Promoting Effect of V, Mo, W, and Re on the Rate of C–O Bond Dissociation of Adsorbed CO in Methanation on Ru/Al_2O_3

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Using pulse surface reaction rate analysis coupled with an emissionless diffuse reflectance infrared spectrometer, it has been found that addition of V, Mo, W, or Re greatly increases the rate of C–O bond dissociation of adsorbed CO in methanation on Ru/Al_2O_3.

Much attention has been paid to the effect of various promoters on the activity and selectivity in Fischer–Tropsch synthesis or methanation.[1,2] It has generally been accepted that these reactions consist of various steps including the adsorption of H_2 and CO, the dissociation of the C–O bond of adsorbed CO to surface $CH_x(a)$ and $OH_y(a)$, and the hydrogenation of $CH_x(a)$ to hydrocarbons with various numbers of carbon atoms.[1,3] The rate measured by conventional methods is an overall value for these complicated processes. Investigation of the effect of various promoters on the rate of individual steps is therefore very useful. We have previously found that the rate constant for the dissociation of the C–O bond of adsorbed CO in methanation over supported Ni and Pd can be determined using pulse surface reaction rate analysis (P.S.R.A.) coupled with an emissionless diffuse reflectance (E.D.R.) i.r. spectrometer.[3] The purpose of this study was to investigate the effect of various additives on the rate of C–O bond dissociation of adsorbed CO in methanation on Ru/Al_2O_3.

Ru/Al_2O_3 (Ru loading, 0.5 wt%) was obtained from Nippon Engelhardt Ltd. Promoted catalysts were prepared by impregnating the Ru/Al_2O_3 with an aqueous solution of $Ca(OAc)_2$, $NH_4TiO(Ox)_2$ (Ox = oxalato), NH_4VO_3, $Cr(OAc)_3$, $Mn(OAc)_2$, $Fe(OH)(OAc)_2$, $Co(OAc)_2$, $Ni(OAc)_2$, $Cu(OAc)_2$, $(NH_4)_6Mo_7O_{24}$, $(NH_4)_{10}W_{12}O_{41}$, or Re_2O_7. The samples were then dried and reduced in flowing H_2 at 728 K. The promoter content was equal to that of Ru in atom %. The amount of CO adsorbed on the catalyst was measured by a conventional pulse adsorption technique at room temperature. It was found to be 14.5 µmol/g for unpromoted Ru/Al_2O_3, and 8.2, 11.0, 5.4, 7.4, 15.7, 12.9, 14.0, 11.7, 17.9, 7.9, 2.0, and 14.9 µmol/g for Ca, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Mo, W, and Re promoted catalysts, respectively. Dynamic experiments were conducted at atmospheric pressure using the P.S.R.A. apparatus coupled with the E.D.R. i.r. spectrometer as described previously.[3]

When a small amount of CO [10 µl (S.T.P.)] was injected onto the Ru/Al_2O_3 sample at 326 K in the P.S.R.A. apparatus, it was immediately adsorbed on the catalyst and exhibited an i.r. band at 2040 cm^{-1} assignable to linearly adsorbed CO. Although the wavenumber of the linear CO increased slightly with an increase in the amount of CO injected, it was almost constant (2040 cm^{-1}) for amounts of CO less than 10 µl (S.T.P.). When the reaction temperature was raised, the adsorbed CO was hydrogenated to form hydrocarbons (almost entirely CH_4); the desorption of CO was negligible under the P.S.R.A. conditions used. Analysis of the dynamic behaviour of the 2040 cm^{-1} band after CO injection with the

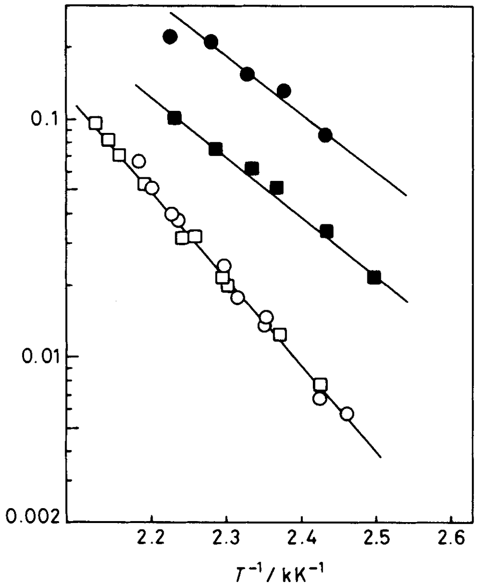

Figure 1. Rate constants (k_{CO} and k_{HC}) for the methanation of CO adsorbed on unpromoted and promoted Ru/Al_2O_3 catalysts. ○: k_{CO} for Ru/Al_2O_3, □: k_{HC} for Ru/Al_2O_3, ●: k_{CO} for V-promoted Ru/Al_2O_3, ■: k_{HC} for V-promoted Ru/Al_2O_3.

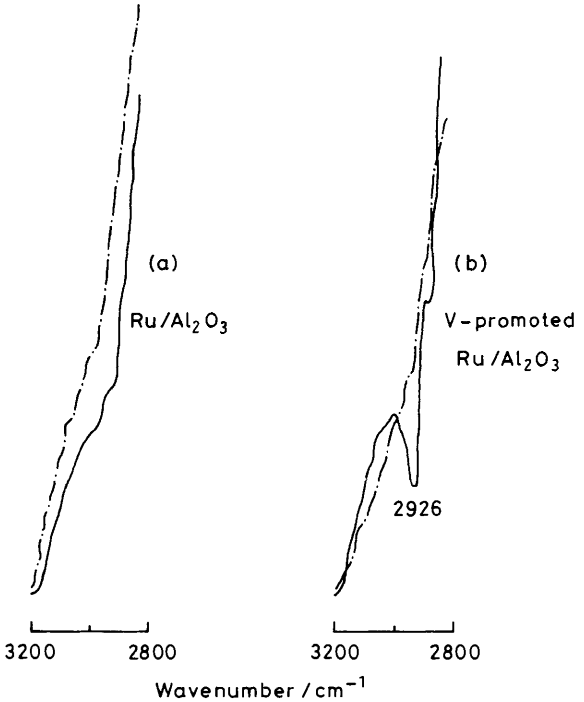

Figure 2. I.r. spectra of catalysts in the steady-state CO–H_2 reaction on (a) unpromoted and (b) V-promoted Ru/Al_2O_3 at 432 K. Partial pressure of CO = 0.018 atm, partial pressure of H_2 = 0.982 atm, total flow rate = 55 cm^3 (S.T.P.)/min. Broken line: background spectra of catalysts in the absence of CO.

Kubelka–Munk equation led to the determination of the rate constant for C–O bond dissociation per adsorbed CO molecule (k_{CO}), while the dynamics for CH_4 led to the rate constant for CH_4 formation per adsorbed CO molecule (k_{HC}). Figure 1 shows the values of k_{CO} and k_{HC} obtained for Ru/Al_2O_3 at various temperatures. k_{CO} is equal to k_{HC} at all temperatures. k_{CO} is the rate constant for the formation of CH_x(a) from CO(a), while k_{HC} is the rate constant for the formation of CH_4 from CO(a). The agreement between k_{CO} and k_{HC} therefore indicates that C–O bond dissociation of adsorbed CO is the rate determining step while the hydrogenation of CH_x(a) to CH_4 proceeds rapidly on unpromoted Ru/Al_2O_3 catalyst.

It was found that the addition of Ca, Ti, Mn, Fe, Co, or Ni slightly decreased k_{HC}, while Cu and Cr caused a more marked decrease. However, as shown in Figure 1, both k_{HC} and k_{CO} for the V-promoted catalyst are much larger than those for unpromoted Ru/Al_2O_3; for example, k_{HC} and k_{CO} for the V-promoted catalyst were 3.2 and 8.5 times larger, respectively than those for Ru/Al_2O_3 at 433 K. Similarly Mo, W, and Re increased the rate constants; k_{HC} for Mo, W, and Re promoted catalysts were 4.2, 2.9, and 2.5 times larger, respectively than k_{HC} for Ru/Al_2O_3 at 433 K, and k_{CO} for Mo, W, and Re promoted catalysts were 9.2, 5.2, and 5.9 times larger, respectively than k_{CO} for Ru/Al_2O_3 at the same temperature. These results clearly indicate the promoting effect of V, Mo, W, or Re on the rate of C–O bond dissociation of adsorbed CO in methanation on Ru/Al_2O_3. It should also be noted in Figure 1 that k_{CO} is larger than k_{HC} for the promoted catalysts, while k_{CO} is equal to k_{HC} for the unpromoted catalyst. These results suggest that there is more of the intermediate CH_x(a) species on the promoted catalyst than on Ru/Al_2O_3. This was confirmed by *in situ* i.r. measurements of the catalyst surface in a steady state reaction. For example, as shown in Figure 2, the V-promoted catalyst exhibited an i.r. absorption band at 2926 cm^{-1} which is assigned to the C–H stretching vibration of the CH_x(a) species,[4] while no noticeable band was observed in the C–H stretching region for the unpromoted catalyst.

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