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Selective oxidation of CO in H_2-rich stream over ZSM5 zeolites supported Ru catalysts: An investigation on the role of the support and the Ru particle size

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ABSTRACT

Selective oxidation of CO in H_2-rich stream was studied over ZSM5 zeolite supported Ru catalysts and the results were compared with those obtained over Ru samples supported on alumina, silica and ceria. ZSM5 zeolite supported Ru catalysts exhibited higher yields to CO_2 than Ru samples on other supports. The SiO_2/Al_2O_3 ratio of the zeolite was found to strongly affect the performance of the Ru/ZSM5 system, the Ru sample supported on the H-ZSM5 with the highest SiO_2/Al_2O_3 ratio (280) being the most efficient towards the CO selective oxidation. The form of the zeolite (H- or Na-) had instead a lower influence. On the basis of characterization data (TEM, XPS, H_2-TPR, NH_3-TPD) it was pointed out that the performance of the Ru/ZSM5 samples are strongly dependent on the Lewis acidity of the zeolite and/or the Ru particle size, a lower number of Lewis acid sites and bigger Ru particles resulting in higher CO_2 yields.

1. Introduction

Polymer electrolyte membrane (PEM) fuel cells are currently considered among the most advanced systems for energy production starting from hydrogen [1]. For this application H_2 streams must be almost free of CO, which poisons the Pt anode catalyst [2]. The selective oxidation of CO in the presence of excess of hydrogen, known as PROX (preferential oxidation), appears a promising technology to reduce the concentration of CO in the hydrogen feed to acceptable ppm levels for PEM fuel cell [1–6], being preferred to CO methanation, which is a more hydrogen consuming reaction. In the PROX, CO oxidation ($CO + 0.5O_2 \rightarrow CO_2$) is the desired reaction, whereas H_2 oxidation ($H_2 + 0.5O_2 \rightarrow H_2O$) must be inhibited. Two other side reactions can also occur in the reaction mixture, namely methanation ($CO + 3H_2 \rightarrow CH_4 + H_2O$) and reverse water-gas shift ($CO_2 + H_2 \leftrightarrow CO + H_2O$).

Oxide supported noble metals (Pt, Rh, Ru and Au) and their alloys with a second metal have been investigated as catalysts for the PROX reaction [7–14]. In the last years copper based catalysts, mainly the CuO-CeO_2 system, have been also found highly selective for the PROX [15–17]. The role of the support on the PROX performance has been also object of several studies. For instance, a variety of metal oxides such as Al_2O_3, SiO_2, TiO_2, CeO_2, and different zeolites (A, ZSM5, Faujasite, etc.) were taken into consideration for supported Pt catalysts. In particular Pt/zeolite samples were investigated in the PROX reaction by the research group of Watanabe [18–21]. They found that Pt supported on A zeolite exhibited fairly high conversion [18,19]. A high Pt dispersion and a good stabilization of metal nanocrystallites on Pt/ZSM5 or Pt/mordenite were reported [20], resulting in a significant improvement of CO conversion and selectivity. Superior performances were obtained by using Pt–Fe/mordenite systems both as powders and honeycomb catalysts [20,21].

A lower number of articles dealt with Ru-based catalysts, even though they were reported to be more active and selective than Pt ones below 150 °C, in a temperature range where methanation and reverse water gas shift reaction do not occur [22]. The use of different Ru precursors has been reported to affect the PROX performance of catalysts, ruthenium nitrosylnitrate being the most appropriate Ru precursor when supported Ru catalysts were prepared by impregnation [23,24].

A crucial importance was also attributed to the choice of the support. Up to now, the research has been focused on Ru catalysts supported on Al_2O_3 [8,25–27], TiO_2 [27,28] and mesoporous silica [29,30]. In particular Wang et al. studied four Ru catalysts supported on MCM-41, MCM-48, SBA-15 and KIT-6. They found that

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Ru/MCM-41 was the most selective and stable system among the investigated ones, attributing this behavior to both high Ru dispersion and strong Ru-support interaction [30]. The use in the PROX of Ru/zeolite catalysts was investigated in two papers by Rosso et al. [31,32] who compared the performance of Ru/Al_2O_3 and Ru/A zeolites (3A, 4A and 5A). To our knowledge no other paper deal with the use of other Ru/zeolite systems.

On the basis of the above considerations we here report a study of the PROX reaction over Ru supported on ZSM5 zeolite, investigating in detail the effect that different silica/alumina ratios (30 and 280) and forms of the zeolite (H- or Na-) play on the performance of these catalysts towards the selective removal of CO in excess of H_2.

2. Experimental

The preparation of Ru/ZSM5 catalysts (1 wt% Ru) was carried out by incipient wet impregnation of the support with an aqueous solution of the precursor, $Ru(NO)(NO_3)_3$ from Alfa Aesar. Two H-ZSM5 (Zeolyst, ~400 $m^2 g^{-1}$), with SiO_2/Al_2O_3 ratios of 30 and 280 respectively, and two Na-ZSM5, prepared by ionic exchange with NaCl solution of the corresponding H-ZSM5 sample, were used as support. These four samples were coded as Ru/HMFI30, Ru/HMFI280, Ru/NaMFI30 and Ru/NaMFI280 respectively. Three additional Ru (1 wt%) samples supported on $\gamma-Al_2O_3$ (Alfa Aesar, 221 $m^2 g^{-1}$), SiO_2 (Grace, 306 $m^2 g^{-1}$) and CeO_2 (prepared according to ref. [33], 110 $m^2 g^{-1}$) were used as reference catalysts, being coded as Ru/Al_2O_3, Ru/SiO_2 and Ru/CeO_2 respectively.

Catalytic activity tests were carried out in the gas phase at atmospheric pressure in a continuous-flow micro-reactor filled with the catalyst (0.05-0.5 g, 80–140 mesh) diluted with an inert glass powder. The gas composition (total flow rate: 80 ml/min) was 1 vol.% of CO, 1 vol.% of O_2, the rest being H_2. Some experiments were carried out in the presence of water vapor (2 vol.%) or carbon dioxide (5 vol.%). Before activity tests, catalysts were reduced in H_2 at 350 °C. A space velocity (GHSV) of 3.92×10^{-2} $mol_{CO}\ h^{-1}\ g_{cat}{}^{-1}$ was used. The effluent gases were analyzed by an online gas chromatograph with a packed column (Carboxen 1000) and TCD. CO and O_2 conversions, selectivity (defined as the ratio of O_2 consumption for the CO oxidation over the total O_2 consumption) and CO_2 yield were calculated by the following equations:

$$\text{COconversion}(\%) = ([CO_2]_{out}/[CO]_{in}) \times 100$$

$$O_2\text{conversion}(\%) = (([O_2]_{in} - [O_2]_{out})/[O_2]_{in}) \times 100$$

$$\text{Selectivity}(\%) = (0.5 \times [CO_2]\text{out}/([O_2]_{in} - [O_2]_{out})) \times 100$$

$$CO_2\text{yield}(\%) = (\text{COconversion} \times \text{Selectivity})/100$$

Temperature programmed reduction (H_2-TPR) tests were carried out in a conventional flow apparatus with a TCD detector, at heating rate of 10 °C/min using 5 vol.% H_2 in Ar. CuO powder was used to calibrate the detector signal.

Surface area measurements were carried out using the BET nitrogen adsorption method with a Sorptomatic series 1990 (Thermo Quest). Before BET tests, samples were outgassed in N_2 at 120 °C and 1×10^{-3} Torr.

Ru particles were characterized by transmission electron microscopy using a TEM JEOL 2010 F instrument, equipped with the Gatan imaginiing filter, operating at 200 KeV. The powdered samples were ultrasonically dispersed in isopropyl alcohol and a few droplets of the suspension were deposited on a Cu grid coated by a holey carbon film. After the solvent evaporated, the specimens were introduced into the microscope column. The average metal size diameter estimated by TEM (d_{TEM}) was calculated using the following formula: $d_{TEM} = \Sigma(n_i d_i)/n_i$, where n_i is the number of Ru particles of diameter d_i. In order to obtain a good statistical particle size distribution several different areas of the grid were observed and more than 150 Ru particles measured for each sample. Before TEM measurements, samples were reduced in H_2 flowing for 1 h at 350 °C.

X-ray photoelectron spectra (XPS) of the sample powders pressed on an indium foil were measured at 45° relative to the sample stage plane with a PHI 5600 Multi Technique System which gives a good control of the electron take-off angle (base pressure of the main chamber 3×10^{-10} Torr). Spectra were excited with Al-Kα radiation and structures due to satellites were subtracted before data processing. XPS peak intensities were obtained after Shirley background removal [34,35]. Spectra calibration was achieved by fixing the C1s peak of the aliphatic C—C bond at 285.0 eV. Experimental uncertainties in binding energies lie within ±0.4 eV. Spectra deconvolution was carried out by fitting the experimental profiles with symmetrical Gaussian peaks after subtraction of the background [34]. This process involves data refinement, based on the method of the least squares fitting, carried out until there was the highest possible correlation between the experimental spectrum and the theoretical profile. The R-factor (residual or agreement factor), $R = [\Sigma(F_o - F_c)^2/\Sigma(F_o)^2]^{1/2}$, after minimization of the function $\Sigma(F_o - F_c)^2$ converged to R values ≤ 0.038. XPS was performed on sample powders after reduction under H_2 at 350 °C as in the catalytic tests.

NH_3-TPD experiments were carried out in a quartz U-shape reactor in a flow of He with a constant heating rate of 10 °C/min. The desorbed products were detected by a quadrupole mass spectrometer (Sensorlab VG Quadrupoles). Before TPD all samples were reduced in flowing H_2 for 1 h at 350 °C, heated and maintained in flowing He for 30 min at 600 °C and then cooled to 30 °C in a flow of He.

3. Results

3.1. Catalytic activity

Fig. 1 reports catalytic activity results of variously supported Ru catalysts in terms of CO conversion (Fig. 1A), O_2 conversion (Fig. 1B) and selectivity towards CO oxidation (Fig. 1C), defined as the ratio of O_2 consumption for the CO oxidation over the total O_2 consumption. On all investigated samples no methane was formed up to 140 °C, whereas at higher temperatures the CO methanation occurred only at a very small extent with formation of small amounts of methane. It must be also reminded that under the same experimental conditions no significant CO conversion was observed on bare zeolites.

Fig. 1A shows that the trend of CO conversion versus reaction temperature is similar on all investigated samples, increasing on increasing the reaction temperature, reaching a maximum and then decreasing at higher temperature. Interestingly both the highest conversion value and the temperature of this maximum is dependent on the oxide used as support. In particular zeolite supported Ru catalysts exhibited very high values of maximum CO conversion (96.2 and 88.0 on Ru/HMFI280 and Ru/HMFI30, respectively), whereas these values were much lower on Ru/CeO_2, Ru/Al_2O_3 and Ru/SiO_2 (51.7, 63.1 and 66.2, respectively). The temperature at which the maximum of CO conversion was reached showed the following order: Ru/CeO_2 (100 °C) < Ru/HMFI280 (120 °C) < Ru/HMFI30 (140 °C) = Ru/SiO_2 (140 °C) < Ru/Al_2O_3 (150 °C).

Data of O_2 conversion (Fig. 1B) point out that Ru/CeO_2 is far the most active catalyst, with 100% conversion reached at 100 °C, i.e. around 40 °C less than on Ru/HMFI280 and 60 °C less than on Ru/HMFI30, Ru/SiO_2 and Ru/Al_2O_3 samples.