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Catalytic performance and characterization of $RhVO_4/SiO_2$ for hydroformylation and CO hydrogenation

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Abstract

Effect of addition of vanadium oxide (vanadia) to Rh/SiO_2 in hydroformylation of ethylene and CO hydrogenation was investigated. In the hydroformylation of ethylene, the addition of vanadia enhanced hydroformylation activity and selectivity; especially the selectivity for 1-propanol formation was drastically promoted. The promoting effect was observed more significantly on the catalyst calcined at higher temperature such as 973 K. It is found that the effect is related to the formation of the $RhVO_4$ phase, and it is suggested that the active site consists of Rh metal and partially reduced VO_x, which is formed by the reduction of $RhVO_4$. This can make the interaction between Rh and VO_x more intimate. This catalyst was also effective for the alcohol formation in CO hydrogenation. Based on the catalyst characterization by means of the adsorption measurements of H_2 and CO, H_2–D_2 exchange rate under the presence of CO, temperature-programmed desorption (TPD) of CO, temperature-programmed reduction (TPR) with H_2 and temperature-programmed surface reaction (TPSR) of adsorbed CO with H_2, it is suggested that the sites for H_2 activation, which cannot be inhibited by the presence of CO, play an important role in the promotion of alcohol formation in hydroformylation and CO hydrogenation.

Keywords: Hydroformylation; Ethylene; 1-Propanol; $RhVO_4$; SMOI; Rh–VO_x interaction

1. Introduction

Hydroformylation is one of important industrial processes for producing oxygen-containing compounds (especially aldehyde) from olefin. Therefore, the catalysts for the gas phase [1–3] and liquid phase [4–7] hydroformylation have been developed. It is well known that Rh is active species for hydroformylation reaction. Especially the additive effect of various components over heterogeneous Rh catalysts has been investigated in order to enhance the catalytic activity and selectivity [1,8–15]. In hydroformylation reaction, the insertion of CO to an alkyl group is an important elementary step. In addition, it has been reported that Rh is an effective species for C2 oxygenates formation in CO hydrogenation [3]. This property is related to high performance in CO insertion. There are also reports on addition of metal or metal oxide to Rh-based catalysts for CO hydrogenation [1,8,11,16–27]. In both reactions, the additives produced a significant effect on conversion and product distribution. In many cases, the interaction between Rh and additive component is important in the catalytic promotion mechanism, especially if the additive can be located near Rh site in an atomic scale [20,28–30].

One method for making the intimate interaction is preparation of catalysts via mixed oxide crystallites [22–25,31,32]. Our group has found that mixed oxides such as $RhVO_4$, $RhNbO_4$ and Rh_2MnO_4 can be formed on SiO_2 support by the calcination at high temperature (973–1173 K) [22,24]. $RhVO_4$ was decomposed to highly dispersed Rh metal particles covered with partially reduced vanadia species (VO_x) by H_2 reduction above 473 K, and a strong metal–oxide (Rh–VO_x) interaction (SMOI) was induced on SiO_2 support [22,23,25].

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In this article, we investigated the performance of vanadia promoted Rh/SiO_2 (V–Rh/SiO_2) catalysts prepared via $RhVO_4$ mixed oxide in hydroformylation of olefins (ethylene and propylene) and CO hydrogenation under atmospheric pressure. In addition, from the catalyst characterization data, the mechanism of the promotion by vanadium oxide is discussed.

2. Experimental

2.1. Catalyst preparation

All catalysts were prepared by impregnating SiO_2 support (Q-100 or G-6; Fuji Silysia Chemical Ltd.) with aqueous solution of metal salts. Before the impregnation, SiO_2 was calcined in air at 1173 K for 1 h to avoid the structural change during the catalyst preparation. The BET surface areas of the SiO_2 (Q-100 and G-6) after the calcination were 38 and 535 m^2/g, respectively. Rh/SiO_2 (Q-100 and G-6) catalysts were prepared by the incipient wetness method using $RhCl_3{\cdot}3H_2O$ (N.E. Chemcat Corporation, >98%). Unless otherwise stated, the SiO_2 (Q-100) support was used. The method of preparing modified Rh catalysts (M-Rh/SiO_2, M = V, Fe, Zn, Mo, Co, Zr and Nb) was as follows: after the impregnation of SiO_2 with $RhCl_3{\cdot}3H_2O$ aqueous solution and drying at 383 K for 12 h, the modification with additive component was carried out by the subsequent impregnation using the aqueous solution of NH_4VO_3 (WAKO Pure Chemical Industries Ltd., >99.5%), $Fe(NO_3)_3{\cdot}9H_2O$ (WAKO Pure Chemical Industries Ltd., >99%), $Zn(NO_3)_2{\cdot}6H_2O$ (WAKO Pure Chemical Industries Ltd., >99%), $(NH_4)_6Mo_7O_{24}{\cdot}4H_2O$ (WAKO Pure Chemical Industries Ltd., >99%), $Co(NO_3)_2{\cdot}6H_2O$ (WAKO Pure Chemical Industries Ltd., >98%), $ZrO(NO_3)_2{\cdot}2H_2O$ (SOEKAWA CHEMICALS, >99%) and $(NH_4)_3[NbO(C_2O_4)_3]$ (CBMM International LDTA, AD-382). After the catalysts were dried at 383 K for 12 h again, they were calcined in air at 573–973 K for 3 h. The loading amount of Rh was 4 wt%, and the amount of additive was adjusted to molar ratio of M/Rh = 1. V_2O_5/SiO_2 was prepared by impregnating SiO_2 (Q-100) with the aqueous solution of NH_4VO_3. After the sample was dried at 383 K for 12 h, it was calcined at 773 K for 3 h. Loading amount of vanadium was adjusted to that of V–Rh/SiO_2.

2.2. Catalyst characterization

X-ray diffraction (XRD) measurements were carried out with an X-ray diffractometer (Philips X'Pert MRD) equipped with a graphite monochromator for Cu Kα (40 kV, 20 mA) radiation. The mean particle size was calculated from the XRD line broadening measurement using Scherrer equation [31,33]. Transmission electron microscope (TEM, JEOL JEM-2010) observation was carried out for V–Rh/SiO_2 catalysts after reduction, CO hydrogenation and ethylene hydroformylation. The amounts of H_2 and CO chemisorption were measured in a conventional volumetric adsorption apparatus; detailed procedures were described elsewhere [34,35]. The amounts of the total H_2 chemisorption (H/Rh) and the irreversible CO chemisorption (CO/Rh) were measured at room temperature after H_2 reduction and evacuation at 573 K.

Temperature-programmed reduction (TPR) was carried out in a fix bed reactor equipped with a TCD detector using 5% H_2 diluted with Ar (30 ml/min). The amount of catalyst was 0.05 g, and the temperature was increased from room temperature to 1123 K at the heating rate of 10 K/min. Temperature-programmed desorption (TPD) of CO adsorbed on the catalyst was carried out in a closed circulation system equipped with a quadrupole mass spectrometer (Balzers QMS 200F). The amount of the catalyst was 0.10 g and the temperature was increased from room temperature to 773 K at the rate of 10 K/min. The catalyst was exposed to CO (7 kPa) at room temperature after reduction in H_2 (7 kPa) and evacuation at 573 K before TPD measurements.

Temperature-programmed surface reaction (TPSR) of adsorbed CO with H_2 was carried out in the fixed bed flow reactor under atmospheric pressure. The effluent gas was analyzed by FID-gas chromatograph (Shimadzu GC-14B) equipped with a methanator using a Gaschropak 54 column every 30 s. The catalyst weight was 0.1 g, and the temperature was increased from room temperature to 600 K at the heating rate of 10 K/min under the flow of 10% H_2 (total flow rate: 10 ml/min, balanced with He). The catalyst was exposed to CO (5 kPa, total flow rate 10 ml/min, balanced with He) at room temperature after H_2 reduction and purge with He at 573 K before TPSR measurements.

Fourier transform infrared spectra (FTIR) of CO adsorption was recorded at room temperature by an FTIR spectrometer (Nicolet, Magna-IR 550 spectrometer) in the transmission mode using a quartz glass IR cell with CaF_2 windows connected to the vacuum-closed circulating system. The catalyst was well mixed with the same weight of SiO_2 (fine powder, AEROSIL SiO_2 380, BET 380 m^2/g), and it was pressed into a disk of 20 mm Ø and a weight of about 0.03 g. The catalyst was exposed to CO (7 kPa) at room temperature after the reduction with 7 kPa H_2 and evacuation at 573 K. After CO adsorption, the gas was evacuated. FTIR spectra of adsorbed CO were obtained under vacuum. H_2–D_2 exchange reaction under presence of CO was carried out in the closed circulation system equipped with the quadrupole mass spectrometer. The catalyst amount was 0.5 g, and the catalyst sample was reduced in 33.3 kPa of H_2 at 573 K for Rh-based catalyst and at 1023 K for V_2O_5/SiO_2, and subsequently evacuated at the same temperature. After the temperature reached the reaction temperature, reactant gases ($P_{H_2} = P_{D_2} = P_{CO} = 20$ kPa, $P_{Ar} = 6$ kPa as internal standard gas) were introduced and they were continuously circulated during the reaction. The reaction was carried out in the range of room temperature to 353 K, and the gas phase was analyzed by the quadrupole mass spectrometer every 4.5 min.

2.3. Hydroformylation of ethylene and propylene

Ethylene hydroformylation was carried out in the fixed bed flow reactor system under atmospheric pressure. The catalyst was pretreated under hydrogen flow (30 ml/min) at 573 K for 1 h. After the reactor was cooled down to room temperature, the reactant gases for hydroformylation of ethylene ($P_{C_2H_4} = P_{CO} = P_{H_2} = 33.8$ kPa) were fed to the catalyst bed, and then