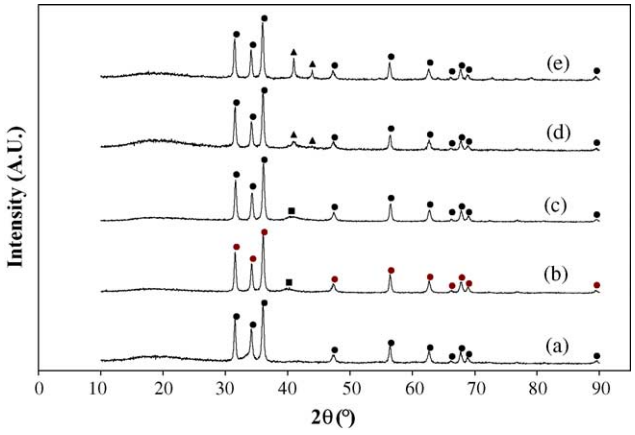

Fig. 3. X-ray diffraction patterns for 10% Pd/ZnO catalysts following reduction at different temperatures using 4% H_2 in N_2 for 1 h. The circles correspond to peaks for ZnO, squares correspond to peaks for Pd, and triangles correspond to peaks for Pd-Zn alloys. (a) Fresh catalyst, (b) reduction at room temperature, (c) reduction at 200 °C, (d) reduction at 300 °C and (e) reduction at 400 °C.

catalyst following reduction at different temperatures are illustrated in Fig. 3. The formation of Pd-Zn alloys was not observed until the reduction temperature was equal to or greater than 300 °C. Similar results were reported by Iwasa et al. [16] for a 10% Pd/ZnO catalyst. They reported the formation of significant amounts of Pd-Zn alloy on reduction at temperatures above 350 °C. Given this and based on the TPR results we concluded that pretreatment in flowing H_2 at 200 °C would be sufficient to reduce PdO in the catalysts without forming Pd-Zn alloys or reducing the ZnO.

3.2. H_2 Chemisorption

Pulsed H_2 chemisorption was used to estimate the density of metallic sites on the catalyst surfaces. Experiments with ZnO and CeO_2 indicated that the supports did not chemisorb hydrogen under the conditions employed. Measurements with adsorption temperatures between 70 and 100 °C yielded nearly identical H_2 uptakes. For example, the H_2 uptakes following reduction at 200 °C for the 2% Pd/CeO_2 catalyst at 70, 80 and 100 °C were 44.6, 42.4 and 45.5 μmol/g, respectively. Table 1 lists H_2 uptakes at 70 °C for the various catalysts following different reduction treatments. The uptake increased with increased loading for catalysts that were reduced at 200 °C for 1 h. Reducing the 2% Pd/ZnO or Pd/CeO_2 catalysts at temperatures higher than approximately 300 °C caused a significant decrease in the uptake. For the Pd/ZnO catalysts, the decrease in H_2 uptake may have been a consequence of the formation of Pd-Zn alloys. It is also likely that Pd particles on the ZnO and CeO_2 supports sintered at the higher reduction temperatures. The H_2 chemisorption and TPR results suggest the use of 200 °C reduction temperature prior to measurement of the MSR rates and selectivities.

Table 1
Hydrogen chemisorption uptakes and metal dispersions as a function of reduction temperature and Pd loading for ZnO and CeO_2 supported catalysts

Catalyst	Reduction temperature (°C)	Hydrogen uptake (μmol/g)	Pd dispersion (%)
2% Pd/ZnO	200	8 ± 1	8.6
2% Pd/ZnO	300	8 ± 2	8.6
2% Pd/ZnO	400	2.7 ± 0.4	2.9
2% Pd/ZnO	500	3.1 ± 0.4	3.3
6% Pd/ZnO	200	17 ± 2	6.2
10% Pd/ZnO	200	25 ± 4	5.4
2% Pd/CeO_2	200	45 ± 9	48
2% Pd/CeO_2	400	36 ± 5	38
2% Pd/CeO_2	550	12 ± 2	13
6% Pd/CeO_2	200	98 ± 18	34
10% Pd/CeO_2	200	116 ± 18	25

The Pd dispersions estimated using a H/Pd stoichiometry of one ranged from approximately 3% to nearly 50% (Table 1). Some of these values are similar to those reported by Iwasa et al. [13]. For a 10% Pd/ZnO catalyst, they obtained a dispersion of 2.2% while a dispersion of 36% was reported for a 10% Pd/CeO_2 catalyst following reduction in 4% H_2/N_2 at 500 °C. These H_2 chemisorption experiments were carried out at 100 °C. Pfeifer et al. [26] measured dispersions for Pd-Zn alloys in a 1% Pd/ZnO catalyst with varying reduction temperatures using both H_2 (40 °C) and CO (−73 °C) as the chemisorbates. They observed that reducing the catalyst at temperatures greater than 400 °C caused a significant decrease in the dispersion and they attributed this to sintering.

3.3. Temperature programmed desorption

Temperature programmed desorption was used primarily to characterize the oxide surfaces. In particular, CO_2 and NH_3 TPD are used to characterize the base and acid sites, respectively [27,28]. These types of sites may have participated in catalyzing MSR or reactions of the intermediates. The CO_2 and NH_3 TPD spectra for ZnO, Pd/ZnO, CeO_2, and Pd/CeO_2 are compared with their He TPD spectra in Figs. 4–7, respectively. Carbon dioxide

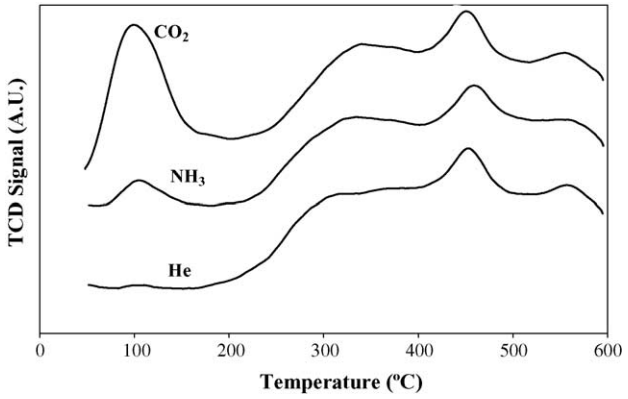

Fig. 4. Helium, NH_3 and CO_2 TPD spectra for ZnO following reduction in 5% H_2 in Ar at 200 °C for 1 h. The heating rate was 10 °C/min.