Characterization of Ru/Q10 catalysts containing Zr or Mn and their activity for Fischer-Tropsch synthesis

Mohammad Nurunnabi*, Scott Q. Turn

*Hawaii Natural Energy Institute, University of Hawaii at Manoa,
1680 East-West Road, POST 109, Honolulu, Hawaii 96822, USA*

* Corresponding author (M. Nurunnabi)

E-mail address: nurunnab@hawaii.edu (M. Nurunnabi)

drmnabi@yahoo.com (M. Nurunnabi)

sturn@hawaii.edu (S. Q. Turn)

Phone number: +1-808-956-0877 (M. Nurunnabi)

+1-808-956-2346 (S. Q. Turn)

Abstract

Catalyst characterization and activity of Zr or Mn containing Ru/Q10 were investigated for Fischer–Tropsch synthesis in a stirred slurry tank reactor. The addition of Zr or Mn in Ru/Q10 enhanced CO conversion, C₅₊ selectivity and space time yield at 503 K, 5.0 MPa and 1800 h⁻¹, and the catalyst activity was highly stable during the reaction. The addition of Zr or Mn can inhibit the oxidation of Ru species and it can maintain the

active reduced Ru atoms on the catalyst surface. Ru/Q10 showed lower activity compared to Zr or Mn containing catalysts and it was deactivated due to the oxidation of active and reduced Ru species. Catalyst characterization results of BET, BJH, XRD, TPR, H₂ chemisorption, TEM, EDS and XPS were studied, it suggests that the small amount of Zr or Mn addition can increase the surface atomic concentration of Ru due to inhibit the oxidation of Ru species. ZrO₂ in Ru/Zr/Q10 and MnO in Ru/Mn/Q10 were formed on the catalyst surface, and it can be related to maintain Ru species in a reduced state, resulting to enhance catalyst activity and stability.

Keywords: Catalyst activity; Deactivation; Zr or Mn; Ru; Q10; Fischer–Tropsch synthesis

1. Introduction

Fischer-Tropsch (FT) synthesis, whose main reaction is $[\text{CO} + 2\text{H}_2 \rightarrow -(\text{CH}_2)_n + n\text{H}_2\text{O} - \Delta H]$, is a thermocatalytic conversion process that produces a distribution of hydrocarbons from synthesis gas (a mixture of CO and H₂) that can be derived from reforming natural gas or gasifying coal or biomass [1-6]. These hydrocarbons can be upgraded to produce high-quality, light hydrocarbons, gasoline, diesel, jet fuels, lubricants, and waxes. About 40 percent of crude oil and petroleum products in the United States were imported in 2012. In use, the imported oils produce oxides of sulphur, oxides of nitrogen and particulate matter (Source: U.S. Energy Information Administration. Monthly Energy Review, April 2013). Energy programs in the United States, Japan and Europe support the development of FT processes to advance energy policies and reduce green house gas

emissions. FT fuels can reduce the net emission of CO₂ as well as oxides of sulphur and nitrogen; the latter are EPA (Environmental Protection Agency) criteria atmospheric pollutants. FT diesel has a very high cetane number and very low sulphur and aromatic content. These qualities significantly reduce exhaust gas pollutant emissions, thereby benefiting the environment. FT fuels are compatible with existing fuel distribution infrastructures, and with current and envisaged-future engine and exhaust gas after-treatment technologies.

FT synthesis is exothermic and a stirred slurry tank reactor is an effective method of enhancing mixing and heat transfer from the catalyst. Ru is a very active FT catalyst, and at low temperature (~500 K) it is more active than Co, Fe, Ni, Pt, Pd, Rh and Re [7-13]. Higher CO conversion, hydrocarbon productivities, and carbon chain growth probabilities, and lower deactivation rates and CH₄ and CO₂ selectivities can be achieved with Ru-based catalysts [14-19]. Deactivation of FT catalysts due to wax deposition onto the catalyst surface is a major problem. Ru-based catalysts can be inhibited the catalyst deactivation, and it can be performed as high activity and selectivity for the production of liquid fuels. In this case, heavy hydrocarbons such as wax can be decomposed on the catalyst surface in situ to produce diesel fuels, and the lifetime of catalysts can be significantly extended.

Al₂O₃ and SiO₂ are attractive supports for FT catalyst, and SiO₂ is more promising for Ru catalyst due to low cost and availability. Catalyst activity depends on the properties of the support, and the mesoporous SiO₂ support with 10 nm pore diameter and a particle size range from 0.075–0.15 μm was selected for the impregnation methods described previously [20]. This article reports the results of an investigation of the catalytic activity of Ru/Q10 catalysts containing Zr or Mn for FT synthesis in a stirred slurry tank reactor under pressurized conditions. Small amounts of Zr or Mn added to Ru/Q10 produced high

and stable catalytic activity, whereas Ru/Q10 was deactivated. Catalyst characteristics and behavior are reported.

2. Experimental

2.1. Catalyst preparation

Ru catalyst was prepared by an impregnation method using mesoporous CARiACT silica spherical support, Q10 (Fuji Silysia Chemical Ltd., Japan). Q10 particle sizes ranged from 0.075-0.150 mm and have a surface area of 300 m²/g pore volume of 1.0 mL/g, and average pore diameter of 10 nm. The support was impregnated with an aqueous solution (water, CAS 7732-18-5, Fisher Scientific, HPLC Grade) of RuCl₃·nH₂O (Acros Organics, USA; 35-40% Ru, n=unknown) at a Ru to Q10 weight ratio of 5:100. After impregnation, the bulk of the water was removed by evaporation at 348 K, followed by drying at 383 K for ~12 h. The catalysts were subsequently calcined in air at 673 K for 4 h. The prepared catalysts are denoted as Ru/Q10.

The addition of Mn or Zr to Ru/Q10, denoted as Ru/Mn/Q10 or Ru/Zr/Q10, was prepared in two steps. In the first step, the Q10 support was impregnated with an aqueous solution (water, CAS 7732-18-5, Fisher Scientific, HPLC Grade) of Mn(NO₃)₂·4H₂O (Acros organics, USA; 99.9%) or ZrO(NO₃)₂·xH₂O (Acros organics, USA; 99.5%, x=6.6) at a weight ratio of Mn:Si or Zr:Si of 1:30. After impregnation, the bulk of the water was removed by evaporation at 348 K, followed by drying at 383 K for ~12 h. This intermediate product was then calcined at 873 K for 5 h. The concentration of solution was maintained to be about 10 wt%. In the second step, the intermediate product was

impregnated with Ru using a procedure identical to the reference Ru/Q10 preparation with a Ru to Q10 weight ratio of 5:100.

2.2. Catalyst characterization

Hydrogen chemisorption of the catalysts was determined using a fully automatic Quantachrome Autosorb iQ apparatus (Quantachrome Instruments, Boynton Beach, FL) at 313 K. Sample masses of 0.500 ± 0.005 g were analyzed in a Y-shaped chemisorption cell. Before H₂ adsorption, the samples were pretreated in He for 30 min at 393 K, then reduced at 673 K under H₂ flow for 2 h followed by evacuation for 2 h. After pretreatment, the samples were cooled and stabilized at 313 K and hydrogen chemisorption was measured under evacuated conditions. The measurement method was validated using a standard 2% Pt/Al₂O₃ chemisorption reference material with dispersion of $36.4 \pm 1.5\%$ and average crystallite size of 3.1 ± 0.3 nm (Catalog No. 7001, Quantachrome Instruments, Florida).

The Brunauer-Emmett-Teller (BET) surface area and the Barrett-Joyner-Halenda (BJH) pore size distribution of the catalysts were determined using an automatic Quantachrome Autosorb iQ (Quantachrome Instruments, Boynton Beach, FL) and an adsorption–desorption isotherm of N₂ at 77 K. Prior to analysis, the samples were degassed in a standard physisorption cell at 573 K for minimum 3 h under vacuum. The measurement method was validated using a certified TiO₂ reference material with BET surface area of 96.6 ± 1.7 m²/g and a desorption modal pore diameter of 8.2 ± 1.0 nm (BAM-P106, BAM Federal Institute for Materials Research and Testing, Berlin) and a non-certified standard Al₂O₃ reference material with BET surface area of 105.7 ± 1.5 m²/g and a desorption pore diameter of 9.5 ± 1.0 nm (Catalog No. 2005, Quantachrome Instruments, Florida).

X-ray diffraction (XRD) was measured after catalyst calcination and reduction by using a Rigaku MiniFlex II diffractometer (Rigaku Americas, The Woodlands, TX) with Cu K α radiation at 30 kV and 15 mA.

Using samples of 0.200 $\pm$ 0.005 g, temperature-programmed reduction (H₂-TPR) was measured in a Y-shaped TPR cell with a thermal conductivity detector (TCD) using TPRWin software (Autosorb iQ, Quantachrome Instruments, Boynton Beach, FL). The samples were automatically heated at 773 K for 30 min under high purity He gas flow of 45 ml/min to remove any adsorbed species such as CO₂, then cooled to 308 K under He flow. The TPR cell was then heated from 308 K to 1000 K at a heating rate of 20 K/min in a 45 ml/min gas flow of 5% H₂ in N₂. When the TPR analysis was completed, the system was cooled to room temperature under He flowing at 45 ml/min.

The catalyst samples, reduced by H₂ at 483 K for 3 h at 2.0 MPa, were analyzed using transmission electron microscope (TEM) (Model HT7700, Hitachi High Technologies America) operating at 100 kV. The powdered sample was distributed on a carbon-coated Formvar-coated copper grid. A range of metallic catalyst particles (45–80 nm) were examined and measured. Average particle size, d (nm), was estimated using equation (1).

$$d = \sum_i n_i d_i^3 / \sum_i n_i d_i^2 \quad (1)$$

Where n_i is the number of the particles of diameter d_i (nm).

The reduced catalysts were analyzed using field-emission scanning electron microscope (FESEM) (Hitachi S-4800) at an accelerating voltage of 30 kV. Specimens were mounted on aluminum stubs with double-stick carbon tape. Energy dispersive X-ray

spectroscopy (EDS) was used to identify the sample composition with an Oxford INCA PentaFET-x3 Si(Li) EDS detector system.

X-ray photoelectron spectroscopy (XPS) of the samples was obtained using a Kratos Axis 165 Photoelectron Spectroscopy System (Kratos Analytical, Manchester, UK) operated by the Surface Chemistry Lab in the Material Research Center at Missouri University of Science and Technology. The samples were placed on conductive carbon tape (to reduce the effects of sample charging) that was then adhered to specifically design sample holders, of either stainless steel or copper composition. The sample analysis area was 120 microns. Within the sample analysis chamber, immediate surface analysis was performed at ultra-high vacuum levels of 1.3 μ Pa or higher. A monochromatic 150 W source was used for material excitation.

2.3. Catalytic reaction

FT synthesis was carried out under pressurized conditions in a 1.0 L continuously-stirred slurry tank reactor (CSTR) (EZE Seal, Autoclave Engineers, USA) with an inner diameter of 75.5 mm and an inner height of 240 mm. A schematic flow diagram of FT synthesis is shown in Figure 1. The catalyst was loaded into the reactor and then reduced under hydrogen at 483 K and 2.0 MPa for 6 h. 2.5 g of catalyst was suspended in 110 g hexadecane as a solvent under atmospheric pressure and room temperature. The partial pressure ratio of reactants was $H_2/CO/N_2/Ar = 6/3/0.7/0.3$. The reactions were carried out at $T = 503$ K, $P = 5.0$ MPa, GHSV = 1800 h^{-1} , stirring rate = 500 rpm. The feed gas flow rate was adjusted with a mass flow controller (MFC), and the reaction temperature was monitored by thermocouples located inside and outside of the CSTR. The effluent gas was periodically analyzed with two on-line gas chromatographs (GC). One GC (Arnel Clarus

680, PerkinElmer, Shelton, CT) was equipped with an RT-Alumina bond/Na₂SO₄ capillary column (Restek Corp., Bellefonte, PA) and a flame ionization detector and analyzed for vapor phase organic compounds from methane to decane. The second GC (Arnel Clarus 580, PerkinElmer, Shelton, CT) was equipped with four HayeSep columns, two mole sieve columns, and three thermal conductivity detectors (TCD Clarus 580) and analyzed H₂, Ar, O₂, N₂, CH₄, CO, CO₂, the C₂'s and H₂S in the gas stream exiting the reactor. A hydrocarbon analysis was conducted on the liquids recovered from the reactor after each test was completed using a third GC (Autosystem, PerkinElmer) equipped with a capillary column (Rtx-1, Restek Corp.) and flame ionization detector.

2.4. Data reduction

Data collected from the experiments were used to calculate the performance indicators shown in equations (2) to (5)

$$\eta_{CO,t} = 100 \cdot \frac{\dot{m}_{CO,in} - \dot{m}_{CO,out}}{\dot{m}_{CO,in}} \quad (2)$$

$$D = 100 \cdot \frac{\eta_{CO,t_0} - \eta_{CO,t}}{\eta_{CO,t_0}} \quad (3)$$

$$S_t = 100 \cdot \left(1 - \frac{\sum_{n=1}^{n=4} \dot{m}_{C_{n,out}} \cdot n}{\dot{m}_{CO,in} \cdot \eta_{CO,t}} \right) \quad (4)$$

$$STY_t = \frac{\dot{m}_{CO,in} \cdot \eta_{CO,t} \cdot S_t \cdot M_C}{W} \quad (5)$$

Where

$\eta_{CO,t}$ (%) is the CO conversion rate at time, t ,

t (h) is time on stream or elapsed time that reactants are metered to the reactor,

$\dot{m}_{CO,in}$ (gmol/h) is the molar flow rate of CO at the reactor inlet,

$\dot{m}_{CO,out}$ (gmol/h) is the molar flow rate of CO at the reactor outlet,

D (%) is the deactivation rate,

S_t (%) is the C_{5+} selectivity at time, t ,

$\dot{m}_{Cn, out}$ (gmol/h) is the molar flow rate of gas-phase, carbon-containing species, C_n ,
at the reactor outlet,

n is the number of carbon atoms with values of 1, 2, 3, and 4,

STY_t (g/kg·h) is the space time yield at time, t , of C converted to C_{5+} hydrocarbons
per kg of catalyst per unit time,

W (kg) is the catalyst weight,

M_C (g/gmol) is the atomic weight of C.

2.5. The analysis of uncertainty

Uncertainty of measurement is the doubt that exists about the result of any measurement. All contributing uncertainties are expressed at the same confidence level, by converting them into standard uncertainties. Calculating the combined standard uncertainty is a two step process. The first step is to determine the uncertainties measured from the standard deviation, and the second step is combine the uncertainties using summation in quadrature, which is also known as root sum of the squares.

$$u_c = \sqrt{u_1^2 + u_2^2 + u_3^2} \quad (6)$$

Where

u_c is the combined standard uncertainty,

u_1, u_2, u_3 are the standard uncertainties.

Multiplying the combined standard uncertainty (u_c) by a coverage factor (k) gives a result which is called the expanded standard uncertainty (U).

$$U = ku_c \quad (7)$$

Where

U is the expanded uncertainty,

k is the coverage factor.

A particular value of coverage factor gives a particular confidence level for the expanded uncertainty. We scaled the overall uncertainty by using the coverage factor $k = 2$, to give a level of confidence of approximately 95 percent. The expanded uncertainty was determined using a coverage factor, $k = 2$ in the experimental parameters.

The expanded uncertainty values were $\pm 4\%$ for CO conversion, $\pm 6\%$ for C_{5+} selectivity, ± 10 g/kg_{cat}.h for space time yield, and $\pm 6\%$ for catalyst deactivation. These give a level of confidence of about 95%. GC's were calibrated using external custom blend standard gas mixtures (Airgas Specialty Gases, Port Allen, LA) and custom blend standard liquid mixtures (AccuStandard, Inc., New Haven, CT) of known compositions. The calibration uncertainty was 0.1% at a coverage factor $k = 2$.

For a coverage factor $k = 2$, the expanded uncertainty values were $\pm 3.0\%$ for dispersion, ± 0.6 nm for average crystallite size, ± 4 m²/g for BET surface area and ± 2.0 nm for pore diameter. For Quantachrome Autosorb iQ apparatus, the calibration uncertainty was negligible.

The expanded uncertainty of the surface atomic concentration was $\pm 0.04\%$ for EDS and $\pm 0.04\%$ for XPS measurements by a coverage factor $k = 2$, providing a level of confidence of approximately 95%.

3. Results and Discussion

3.1. Catalyst characterization

The measured surface areas ($270\text{--}290\text{ m}^2/\text{g}$), pore volumes ($1.1\text{ cm}^3/\text{g}$), and pore diameters (12.4 nm) for the three catalyst samples presented in Table 1 are quite similar, indicating that the small addition of Mn or Zr (weight ratio of Zr:Si or Mn:Si = 1:30) had no significant effects.

Figure 2 shows the XRD diffractograms of (a) Ru/Mn/Q10 after calcination, (b) Ru/Mn/Q10, (c) Ru/Zr/Q10 and (d) Ru/Q10 after reduction. The peak assigned to SiO_2 [21] was observed over all catalysts after calcination and reduction. The peak intensity of SiO_2 after catalyst reduction was stronger than that observed after calcination. The peak assigned to RuO_2 [22] was clearly observed for the Ru/Mn/Q10 sample after calcination in Fig. 2(a). As anticipated, the diffraction peak assigned to Ru metal [23] was observed in the Figs 2(b-d) samples after RuO_2 on the catalyst surface was completely reduced ($\text{RuO}_2 + 2\text{H}_2 \rightarrow \text{Ru}^0 + 2\text{H}_2\text{O}$). The main ruthenium peak occurred at $2\theta = 44^\circ$. The crystallite size of Ru was calculated to be 5–6 nm using the Scherrer equation and these sizes are presented in Table 1. Ru/Zr/Q10 in Fig. 2(c) showed stronger Ru metal peak intensity than that of Ru/Q10 (Fig. 2(d)). This indicates that there is poor interaction of Ru-Zr species and that Ru/Zr/Q10 can be reduced at lower temperature. Different behavior is shown for Ru/Mn/Q10 in Fig. 2(b), displaying a weaker Ru metal peak intensity than that of

Ru/Zr/Q10 and Ru/Q10 (Fig. 2(c,d)). This suggests that the interaction of Ru-Mn species is stronger than Ru-Zr species, and that a higher reduction temperature is needed for Ru/Mn/Q10. This phenomenon can be explained in the TPR profile.

Figure 3 shows the TPR profiles of Ru/Q10, Ru/Zr/Q10 and Ru/Mn/Q10 catalysts. One hydrogen reduction peak was present for all three catalysts, and no reduction peaks assigned to ruthenium chloride (RuCl_3) or ruthenium oxychloride (RuCl_xO_y) were observed in the profiles [24,25]. Ru/Q10 in Fig. 3(a) showed a reduction peak centered at 482 K assigned to the reduction of RuO_2 to Ru^0 ($\text{RuO}_2 + 2\text{H}_2 \rightarrow \text{Ru}^0 + 2\text{H}_2\text{O}$) [24,25]. Ru/Zr/Q10 in Fig 3(b) showed a single strong peak centered at 476 K assigned to the reduction of RuO_2 to Ru^0 . No other peaks assigned to the reduction of Zr-species were observed for this catalyst. The Zr additive catalyst was reduced at a lower temperature than Ru alone catalyst. Ru/Mn/Q10 in Fig. 3(c) showed a broader RuO_2 to Ru^0 reduction peak centered at 508 K. No other reduction peaks assigned to Mn-species were observed for this catalyst. Ru/Mn/Q10 showed a reduction peak delayed by ~ 30 K compared to Ru/Zr/Q10 and Ru/Q10. This suggests a possible interaction of Ru-Mn species forcing the RuO_2 phase to be reduced at a higher temperature and that the interaction of Ru-Mn species is stronger than the interaction of Ru-Zr species on the catalyst surface. These results also agree with XRD profiles in Fig. 2.

Figure 4 shows the TEM images and ruthenium particle size distributions of Ru/Q10, Ru/Zr/Q10 and Ru/Mn/Q10 catalysts after H_2 reduction. A significant difference of ruthenium particle sizes and numbers of particles was observed for these three catalysts. Small particles, corresponding to Ru metal dispersed over the Ru/Q10 and Ru/Zr/Q10 catalysts are apparent. Uniformly-dispersed, round Ru particles were observed on the Ru/Mn/Q10 catalyst. Average ruthenium particle sizes (d) were determined using equation (1) and are listed in Table 1 (far right column). The average particle sizes for the three

catalysts were ~ 7 nm and are consistent with those estimated from XRD and H_2 chemisorption. Surface concentration and dispersion of ruthenium from H_2 chemisorption are shown in Table 1. The surface concentration (S_{conc}) and dispersion (D_{disp}) of Ru on Ru/Q10 was $51 \text{ m}^2/\text{g}$ and 14%, respectively, and values for Ru on Ru/Zr/Q10 were very similar. Ru/Mn/Q10, however, exhibited much higher Ru concentrations and dispersions of $70 \text{ m}^2/\text{g}$ and 19%, respectively, indicating that Mn is an effective additive to enhance the number of Ru particle active sites on the catalyst surface.

Figure 5 presents the SEM images and EDS spectra of Ru/Q10, Ru/Zr/Q10 and Ru/Mn/Q10 after H_2 reduction. The EDS spectra for Ru, Mn, Zr, Cl, Si and O were obtained from the area in the rectangle shown on the SEM catalyst images. In the XRD profile (Fig. 2), the diffraction peaks assigned to Zr and Mn-species were not observed, possibly because the Zr and Mn concentrations were below the XRD limit of detection. EDS results also agree with TPR profiles in Fig. 3, as reduction peaks assigned to ruthenium chloride ($RuCl_3$) or ruthenium oxychloride ($RuCl_xO_y$) were not observed in either case. Although possessing weaker signals, the EDS analysis confirmed the presence of Zr on Ru/Zr/Q10 catalyst, Mn on Ru/Mn/Q10 catalyst, and Cl on the surface of Ru/Q10 and Ru/Zr/Q10 catalysts. The surface atomic concentrations of Ru, Mn, Zr, Cl, Si, and O and their ratios to Si are presented in Table 2. The concentrations of Ru (0.2 to 0.5%), O (89-92%), and Si (7-10%) were in relatively narrow ranges for all three catalysts. Measured concentrations of Zr on Ru/Zr/Q10, Mn on Ru/Mn/Q10, and Cl on Ru/Q10 and Ru/Zr/Q10 were all 0.1%. The ratio of Ru/Si for Ru/Q10 was 0.02, and this value was lower than the values of Ru/Zr/Q10 ($Ru/Si = 0.05$) and Ru/Mn/Q10 ($Ru/Si = 0.07$). These results are consistent with the data from H_2 chemisorption in Table 1. The ratio of Zr/Si for Ru/Zr/Q10 and Mn/Si for Ru/Mn/Q10 was 0.01. In the catalyst preparations, Zr/Si and

Mn/Si molar ratios were 1:30 (0.03:1) during impregnation and the lower values determined by EDS are therefore consistent.

Figure 6 shows the XPS survey spectra of Ru/Q10, Ru/Zr/Q10 and Ru/Mn/Q10 catalysts. The signal of Ru 3s, Ru 3p, Ru 3d, Mn 2p, Zr 3p, Zr 3d, Cl 2p, O 1s, O 2s, Si 2s and Si 2p was observed in a range of binding energy from 0–1100 eV at 80 pass energy (pe) of higher sensitivity resolution scans, indicating the presence of Ru, Mn, Zr, Cl, O and Si on the surface of catalysts. Well defined peaks assigned to Ru, O and Si are evident for all catalysts. Weaker peaks corresponding to Cl 2p, Zr 3d and Mn 2p were detected at ~197 eV, ~181 eV and ~640 eV binding energy, respectively. The surface atomic concentrations and binding energies of Ru 3p, Mn 2p, Zr 3d, Cl 2p, O 1s and Si 2p are presented in Table 3. The ratio of O/Si for all of the catalysts was ~2.5, consistent with the presence of SiO₂. The surface concentration of Ru for Ru/Q10, Ru/Zr/Q10 and Ru/Mn/Q10 catalysts was 0.9, 1.2 and 3.6%, respectively. These data are in agreement with the results of H₂ chemisorption (Table 1) and EDS analysis (Table 2), where Ru/Mn/Q10 exhibited high concentration of Ru active atoms on the catalyst surface. Moreover, the atomic concentration of Zr in Ru/Zr/Q10 and Mn in Ru/Mn/Q10 was also observed to be 0.3 and 1.7%, respectively, indicating that the presence of small amounts of Zr and Mn increases the active Ru atom concentration compared to the surface of Ru/Q10 catalyst. XPS detected trace amounts of Cl (0.3–0.5%) on the Ru/Zr/Q10 and Ru/Mn/Q10 catalysts, whereas EDS identified Cl on the Ru/Q10 and Ru/Zr/Q10 catalysts. These inconsistent results preclude interpretation of the role of Cl in increasing Ru active catalyst activity.

Figure 7 shows the Ru 3p, Zr 3d, Mn 2p, Cl 2p, O 1s and Si 2p XPS spectra of Ru/Q10, Ru/Zr/Q10 and Ru/Mn/Q10 catalysts at 20 pe resolution scans. The binding energies of elements are also listed in Table 3. For Ru 3p in Fig. 7(i), two energy peaks of Ru 3p_{3/2} and Ru 3p_{1/2} were observed over Ru/Q10, Ru/Zr/Q10 and Ru/Mn/Q10 catalysts,

and these peaks were located at a binding energy of 461.2-461.8 and 484.0 eV, respectively. The peak shape and intensity were very weak for Ru/Q10 and Ru/Zr/Q10 catalysts compared to Ru/Mn/Q10. According to the binding energy of Ru 3p_{3/2} at 461.2-461.8 eV, this peak correspond to atomic ruthenium (Ru⁰) [26,27]. Ruthenium peaks were also confirmed in XRD, TPR and EDS profiles (Figs. 2, 3 and 5). For Zr 3d in Fig. 7(ii), Ru/Zr/Q10 showed two energy peaks of Zr 3d_{5/2} and Zr 3d_{3/2} at a binding energy position of 181.4 and 183.9 eV, respectively. These peaks can be assigned to ZrO₂ [28-30]. For Mn 2p in Fig. 7(iii), Ru/Mn/Q10 showed two energy peaks of Mn 2p_{3/2} and Mn 2p_{1/2} at a binding energy position of 640.1 and 651.0 eV, respectively. These values correspond to the formation of MnO [31-34]. XRD and TPR profiles (Figs. 2 and 3) did not display peaks for ZrO₂ or MnO, perhaps due to the trace amount of Zr or Mn added. EDS (Fig. 5) showed Zr, Mn and O peaks. It is clear that the Cl 2p peak was not present in the XPS spectra of the catalysts (Fig. 7(iv)) and the surface concentration of Cl on the catalysts was negligible (Table 3). Chlorine species were also not detected by XRD and TPR. This suggests that there was no effect of chlorine on catalyst activity using ruthenium chloride precursor in aqueous solution. Si 2p presented one energy peak in Fig. 7(v) at a binding energy position of 102-103 eV. This energy position corresponds to the formation of SiO₂ [35,36]. One peak at a binding energy position of 531-532 eV was observed for O 1s in Fig. 7(vi) for all catalysts. This energy position can be assigned to the formation of SiO₂ [35,36], ZrO₂ [28-30] and MnO [31-34].

3.2. Catalyst activity

CO conversion (Eq. 2), C₅₊ selectivity (Eq. 4) and space time yield (Eq. 5) using Ru/Q10, Ru/Zr/Q10 and Ru/Mn/Q10 catalysts for FT synthesis at 503 K, 5.0 MPa and

1800 h⁻¹ are presented in Figure 8. Under these conditions, Ru/Zr/Q10 and Ru/Mn/Q10 produced consistently higher values than Ru/Q10 for all three performance indicators over the test durations and Ru/Mn/Q10 showed comparable but slightly higher values than Ru/Zr/Q10. The CO conversion was nearly constant with time on stream (TOS) for Ru/Zr/Q10 and Ru/Mn/Q10 catalysts, whereas Ru/Q10 decreased gradually toward 87% at 50 h, indicating catalyst deactivation (Eq. 3). The Zr and Mn augmented catalysts showed relatively constant performance for the 50 h test period for both C₅₊ selectivity and space time yield while Ru/Q10's performance continued to decline. This indicates that small amounts of Zr or Mn added to Ru/Q10 can prevent catalyst deactivation by maintaining the surface atomic concentration of Ru in a reduced position. Uncertainty values were $\pm 4\%$ for CO conversion, $\pm 6\%$ for C₅₊ selectivity and ± 10 g/kg_{cat}·h for space time yield for all three catalysts. Observed differences between the Ru/Q10 and both Ru/Zr/Q10 and Ru/Mn/Q10 catalysts are greater than these uncertainty values. Differences in performance between Ru/Mn/Q10 and Ru/Zr/Q10, however, were not.

Detailed results at the conclusion of the 51 hour tests are presented in Table 4 for CO conversion, CO₂ selectivity, CH₄ selectivity, C₅₊ selectivity, STY, deactivation rate, and carbon chain growth probability (α). CO conversion on Ru/Q10, Ru/Zr/Q10 and Ru/Mn/Q10 was ~88, 97 and 98%, respectively. CO₂ and CH₄ selectivity had comparable values for Ru/Q10 (7%), Ru/Zr/Q10 (4%), and Ru/Mn/Q10 (3%). The addition of Mn to Ru/Q10 improved performance by more than 100% (relative). C₅₊ selectivity on Ru/Q10, Ru/Zr/Q10 and Ru/Mn/Q10 was 85, 91 and 92%, respectively. The results of STY for Ru/Q10, Ru/Zr/Q10 and Ru/Mn/Q10 were 248, 292 and 302 g/kg_{cat}·h, respectively, and the addition of Zr or Mn produced significant improvement in catalyst performance. The catalyst deactivation rates for Ru/Zr/Q10 and Ru/Mn/Q10 catalysts were <2%, whereas the

value for Ru/Q10 was >10% at 51 TOS. Little difference was apparent for carbon chain growth probability (α), with all three catalysts having values of ~0.9.

According to the catalyst characterization, Ru/Q10, Ru/Zr/Q10 and Ru/Mn/Q10 showed similar BET surface area and porosity indicating that the trace amount of Zr and Mn added to Ru/Q10 had little effect (Table 1). Clear differences in catalytic activity and stability were demonstrated, however, by the catalysts under FT operating conditions (Fig. 8 and Table 4). XRD and TPR profiles (Figs. 2 and 3) identified Ru metal on the surface of the catalyst due to complete reduction of ruthenium oxide. Ru particle size from H_2 adsorption, XRD and TEM analyses ranged from 5 to 10 nm (Table 1). H_2 chemisorption, EDS and XPS results showed clear differences in the concentrations of ruthenium atoms between the Ru/Q10, Ru/Zr/Q10 and Ru/Mn/Q10 catalysts (Tables 1-3). From these results, Ru/Zr/Q10 and Ru/Mn/Q10 presented higher surface concentration of Ru atoms than that on Ru/Q10. This behavior can be explained by the formation of ZrO_2 and MnO. XPS results confirmed the formation of ZrO_2 in Ru/Zr/Q10 and MnO in Ru/Mn/Q10 (Fig. 7 and Table 3), and this can be related to improvement in the Ru active atoms on the catalyst surface. The addition of Zr or Mn can inhibit the oxidation of Ru species and it can maintain the active reduced Ru atoms on the surface. Therefore, Ru/Q10 deactivated due to the oxidation of active and reduced Ru species. Zr or Mn is an effective additive to Ru/Q10 to enhance the concentration of active Ru atoms on the catalyst surface, and these catalysts showed high catalytic activity and stability for FT synthesis.

4. Conclusions

Ru/Q10 catalyst showed 88% CO conversion under typical FT conditions. However, this catalyst was deactivated with time on stream with a deactivation value of 10%

measured after 51 h of reaction. The results indicate that Ru/Q10 lost catalytic activity due to the oxidation of active, reduced Ru species. Ru/Zr/Q10 and Ru/Mn/Q10 showed 10% (absolute) higher CO conversion compared to Ru/Q10. CO conversion and deactivation rate for the two catalysts were ~97% and ~2%, respectively, and STY ranged from 290 to 300 g/kg_{cat}·h. The addition of Zr or Mn inhibited the oxidation of Ru species and maintained catalyst activity and stability. Based on catalyst characterization by XRD, TPR, H₂ chemisorption, TEM, EDS and XPS, Ru/Zr/Q10 and Ru/Mn/Q10 exhibited high surface concentration of Ru active atoms compared to Ru/Q10. XPS results confirmed the formation of ZrO₂ in Ru/Zr/Q10 and MnO in Ru/Mn/Q10, and their presence can be related to increased concentrations of Ru active atoms on the catalyst surface and associated performance improvements.

Acknowledgements

This article was made possible by Grant Number N00014-10-1-0310 from the Office of Naval Research.

References

- [1] J.R. Rostrup-Nielsen, Fuels and energy for the future: The role of catalysis, *Catal. Rev. Sci. Eng.* 46 (2004) 247-270.
- [2] R.B. Anderson, *The Fischer–Tropsch synthesis*, Academic Press, Orlando, FL, 1984.
- [3] B.H. Davis, M.L. Occelli (edited), *Advances in Fischer–Tropsch synthesis, catalysts, and catalysis*, Vol. 128, CRC Press, New York, 2009.
- [4] J.R.H. Ross, A.N.J. van Keulen, M.E.S. Hegarty, K. Seshan, The catalytic conversion of natural gas to useful products, *Catal. Today* 30 (1996) 193-199.
- [5] M. Nurunnabi, Y. Mukainakano, S. Kado, T. Miyao, S. Naito, K. Okumura, K. Kunimori, K. Tomishige, Catalytic performance and characterization of Pd/Ni_{0.2}Mg_{0.8}Al₂O₄ in oxidative steam reforming of methane under atmospheric and pressurized conditions, *Appl. Catal. A: Gen.* 325 (2007) 154-162.
- [6] M. Nurunnabi, S. Kado, K. Suzuki, K.I. Fujimoto, K. Kunimori, K. Tomishige, Synergistic effect of Pd and Ni on resistance to carbon deposition over NiO-MgO solid solution supported Pd catalysts in oxidative steam reforming of methane under pressurized conditions, *Catal. Commun.* 7 (2006) 488-493.
- [7] M.E. Dry, FT catalysts, *Stud. Surf. Sci. Catal.* 152 (2004) 533-600.
- [8] M. Nurunnabi, K. Murata, K. Okabe, T. Hanaoka, T. Miyazawa, K. Sakanishi, Effects of ruthenium precursors on Ru/Mn/Al₂O₃ and Ru/Al₂O₃ catalysts for Fischer–Tropsch synthesis, *J. Jpn. Petrol. Inst.* 53 (2010) 75-82.
- [9] M. Nurunnabi, T. Hanaoka, T. Miyazawa, S. Hirata, K. Sakanishi, Fischer–Tropsch synthesis on Ru/Mn/Al₂O₃ catalyst in a BTL plant operation using woody biomass, *J. Jpn. Inst. Energy* 90 (2011) 972-976.

- [10] J.M.G. Carballo, J. Yang, A. Holmen, S. García-Rodríguez, S. Rojas, M. Ojeda, J.L.G. Fierro, Catalytic effects of ruthenium particle size on the Fischer–Tropsch synthesis, *J. Catal.* 284 (2011) 102-108.
- [11] W. Ma, G. Jacobs, R.A. Keogh, D.B. Bukur, B.H. Davis, Fischer–Tropsch synthesis: Effect of Pd, Pt, Re, and Ru noble metal promoters on the activity and selectivity of a 25% Co/Al₂O₃ catalyst, *Appl. Catal. A: Gen.* 437-438 (2012) 1-9.
- [12] Y.P. Li, T.J. Wang, C.Z. Wu, X.X. Qin, N. Tsubaki, Effect of Ru addition to Co/SiO₂/HZSM-5 catalysts on Fischer–Tropsch synthesis of gasoline-range hydrocarbons, *Catal. Commun.* 10 (2009) 1868-1874.
- [13] J.J. Rodrigues, G. Pecchi, F.A.N. Fernandes, M.G.F. Rodrigues, Ruthenium promotion of Co/SBA-15 catalysts for Fischer–Tropsch synthesis in slurry-phase reactors, *J. Nat. Gas Chem.* 21 (2012) 722-728.
- [14] C.N. Hamelinck, A.P.C. Faaij, H. den Uil, H. Boerrigter, Production of FT transportation fuels from biomass; technical options, process analysis and optimisation, and development potential, *Energy* 29 (2004) 1743-1771.
- [15] G.P. van der Laan, A.A.C.M. Beenackers, Kinetics and selectivity of the Fischer–Tropsch synthesis: A literature review, *Catal. Rev. Sci. Eng.* 41 (1999) 255-318.
- [16] J.P. Hindermann, G.J. Hutchings, A. Kiennemann, Mechanistic aspects of the formation of hydrocarbons and alcohols from CO hydrogenation, *Catal. Rev. Sci. Eng.* 35 (1993) 1-127.
- [17] M. Claeys, E. van Steen, On the effect of water during Fischer–Tropsch synthesis with a ruthenium catalyst, *Catal. Today* 71 (2002) 419-427.
- [18] E. Iglesia, S.C. Reyes, R.J. Madon, S.L. Soled, Selectivity control and catalyst design in the Fischer-Tropsch synthesis: sites, pellets, and reactors, *Adv. Catal.* 39 (1993) 221-302.

- [19] J. Kang, S. Zhang, Q. Zhang, Y. Wang, Ruthenium nanoparticles supported on carbon nanotubes as efficient catalysts for selective conversion of synthesis gas to diesel fuel, *Ang. Chem. Int. Ed.* 48 (2009) 2565-2568.
- [20] M. Nurunnabi, S. Turn, Pore size effects on Ru/SiO₂ catalysts with Mn and Zr promoters for Fischer-Tropsch synthesis, *Fuel Process. Technol.* 130 (2015) 155-164.
- [21] International Centre for Diffraction Data (ICDD), 01-071-3839.
- [22] International Centre for Diffraction Data (ICDD), 00-021-1172.
- [23] International Centre for Diffraction Data (ICDD), 00-001-1256.
- [24] V. Mazziere, F. Coloma-Pascual, A. Arcoya, P.C. L'Argentiere, N.S. Figoli, XPS, FTIR and TPR characterization of Ru/Al₂O₃ catalysts, *Appl. Surf. Sci.* 210 (2003) 222-230.
- [25] P.G.J. Koopman, A.P.G. Kieboom, H. Van Bekkum, Characterization of ruthenium catalysts as studied by temperature programmed reduction, *J. Catal.* 69 (1981) 172-179.
- [26] D. Eliche-Quesada, J.M. Mérida-Robles, E. Rodríguez-Castellón, A. Jiménez-López, Ru, Os and Ru-Os supported on mesoporous silica doped with zirconium as mild thio-tolerant catalysts in the hydrogenation and hydrogenolysis/hydrocracking of tetralin, *Appl. Catal. A: Gen.* 279 (2005) 209-221.
- [27] J.F. Moulder, W.F. Stickle, P.E. Sobol, K.D. Bomben, in: J. Chastain (Ed.), *Handbook of X-ray photoelectron spectroscopy*, Perkin-Elmer, Minneapolis, 1992.
- [28] A Lyapin, P.C.J Graat, Quantitative analysis of the X-ray photoelectron spectra of zirconium and zirconium oxide, *Surf. Sci.* 552 (2004) 160-168.
- [29] S. Ardizzone, C.L. Bianchi, Acidity, sulphur coverage and XPS analyses of ZrO₂-SO₄ powders by different procedures, *Appl. Surf. Sci.* 152 (1999) 63-69.

- [30] C. Morant, J.M. Sanz, L. Galán, L. Soriano, F. Rueda, An XPS study of the interaction of oxygen with zirconium, *Surf. Sci.* 218 (1989) 331-345.
- [31] M. Oku, K. Hirokawa, S. Ikeda, X-ray photoelectron spectroscopy of manganese-oxygen systems, *J. Electron Spectrosc. Rel. Phenom.* 7 (1975) 465-473.
- [32] M.C. Biesinger, B.P. Payne, A.P. Grosvenor, L.W.M. Lau, A.R. Gerson, R.St.C. Smart, Resolving surface chemical states in XPS analysis of first row transition metals, oxides and hydroxides: Cr, Mn, Fe, Co and Ni, *Appl. Surf. Sci.* 257 (2011) 2717-2730.
- [33] F. Morales, F.M.F. de Groot, O.L.J. Gijzeman, Ad Mens, O. Stephan, B.M. Weckhuysen, Mn promotion effects in Co/TiO₂ Fischer-Tropsch catalysts as investigated by XPS and STEM-EELS, *J. Catal.* 230 (2005) 301-308.
- [34] F. Kapteijn, A.D. van Langeveld, J.A. Moulijn, A. Andreini, M.A. Vuurman, A.M. Turek, J.M. Jehng, I.E. Wachs, Alumina-supported manganese oxide catalysts, *J. Catal.* 150 (1994) 94-104.
- [35] M. Reinikainen, M.K. Niemela, N. Kakuta, S. Suhonen, Characterisation and activity evaluation of silica supported cobalt and ruthenium catalysts, *Appl. Catal. A: Gen.* 174 (1998) 61-75.
- [36] M.R. Alexander, R.D. Short, F.R. Jones, W. Michaeli, C.J. Blomfield, A study of HMDSO/O₂ plasma deposits using a high-sensitivity and -energy resolution XPS instrument: curve fitting of the Si 2p core level, *Appl. Surf. Sci.* 137 (1999) 179-183.

Figure captions

Fig. 1. Schematic flow diagram for FT synthesis test bed. (MFC-mass flow controller, BPR-back pressure regulator, P-pressure, GC-gas chromatograph, MFM-mass flow meter)

Fig. 2. XRD patterns of (a) Ru/Mn/Q10 after calcination, and (b) Ru/Mn/Q10 after reduction, (c) Ru/Zr/Q10 after reduction, and (d) Ru/Q10 after reduction. ($\diamond$) SiO_2 , (Δ) RuO_2 , (o) Ru^0 .

Fig. 3. TPR profiles of (a) Ru/Q10, (b) Ru/Zr/Q10 and (c) Ru/Mn/Q10 at 300-1000 K.

Fig. 4. TEM images and ruthenium particle size distributions of (a) Ru/Q10, (b) Ru/Zr/Q10 and (c) Ru/Mn/Q10 after H_2 reduction at 483 K.

Fig. 5. SEM images and EDS spectra of (a) Ru/Q10, (b) Ru/Zr/Q10 and (c) Ru/Mn/Q10 after H_2 reduction at 483 K.

Fig. 6. XPS survey spectra of (a) Ru/Q10, (b) Ru/Zr/Q10 and (c) Ru/Mn/Q10 catalysts. Lens mode: hybrid, resolution: 80 pe, anode: mono (Al)(150W), step: 500 meV.

Fig. 7. Ru 3p, Zr 3d, Mn 2p, Cl 2p, O 1s and Si 2p XPS spectra of (a) Ru/Q10, (b) Ru/Zr/Q10 and (c) Ru/Mn/Q10 catalysts. Lens mode: hybrid, resolution: 20 pe, anode: mono (Al)(150W), step: 100 meV.

Fig. 8. Performance of Ru/Q10, Ru/Zr/Q10 and Ru/Mn/Q10 catalysts with (a) CO conversion, (b) C₅₊ selectivity and (c) space time yield for FT synthesis. (□) Ru/Q10, (Δ) Ru/Zr//Q10, (o) Ru/Mn/Q10. Reaction conditions: catalyst weight = 2.5 g, $T = 503$ K, $P = 5.0$ MPa, $GHSV = 1800$ h⁻¹, stirring rate=500 rpm, H₂/CO=2.

Table 1

Summary of results of BET surface area, BJH porosity, H₂ chemisorption, XRD and TEM measurements conducted on samples of Ru/Q10, Ru/Zr/Q10, and Ru/Mn/Q10.

Catalyst	Surface area	Pore volume	Pore diameter	S_{conc} ^a	D_{disp} ^b	Ru particle size (nm)		
	(m ² /g)	(cm ³ /g)	(nm)	(m ² /g)	(%)	H ₂ ^c	XRD ^d	TEM ^e
Ru/Q10	288	1.1	12.4	50.9	14.0	9.6	5.0	6.6
Ru/Zr/Q10	269	1.1	12.4	53.1	14.6	9.2	5.5	7.0
Ru/Mn/Q10	284	1.1	12.4	69.9	19.3	7.0	5.5	7.3

^a Surface concentration of Ru from H₂ chemisorption.

^b Dispersion of Ru from H₂ chemisorption.

^c Particle size obtained from H₂ chemisorption.

^d Particle size obtained from XRD.

^e Particle size obtained from TEM.

Table 2

Surface atomic concentrations and ratios of Ru catalysts using EDS

Catalyst	Surface atomic concentration (%)						Surface atomic ratio			
	Ru	Zr	Mn	Cl	O	Si	Ru/Si	Zr/Si	Mn/Si	Cl/Si
Ru/Q10	0.2	–	–	0.1	90.5	9.2	0.02	–	–	0.01
Ru/Zr/Q10	0.5	0.1	–	0.1	89.6	9.7	0.05	0.01	–	0.01
Ru/Mn/Q10	0.5	–	0.1	–	91.9	7.5	0.07	–	0.01	–

Table 3

Surface concentrations and binding energies of Ru catalysts using XPS

Catalyst	Surface atomic concentration (%)						Binding energy (eV)					
	Ru 3p	Mn 2p	Zr 3d	Cl 2p	O 1s	Si 2p	Ru 3p	Mn 2p	Zr 3d	Cl 2p	O 1s	Si 2p
Ru/Q10	0.9	–	–	–	71.5	27.6	461.8	–	–	–	532.0	102.5
Ru/Zr/Q10	1.2	–	0.3	0.3	69.1	29.1	461.2	–	181.4	195.5	530.9	101.9
Ru/Mn/Q10	3.6	1.7	–	0.5	69.8	24.4	461.3	640.1	–	197.5	531.0	102.0

Table 4

Performance of FT catalysts after 51 hours of reactor operation.

Catalyst	CO conv ^a (%)	CO ₂ sel ^a (%)	CH ₄ sel ^a (%)	C ₅₊ sel ^a (%)	STY ^b (g/kg _{cat.} ·h)	D ^c (%)	α^d
Ru/Q10	87.6	6.6	6.0	84.6	248	10.1	0.89
Ru/Zr/Q10	96.5	3.9	4.0	90.6	292	1.6	0.91
Ru/Mn/Q10	97.8	2.8	2.9	92.4	302	1.0	0.90

Reaction conditions: catalyst weight = 2.5 g, $T = 503$ K, $P = 5.0$ MPa, GHSV = 1800 h⁻¹, stirring rate = 500 rpm, H₂/CO = 2.

^a Results are shown at 51 h TOS.

^b Space time yield on CO conversion and C₅₊ selectivity at 51 h TOS.

^c Deactivation rate: (CO conv. at 7 h – CO conv. at 51 h) / (CO conv. at 7 h) × 100.

^d Carbon chain growth probability.

Fig. 1

Fig. 2

Fig. 3

Fig. 4

Fig. 5

Fig. 6

Fig. 7

Fig. 8