Effects of Addition of Vanadium to Alumina-supported Ruthenium Catalyst on Adsorption and Hydrogenation of Carbon Monoxide

Toshiyuki ENOMOTO, Toshio OKUHARA,* and Makoto MISONO
Department of Synthetic Chemistry, Faculty of Engineering, The University of Tokyo,
Hongo, Bunkyo-ku, Tokyo 113

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The hydrogenation of carbon monoxide to hydrocarbons (Fischer-Tropsch synthesis) was studied over Ru/Al_2O_3 catalysts to which transition metals such as V, Cr, Mn, and Ag were added. Among these additives, V was most effective for the suppression of methane formation, without changing the olefin/paraffin ratio and the propagation probability. The catalytic activity decreased and the infrared band of adsorbed carbon monoxide shifted only slightly upon the V addition, showing little change in the electronic state of Ru. The particle size of the Ru remained almost unchanged, although the degree of hydrogen adsorption decreased to half. This indicates that Ru particles were partially covered by V (or an oxide of V). The effect on the turnover frequency of hydrogenation of CO was compared with those for the hydrogenation of benzene, and the hydrogenolysis of ethane. These effects were found to be very similar to an ensemble effect reported for $Ru-Cu/SiO_2$ catalysts. On the basis of these results, it is concluded that the addition of V brought about an effect similar to the ensemble effect.

In Fischer-Tropsch synthesis, it has been reported that the addition of some transition metal elements sharply changed the activity and selectivity. A Co catalyst containing a Mn oxide showed a high selectivity to ethylene.[1] Mn and V oxides were also important components for producing lower olefins in composite catalysts based on Fe.[2] In the synthesis of C_2-oxygenated compounds over Rh catalysts, transition-metal elements such as Mn, Fe, Zr, and Ti were also effective additives.[3–5] Although little is known about the structure of these catalysts, bimetallic catalysts composed of group-VIII metals and early transition metals are becoming important in CO hydrogenation.[4]

Ru is the most active catalyst among group-VIII metals for Fischer-Tropsch synthesis,[6] but there is now only a little basic research being conducted regarding the role of additives to it.[7] Mori *et al.* reported that the addition of V or Mo to Ru/Al_2O_3 increased the rate of CO dissociation.[8] We observed that the addition of V to Ru/Al_2O_3 suppressed the formation of methane.[9] In addition, Kikuchi *et al.* have reported that V_2O_3 was an effective support for Ru in the formation of lower olefins.[10]

In the present work, the effects of transition metals added to Ru/Al_2O_3 on both the hydrogenation and the adsorption of CO were studied concurrently. Catalysts were characterized by hydrogen adsorption and electron microscopy (EM), and by comparing the effect of these additives on other reactions.

Experimental

Catalysts. A Ru/Al_2O_3 catalyst was prepared by incipient-wetness impregnation of γ-Al_2O_3 with an aqueous solution of $RuCl_3$.[11] The catalysts containing other transition metals were prepared by the co-impregnation of mixed aqueous solutions of $RuCl_3$ and VCl_3, $Co(OCOCH_3)_2$, $Cr(OCOCH_3)_3$, or $Mn(OCOCH_3)_2$ onto Al_2O_3. The catalyst containing Ag was prepared by the impregnation of an aqueous solution of $AgNO_3$ with the Ru/Al_2O_3 dried at 100 °C. After the impregnation, these catalysts were dried at 100 °C for 10 h. They contained 1.6% Ru, and the atomic ratio of additive-metals to Ru was 1. In the case of V and Cr, the amounts added were varied while keeping the amount of Ru constant. Hereafter, these catalysts will be designated *e.g.*, as $Ru-V(1:5)/Al_2O_3$ and $Ru-Cr(1:1)/Al_2O_3$, where the ratio is the atomic ratio of Ru to the additive metals.

Procedure. The hydrogenation of CO was examined in a closed circulation system (200 cm^3) at 220 °C using a 1:2 mixture of CO and H_2 under a total pressure of 500 Torr (1 Torr=133.3 Pa) with a trap kept at liquid-nitrogen temperature in order to suppress any secondary reactions of products. The activities and selectivities were determined in the second run in which the reaction proceeded at a steady rate.[11] The reaction was also performed in a conventional flow reactor at 260 °C under an atmospheric pressure ($H_2/CO=2$) using 0.6—1.2 g of catalysts.[12] The products were analyzed using gas chromatography. CO and methane were analyzed using a Molecular Sieve 5A column at 25 °C. C_1–C_{12} hydrocarbons were analyzed using an FID gas chromatograph (Yanagimoto GC 2800) equipped with a VZ-10 column and a Silicone SE-30 column. The formation of methanol, ethanol, and acetaldehyde was checked using a Porapak R column and was found to be negligible.

The hydrogenolysis of ethane was carried out in the circulation system at 150 °C under 150 Torr of a 1:2 mixture of ethane and H_2. The hydrogenation of benzene was performed using a pulse method at 120 °C. 50 mg of the catalyst was loaded in a glass tubular reactor (8 mm diameter) and benzene (1 μl) was injected into H_2 stream (25 ml/min) at the inlet of the reactor. All these reactions were carried out after the catalysts were pretreated with H_2 at 450 °C for 2 h.

Other Measurements. The adsorption of CO and H_2 was measured at room temperature with a high-vacuum static system after a reduction by H_2 at 450 °C for 2 h.[11] The infrared spectra of the adsorbed CO were recorded using an FT-IR (JEOL IR-10) after the same procedure as described previously.[11] Transmission electron micrographs were obtained with a JEOL JEM 1250 electron microscope (1000 keV, final magnification: ×150000). Particles of the catalysts reduced at 450 °C were suspended in water and collected on a microgrid. More than ten micrographs of each catalyst were taken and the particle-size distributions were estimated from a total of 60—90 particles of Ru.

Results

Hydrogenation of CO. Table 1 summarizes the effects of the addition of various metals to Ru/Al_2O_3 regarding the hydrogenation of CO which was carried out in the closed-circulation system. As for the catalytic activity, no remarkable change was observed, except for the Ag which appreciably lowered the activity. The addition of V suppressed the formation of methane and enhanced the selectivity to C_2–C_4 olefins (suppression of methane formation was also found for Mn to some extent). Then, the effect of the content of V was examined in the same system, and compared with the effect of Cr. When the atomic ratio of Cr to Ru increased from 0.1 to 2, both the activity and selectivity remained almost unchanged. On the other hand, upon the addition of V (V/Ru=5 in atomic ratio), the activity decreased to about 1/5 and the selectivity of C_2–C_4 olefins increased from 42 to 64%, and methane decreased from 28 to 22% in weight. To examine the effect of the addition of V in greater detail, the reaction was carried out in the flow system at 260 °C.

Table 1. Effect of the addition of transition metals to Ru/Al_2O_3 on the hydrogenation of CO[a)]

Additives[b)]	none	V	Ag	Co	Cr	Mn
Catalytic activity[c)]	8.9	5.0	2.1	8.1	7.5	11.4
Selectivity[d)]						
C_1	28	23	37	27	27	23
C_2-C_4 olefins	42	52	46	45	41	38
C_2-C_4 paraffins	7	7	6	11	11	12
$C_{5(+)}$	23	18	11	17	21	27

a) Circulation system, 220 °C, 500 Torr ($H_2/CO=2$). b) Ru : additives = 1 : 1 in atomic ratio. c) 10^2 ml (STP)g-Ru^{-1} h^{-1}. d) Weight percentage.

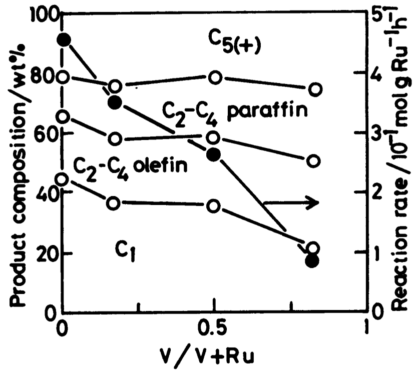

Fig. 1. Effects of the content of V in Ru–V/Al_2O_3 on catalytic activity and selectivity in the CO hydrogenation (flow system, $T=260$ °C, $P=1$ atm, $H_2/CO=2$). The conversion (based on CO) was adjusted in the range of 5—11%.

Figure 1 shows the changes of the reaction rate and selectivity as a function of the V content. The rate decreased monotonously as the V/(V+Ru) ratio increased from 0 to 0.83 (from 0 to 5 in V/Ru ratio). As for the selectivity, the fraction of methane decreased with the increase of the V content; methane was 25% in weight at V/(V+Ru)=0.83, while it was 45% over Ru/Al_2O_3. Due to the difference of the reaction conditions, the selectivity change observed here did not agree quantitatively with that obtained in the circulation system. However, the trend was similar.

The distributions of product hydrocarbons followed the Schultz-Flory plot, as shown in Fig. 2. The propagation probabilities (α) obtained from the slopes were 0.53, 0.53, and 0.57 for Ru/Al_2O_3, Ru–V(1:1)/Al_2O_3 and Ru–V(1:5)/Al_2O_3, respectively. The α values obtained from the intercepts were nearly equal to the α values from the slopes.

Figure 3 shows plots of the distribution of carbon number *vs.* the conversion for Ru/Al_2O_3 and Ru–V(1:5)/Al_2O_3. Over both catalysts, the product distribution was almost independent of the conversion up to about 30%. That is, the lower selectivity to methane observed over Ru–V(1:5)/Al_2O_3 was retained at high conversions.

In Fig. 4, the propene/propane ratio in the product is plotted against the conversion. For comparison, the results for Ru/Al_2O_3 treated with K or P are included in the figure.[9,12] Over these catalysts

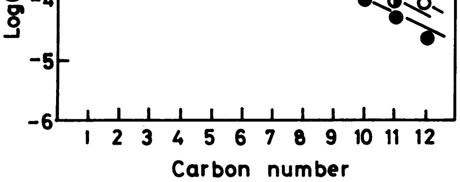

Fig. 2. Schultz-Flory plot (logarithm of (Rate·W_n/n), where W_n is weight percentage, and n is carbon number). The conversion was adjusted in the range of 5—11 %.

○: Ru/Al_2O_3, ◑: Ru–V (1 : 1)/Al_2O_3, ●: Ru–V (1 : 5)/Al_2O_3.

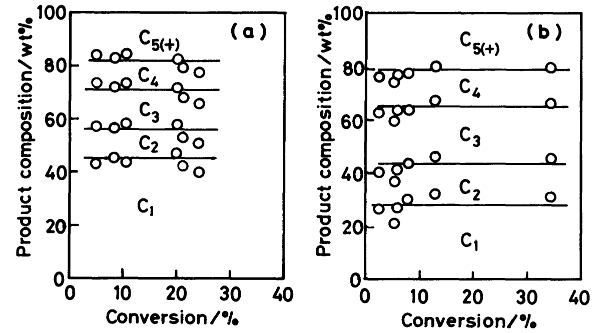

Fig. 3. Product distribution *vs.* conversion for the CO hydrogenation over Ru catalysts at 260 °C under 1 atm ($H_2/CO=2$).
(a): Ru/Al_2O_3, (b): $Ru-V(1:5)/Al_2O_3$

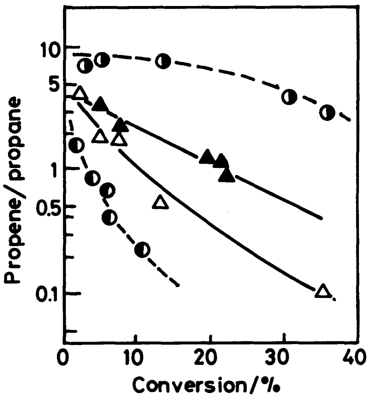

Fig. 4. Effect of conversion on the propene/propane ratio in the CO hydrogenation of CO over various Ru catalysts at 260 °C under 1 atm ($H_2/CO=2$).
▲: Ru/Al_2O_3, △: $Ru-V(1:5)/Al_2O_3$, ◑: Ru/Al_2O_3 treated with K (K; 1 wt%), ◐: Ru/Al_2O_3 treated with P (P; 0.9 wt%).

except for Ru/Al_2O_3 treated with K, the ratio greatly decreased as the conversion increased. The change in the ratio over $Ru-V(1:5)Al_2O_3$ was not very different from that over Ru/Al_2O_3, while the addition of K and P had great effects on the change in the ratio.[12]

Chemisorption of H_2 and CO. Chemisorption data of H_2 and CO are summarized in Table 2, where H/Ru and CO/Ru are respectively the number of hydrogen atoms or CO molecules adsorbed divided by the number of Ru atoms in the catalysts. The H/Ru decreased monotonously from 0.2 to 0.1 as the ratio of V/Ru increased from 0 to 5. Hereafter, the dispersion will be defined as H/Ru, by assuming that a hydrogen atom is adsorbed on a surface Ru atom at 1:1 stoichiometry.[13] The CO/Ru ratio was always greater than H/Ru, and also decreased as the amount of V increased.

Figure 5 shows the infrared spectra of CO adsorbed on Ru/Al_2O_3 and $Ru-V(1:5)/Al_2O_3$. The spectra were recorded at 25 °C after evacuation at several temperatures. In addition to the high frequency band at 2144 cm^{-1}, broad bands at about 1900—2100 cm^{-1} were observed over both catalysts. After an evacuation at above 100 °C, three resolved bands appeared at 2144, 2082, and 2017 cm^{-1} over Ru/Al_2O_3, and were quite similar to that on $Ru-V(1:5)/Al_2O_3$. The difference in the band position was less than about 8 cm^{-1}. The figures in parentheses indicate the integrated intensity of the infrared bands of adsorbed CO. The CO bands of the two catalysts decreased very similarly when the evacuation temperature was raised.

Table 2. Adsorption of CO and H_2 on $Ru-V/Al_2O_3$

V/Ru[a]	0	0.2	1.0	5.0
CO/Ru[b]	0.63	0.54	0.59	0.34
H/Ru[c]	0.20	0.16	0.16	0.10

a) Atomic ratio. b) Irreversible adsorption at 25 °C. c) Total adsorption at 25 °C.

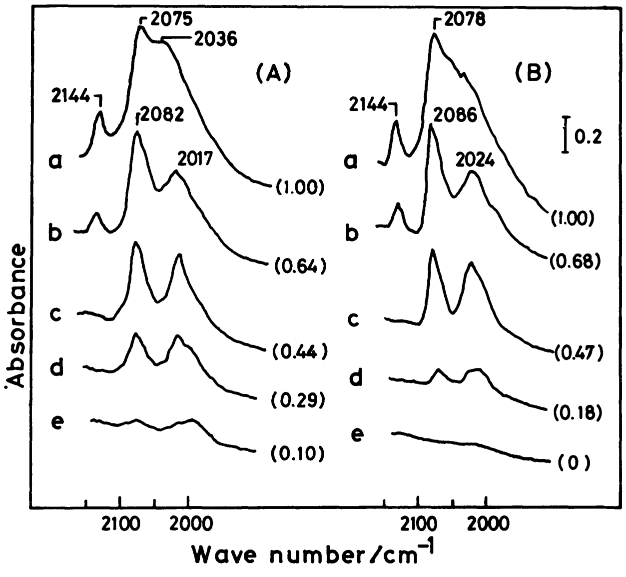

Fig. 5. Infrared spectral changes of adsorbed CO during stepwise thermal desorption on (A) Ru/Al_2O_3 and (B) $Ru-V(1:5)/Al_2O_3$. The spectra of CO were taken at 25 °C after evacuation at (a) 25 °C, (b) 100 °C, (c) 200 °C, (d) 250 °C, and (e) 300 °C. The figures in parentheses are the integrated absorbance relative to that obtained after the evacuation at 25 °C.

Figure 6 shows the particle size distributions of Ru measured by EM after the catalysts were reduced. The distribution pattern on $Ru-V(1:5)/Al_2O_3$ was almost similar to that of Ru/Al_2O_3. The average particle sizes were estimated to be 106 and 104 Å for Ru/Al_2O_3 and $Ru-V(1:5)/Al_2O_3$, respectively.

Effect of V Content on Turnover Frequency. Figure 7 shows the changes in the turnover frequencies (designated as TOF; relative to those over Ru/Al_2O_3) of hydrogenation of CO and benzene, and of hydrogenolysis of ethane as a function of the V content. The TOF values of these reactions all decreased, but the extent of the decrease was greatly

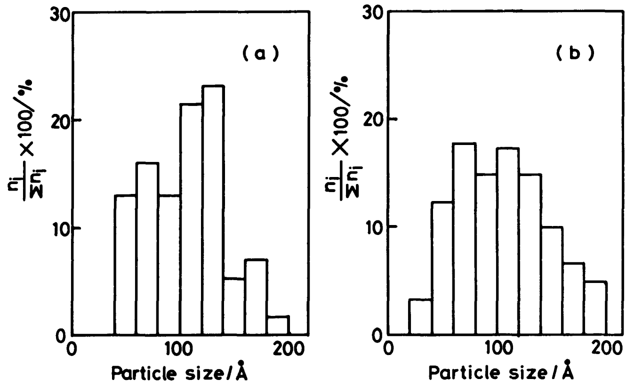

Fig. 6. Distribution of particle size of Ru on (a) Ru/Al$_2$O$_3$ and (b) Ru–V(1 : 5)/Al$_2$O$_3$. n_i is number of particles having i Å of diameter.

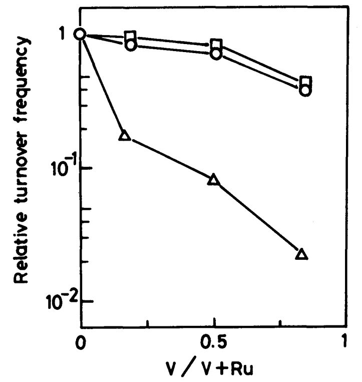

Fig. 7. Changes in TOF of various reactions over Ru–V/Al$_2$O$_3$ as a function of V content.
○: Hydrogenation of CO (260 °C, 1 atm, $H_2/CO=2$). □: Hydrogenation of benzene (120 °C, 1 atm, in a flowing H_2). △: Hydrogenolysis of ethane (150 °C, ethane; 50 Torr, H_2; 100 Torr).

different depending on the kind of reaction. When V/(Ru+V) was 0.83, the TOF for the hydrogenolysis of ethane lowered to 1/50, while the TOF of the other two reactions decreased only to 1/2.5. It was observed that the addition of Cr (Cr/(Cr+Ru)= 0—0.5) decreased only slightly the TOF for the hydrogenolysis of ethane.

Discussion

Effects of Dispersion caused by the V-addition. As shown in Fig. 6, the particle-size distribution of Ru changed only slightly upon the addition of V, while H/Ru decreased considerably (Table 2). Therefore, the reason for the decrease in H/Ru is probably that the surfaces of Ru particles (≈100 Å) were partially covered with V, and H or CO could not be adsorbed on the V-covered surface. The chemical state of V is not clear at present, but the V is probably present in a form of an oxide.

TABLE 3. EFFECTS OF ADDITIVES ON THE HYDROGENATION AND ADSORPTION OF CO OVER Ru/Al$_2$O$_3$

Additives	P	K	V
Activity	+	–	–
Selectivity			
C_1	+	–	–
O/P[a)]	–	+	(–)
α[b)]	–	+	no
CO Adsorption			
Strength	–	+	no
Amount	–	–	–
Frequency of ir band	+	–	no

+: Increase, –: Decrease, (–): Slight decrease, no: No effect. a) Olefin/paraffin ratio. b) Propagation probability.

Several reports[11,14,15)] have shown that the dispersion of Ru on Ru/Al$_2$O$_3$ greatly affects the TOF of the hydrogenation of CO. When the dispersion of Ru was controlled by altering the amount of loaded Ru, the TOF of the CO hydrogenation increased monotonously from $28\times10^{-3}\,s^{-1}$ to $117\times10^{-3}\,s^{-1}$ at 250 °C as the dispersion decreased from 0.60 to 0.23.[14)] However, in the present case, when the dispersion (H/Ru) was lowered by the addition of V (V/Ru = 5) from 0.2 to 0.1, the TOF of the CO hydrogenation decreased (Fig. 7). Thus, the decrease in the TOF after the addition of V cannot be explained by any changes in the dispersion. As for the selectivity *vs.* conversion, it was reported that the product distribution was almost independent of the dispersion of Ru in this dispersion range.[11,14,15)] Therefore, a considerable decrease in the fraction of methane caused by V (Fig. 1) also indicates that the effects of V are different from the dispersion effect reported.

Electronic Effects. It is known that the addition of electron-donating additives like alkali metals and electron-withdrawing additives like P changed the electronic state of catalytically active metals. By this effect, the activity and selectivity varied greatly,[16–18)] and those changes in the electronic state are reflected in the shift of the infrared bands of adsorbed CO.[12)] The effects are summarized in Table 3, in which the effects of V found in the present work are also included. Since no significant shift of the infrared band of adsorbed CO was observed upon the addition of V (Fig. 5), it may be concluded that the change in the electronic state of Ru was small in the case of V-addition.[19)] Mori *et al.* also reported that the infrared band position of CO was unchanged upon the addition of V to Ru/Al$_2$O$_3$.[20)] Furthermore, in contrast to K and P-addition (electronic effect), the olefin/paraffin ratio and the propagation probability little varied upon the addition of V, supporting a small electronic effect for V.

It was reported by Kikuchi *et al.* that when V_2O_3 was used as a suppurt for Ru, the activity was enhanced and the products shifted to higher hydrocarbons.[10] They assumed that the effect of V_2O_3-support was ascribed to an electron transfer from V_2O_3 to Ru (SMSI effect). This effect of V_2O_3-support on both the activity and selectivity is quite different from that of the addition of V to Ru/Al_2O_3 observed in the present study. Although the details are not clear, the difference in the from of V is a possible reason; for example, Ru is partially covered by V in the present study, while it is not covered in the case of V_2O_3-support.

Ensemble Effects. Considering a model of $Ru-V(1:5)/Al_2O_3$, in which part of Ru surface is covered by V, the changes in the surface structure of Ru seem to have affected the catalytic reactions. It is well known that the addition of an inert group-IB metal to group-VIII metals greatly changes the catalytic activities for hydrogenolysis of hydrocarbons and hydrogenation of CO.[21–23] These changes have usually been ascribed to a geometric effect due to the changes in the size of the surface metal ensemble (ensemble effect), and these reactions are regarded as structure-sensitive reactions.[21,22,23] In the case of bimetallic $Ru-Cu/SiO_2$, the addition of Cu to Ru at 1:1 atomic ratio decreased the amount of hydrogen adsorption to about half and decreased the catalytic activity.[23] But the structure-sensitivity varied depending upon the kind of reactions. The TOF of the hydrogenolysis of ethane decreased to about 1/1000, while that of the hydrogenation of CO decreased 1/50, when Cu was added to Ru at 1:1 atomic ratio, though both were reported to be structure-sensitive.[22,23] This difference in the extent of the decrease of the TOF between the two reactions was quite similar to that observed in the present work (Fig. 7). The TOF decreased to about 1/50 and 1/2.5 for the hydrogenolysis of ethane and the hydrogenation of CO by the addition of V (V/Ru=5). Therefore, the changes of the activity and selectivity with the addition of V is presumably due to an effect similar to the ensemble effect. As shown in Fig. 2, there was no effect due to the addition of V on the propagation probability. This is in contrast to the case of K and P[12] and is consistent with the fact that the propagation probability is almost independent of the particle size of Ru.[11,14]

A notable change in the selectivity caused by V was a decrease in methane formation (Fig. 1). There is a possibility that methane was produced mainly by the hydrogenolysis of higher hydrocarbons and the addition of V suppressed the hydrogenolysis, since the rate of hydrogenolysis of ethane was greatly decreased by the addition of V, as shown in Fig. 7. However, most of methane was not a secondary product, since the fraction of methane was independent of the conversion (Fig. 3). The suppression of methane formation by the addition of V is probably due to the ensemble effect, since a decrease in the methane selectivity due to the effect has also been observed for Ru-Cu/zeolite.[24] The lower methane formation reported for Fe and Co catalysts containing V or Mn,[1,2] also seems to be brought about by an effect similar to the ensemble effect.

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