt/TiO_2 and Pt/Mn–CeO_2 catalysts completely oxidized HCHO to CO_2 and H_2O at ambient temperature [1,12], and the order of the HCHO oxidation activity of the TiO_2-supported 1 wt.% noble metal catalysts was Pt ≫ Rh > Pd > Au [1]. However, one of the major barriers for its commercialization is the amount of the noble metal employed for the HCHO oxidation – Pt and Rh in particular – due to their much higher cost than Pd. Zeolite has rarely been employed as a catalyst support for the oxidation of HCHO, although it has strong acidic and adsorption properties.

A recent IR study by Gora-Marek and Datka [16] on the interaction of HCHO molecules with CoZSM-5 suggests that HCHO molecules react with two kinds of adsorption sites on CoZSM-5: zeolitic hydroxyl sites (i.e., Si–OH–Al groups) and Co^{2+} sites. The Co^{2+} cations are more energetically favorable for HCHO adsorption, and thus HCHO molecules bond with the Co^{2+} ions more strongly

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* Corresponding author. Address: School of Environmental Science and Engineering/Department of Chemical Engineering, Pohang University of Science and Technology, San 31 Hyojadong, Pohang 790-784, Republic of Korea. Tel.: +82 54 279 2264; fax: +82 54 279 8299.

E-mail address: isnam@postech.ac.kr (I.-S. Nam).

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than with the zeolytic hydroxyl groups. Their results also illustrated that HCHO molecules are oxidized to formate species by either Co^{3+} or Co^{2+} as oxidants, while Co^{3+} and Co^{2+} are reduced to mostly to Co^{1+} and metallic Co, respectively. For effective decomposition of the formate to CO and its subsequent oxidation to CO_2, Pt has been recognized as the most effective catalyst formulation among other noble metal catalysts as reported earlier [1]. Due to the much higher cost of Pt relative to Pd, however, the recent trend of catalyst formulation has been shifting away from a Pt-based system toward a Pd-based system wherever feasible. HCHO has been recently reported as being completely oxidized over Pd (0.44 wt.%)/Al_2O_3 catalyst at 90 °C. In particular, when Mn as a promoter metal was incorporated into the Pd/Al_2O_3, the catalytic oxidation activity of HCHO was significantly enhanced up to 100% at 70 °C by the oxygen transfer from MnO_2 to the Pd sites through the interaction of Mn with Pd [3,13].

In the present study, the HCHO oxidation reaction over a variety of zeolites as the catalyst support was investigated in the presence of water using Pd as the active metal in order to develop a cost-effective HCHO removal catalytic system. Water vapor was included in the feed gas stream for all catalytic activity tests, since the moisture presence in an indoor air system may adversely affect the catalytic activity through its competitive adsorption with HCHO onto the active adsorption and/or reaction sites on the catalyst surface. For further improvement of the Pd-containing catalyst, a bimetallic catalyst has been developed by the addition of Mn as a promoter for the present catalytic system [13]. Various surface techniques including TPSR, HCHO-TPD, FTIR, H_2-TPR and XPS have been employed for the physicochemical characterization of the catalysts in order to gain deeper insight into the kinetic behavior of the catalysts during HCHO oxidation.

2. Experimental

2.1. Catalyst preparation

Zeolite-supported Pd catalysts containing 0.25 wt.% Pd were prepared by the incipient wetness impregnation method with an aqueous solution of $Pd(NO_3)_2H_2O$ using various zeolite supports including Beta (Si/Al = 150), USY (Si/Al = 90), HZSM5 (Si/Al = 27.5), HM10 (Si/Al = 5) and Zeo13X (Si/Al = 1.25). The Pd/TiO_2 (P-25 and Hombicat), /Al_2O_3 (Alfa) and /Mn–CeO_2 (molar ratio = 1:1) catalysts (each containing 0.25 wt.% Pd) were also prepared as a benchmarking catalyst for a comparative study [1,3,12]. All catalysts prepared in the present study are summarized in Table 1. After impregnation, the catalysts were dried at 110 °C overnight, and then calcined at 500 °C for 5 h under atmospheric condition. The 0.25Pd/20Mn/Beta catalyst was particularly prepared by impregnating Beta zeolite first with an aqueous solution of $Mn(NO_3)_24H_2O$ and then with an appropriate amount of the aqueous solution of $Pd(NO_3)_2H_2O$. The sample was also dried overnight in air at 110 °C followed by calcination at 500 °C for 5 h.

Table 1
Metal oxide- and zeolite-supported Pd catalysts employed in the present study.

Catalyst	Pd (wt.%)	Mn (wt.%)	Si/Al ratio	Pd dispersion (%)	Remarks
0.1Pd/Beta	0.1		150	9.1	
0.25Pd/Beta	0.25		150	10.9	
0.5Pd/Beta	0.5		150	10.3	
0.25Pd/20Mn/Beta	0.25	20	150		
20Mn/Beta		20	150		
0.25Pd/USY	0.25		90		
0.25Pd/Zeo13X	0.25		1.25		
0.25Pd/HZSM5	0.25		27.5		
0.25Pd/HM	0.25		5		
0.25Pd/TiO_2–P	0.25				Dagussa P-25
0.25Pd/TiO_2–H	0.25				Hombicat
0.25Pd/Mn–CeO_2	0.25				
0.25Pd/Al_2O_3	0.25				
0.25Pd/20Mn/Al_2O_3	0.25	20			

2.2. Activity test

Activity tests for the complete oxidation of HCHO over the catalysts were performed using a packed-bed flow reactor system. The powder type catalyst in the 20/30 mesh size for minimizing intraparticle diffusional resistances was charged into a 3/8 inch o.d. quartz tube reactor. Since the indoor atmosphere always contains a certain amount of moisture, the catalytic oxidation activity of HCHO was evaluated under a wet condition based upon its relative humidity. The standard feed gas contained 40 ppm HCHO, 20% O_2, 3% H_2O (relative humidity of 80% at 30 °C) and Ar balance. The gaseous HCHO was introduced into the feed gas stream by a bubbler containing 37% HCHO solution in water (Junsei) with Ar. To prevent the feed gas from condensing in the reactor system, all reactor lines were electrically heated to 150 °C. No decomposition of HCHO was observed over the empty reactor without catalyst. The conversion of HCHO and the formation of CO_2 were determined by an on-line FT-IR equipped with a 2 m gas-cell (Nicolet 6700, Thermo Electron Co.). The temperature difference between the top and bottom of the vertical catalyst bed was always maintained within 2 °C as measured by K-type thermocouples. The reactor space velocity defined as the ratio of the feed gas flow rate to the reactor volume occupied by catalyst was typically at 50,000 h^{-1} or 200,000 h^{-1}.

2.3. Catalyst characterization

A temperature programmed surface reaction (TPSR) study was carried out over a fixed-bed flow reactor system equipped with an on-line mass spectrometer (Pfeiffer/Balzers Quadstar QMI 422 and QME125). The catalyst (100 mg) was activated in situ by heating to 500 °C at a rate of 10 °C/min, kept for 1 h in a total flow of 100 cc/min containing 5% H_2 in Ar balance, cooled to 40 °C under flowing Ar (100 cc/min STP), and then exposed to a gas flow containing 40 ppm HCHO and 3% H_2O in Ar balance for 30 min at 40 °C. The catalysts were then purged by Ar and heated to 500 °C at 10 °C/min, again under flowing 20% O_2; the reaction products including CO_2, HCHO, and formate species were continuously monitored by the mass spectrometer (Pfeiffer/Balzers Quadstar QMI 422 and QME125).

HCHO temperature programmed desorption (TPD) was also performed in a quartz tubular fixed-bed microreactor system. The sample (100 mg) was pretreated by heating in 5% H_2 in Ar balance (100 cc/min STP) to 500 °C for 1 h, then subsequently cooled to 40 °C in Ar and exposed to a gas stream containing 40 ppm HCHO and 3% H_2O in Ar balance for 30 min. After flushing with Ar at 40 °C for 20 min to remove the physisorbed and gaseous HCHO species in the reactor system, the catalyst was heated to 500 °C at 10 °C/min under flowing Ar (100 cc/min STP) while HCHO and its cracking fragments (m/z = 29, 30 and 31) were continuously monitored by the on-line mass spectrometers (Pfeiffer/Balzers Quadstar QMI 422 and QME 125).

An FT-IR spectroscopic study was conducted using an M2000 series FTIR spectrometer (MIDAC Corp.) equipped with an in situ sample cell in the range of the IR wave numbers, 4000–400 cm^{-1} at a resolution of 4 cm^{-1} (number of scans: 5). The catalyst sample (10 mg) was prepared into a self-supporting disk (13 mm dia.) and placed in the IR cell, which allowed thermal treatment of the