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Ru/MnCo₂O₄ as a catalyst for tunable synthesis of 2,5-bis(hydroxymethyl) furan or 2,5-bis(hydroxymethyl)tetrahydrofuran from hydrogenation of 5hydroxymethylfurfural

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ABSTRACT

Manganese and cobalt metals-based mixed oxide (MnCo2O4) spinels supported ruthenium (Ru) nanoparticles, Ru/MnCo2O4, is found to be an active catalyst to execute outstandingly the hydrogenation of 5-hydroxymethylfurfural (HMF) to produce two useful furan diols such as 2,5-bis(hydroxymethyl)furan (BHMF) and 2,5bis(hydroxymethyl)tetrahydrofuran (BHMTHF) in highly selective fashion without any additive. It could found that Ru/MnCo₂O₄ was able to catalyze not only the oxidation but also the reduction of HMF due to the redox properties of the MnCo₂O₄. Moreover, the characterization details responsible for the high activity of this catalyst in the hydrogenation of HMF were investigated by several spectroscopic methods. In order to maximize the products yield and HMF conversion, the effect of reaction variables such as time, temperature, pressure, and various metal oxides supported Ru nanoparticles was also investigated. Furthermore, the reusability tests exhibited that Ru/MnCo₂O₄ catalyst could be reused at several consecutive cycles, retaining almost its original activity.

Introduction

Since last few decades, the foremost commodity chemicals, fuels, and polymeric materials have been produced mostly from the non-renewable sources, and consequently, the fossil fuel sources are depleting whereas the demands of all these useful materials are increasing considerably. In these circumstances, the modern society is being forced to depend on biomass as an alternative source to produce bio-based materials. Recently, lignocellulosic biomass is known to be the most potential raw materials for the synthesis of value-added products [1-4]. Several bio-based fuels and chemicals have been successfully synthesized directly from lignocellulosic biomass as a renewable feedstock or its furan derivatives chemicals [5-14]. Among them, 5-hydroxymethylfurfural (HMF) is attracting platform chemical and thus can be used as a precursor for producing furan-based biofuels and several other valuable products. The synthesis of HMF from sugars or cellulose derived from lignocellulosic biomassis is documented well in the literature [15–18]. The availability of multifunctional groups such as aldehyde, alcohol, and furan ring makes HMF more supple and convertible into several valuable products via hydrogenation [19,20], oxidation [21-23], decarbonylation [24], and etherification [25]. Among all, hydrogenation of HMF is of great importance that leads to an useful approach for generating partly reduced (functional group reduction) or fully reduced (furan ring saturation) products. Many other useful products obtained from HMF are 5-methyl furfural (MF), 5-methyl-2-furan methanol (MFM), 2,5-dimethylfuran (DMF), and dimethyl tetrahydrofuran (DMTHF) [19]. Especially, 2,5-bis(hydroxymethyl) furan (BHMF) and 2,5-bis(hydroxymethyl)tetrahydrofuran (BHMTHF) are identified as important bio-based monomers for the preparation of polyurethanes and polyesters, and the possible polymers can be extended to 6,6-nylon by ring opening of BHMTHF to afford 1,6-hexanediol [26-31]. Meanwhile, it would be of great interest to tune the production of not only BHMF but also BHMTHF using molecular hydrogen in the same reactor. Undoubtedly, hydrogenation of HMF to produce BHMF/BHMTHF has been carried out using quite a lot of metal-based catalysts such as ruthenium (Ru), nickel (Ni), gold (Au),

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platinum (Pt), and palladium (Pd). For example, Chatterjee et al. have investigated the aqueous phase of hydrogenation of HMF using Pt/ MCM-41 catalyst under mild conditions (at 35 °C and 0.8 MPa of H₂ pressure for 2 h) wherein 98.9 % yield of BHMF could be achieved [32]. Ohyama et al. reported alumina supported gold (Au) sub-nano clusters as catalyst for hydrogenation of HMF to BHMF (96.0 % yield) at 120 °C under 6.5 MPa of H₂ pressure for 2 h [33]. Nakagawa et al. reported a new class of Ni-Pd-based bimetallic catalyst (Ni/Pd = 7) which delivered 96.0 % of BHMTHF from hydrogenation of HMF at 40 °C and 8.0 MPa of hydrogen pressure for 2 h [34,35]. However, the use of expensive Pt, Au, and Pd metal-based catalysts makes the process a hurdle to industrial application. Compared to these expensive metal-based catalysts, ruthenium (Ru) metal is thought to be less expensive. Nanosized mesoporous zirconium silica (Ru/MSN-Zr) catalyst is also known to be an active catalyst which gave 92.1 % yield of BHMF at 98.1 %conversion of HMF under mild reaction conditions (at the initial H₂ pressure of 5 bar and at 25 °C). However, the yield of BHMTHF product was quite low as only 5.2 % [36]. Alamillo and co-workers reported the hydrogenation of HMF in a biphasic system of water and 1-butanol as mixed solvent and single phase water system, which delivered maximum 81.0 % yield of BHMF using Ru/CeO2 catalyst at 130 °C and 2.8 MPa of H₂ pressure [37]. Recently, Tamura et al. reported 99.0 % yield of BHMF from the hydrogenation of HMF over Ir-ReOx/SiO2 catalyst under applied reaction conditions (at 30 °C and 0.8 MPa of hydrogen pressure for 6 h) [38]. Kumalaputri and co-workers described the hydrogenation of HMF to form a mixture of BHMF and DMF using porous metal oxide doped copper wherein 97.0 % yield of BHMF was obtained at 100 °C and 5.0 MPa of H_2 pressure after 3 h [39]. Kong et al. reported the switchable synthesis of DMF (88.5 %) and BHMTHF (96.0 %) yields from the hydrogenation of HMF over a traditional RANEY® Ni catalyst [40]. Lima et al. reported a continuous-flow process for hydrogenation of HMF to form BHMF with 92.0 % yield and BHMTHF with 98.0 %yield over RANEY®Cu and Ni-based catalysts [41]. Most recently, Fulignati et al. reported the hydrogenation of pure and crude HMF to BHMTHF using a huge amount of Ru/C catalyst (HMF/Ru = 1) wherein 88.6 % yield of BHMTHF could be found at complete conversion of HMF under the applied reaction conditions (at 140 °C and 7.0 MPa of hydrogen pressure after 60 min.) [42]. Although several examples of hydrogenation of HMF have already been reported, and in most cases, the harsh reaction conditions were needed.

We have previously reported that $Ru/MnCo_2O_4$ is a highly effective catalyst for the aerobic oxidation of HMF to selectively produce 2,5furandicarboxylic acid (FDCA) under base-free conditions where the physicochemical characteristics of $MnCo_2O_4$ used as support material were highlighted [17]. Since the $MnCo_2O_4$ is promising support and thus it has been used as electrode materials. Indeed, many previous studies have also demonstrated that Mn and Co-based bimetal species with multiple oxidation states could promote the water-oxidation and water-reduction reactions [22,43]. Being motivated by these facts, Ru/ $MnCo_2O_4$ is tested as a catalyst for the possible production of BHMF or BHMTHF from hydrogenation of HMF. In this context, we demonstrate the applicability of $Ru/MnCo_2O_4$ as a switchable catalyst for selective hydrogenation of HMF to produce either BHMF or BHMTHF depending on the reaction conditions.

Experimental

Chemicals

Commercially available manganese (II) acetate tetrahydrate cobalt (II) acetate tetrahydrate, ruthenium (III) chloride hydrate (RuCl₃.xH₂O), ammonium sulfate, ammonium bicarbonate, and sodium borohydride (NaBH₄) were purchased from Sigma-Aldrich Company. 5-hydroxymethyl-2-furfural (HMF) was received from the Shanghai Research Institute of Chemical Industry Testing Centre and used for standard calibration. 2,5-bis(hydroxymethyl)furan (BHMF, 95 %) was

purchased from U CHEM Co., LTD, South Korea. 2,5-bis(hydroxymethyl)tetrahydrofuran (BHMTHF, 98 %) were purchased from Jiangxi Yongtong Technology CO., LTD. During the preparation of MnCo₂O₄ and Ru/MnCo₂O₄ catalyst, freshly distilled water was used. Metal oxides such as cerium (IV) oxide (CeO₂, powder, < 5 µm, 99.9 % Trace metals basis), aluminum oxide (Al₂O₃, activated basic, Brockman I), silicon oxide (SiO₂), nanopowder, 10 – 20 nm particle size, and ruthenium on carbon (extent of loading: 5.0 wt%) were purchased from Sigma-Aldrich Company. Methanol was used solvent for the hydrogenation of HMF which was purchased from Samchun Pure Chemicals Company, South Korea.

Synthesis of Ru/MnCo₂O₄catalyst

MnCo₂O₄ spinels were synthesized by following the facile co-precipitation method as described in the literatures [21,22]. Images of solid MnCo₂CO₃ (pink) and MnCo₂O₄spinels (black) are provided in Fig. S1. Ru/MnCo₂O₄ catalyst was prepared by an impregnation-reduction method which is described in our previously published papers [22,23,44]. To support Ru (4.0 % by weight) on MnCo₂O₄ spinels, 20 g of MnCo₂O₄ and RuCl₃.3H₂O (1.69 g) were used. Then, aqueous solution of NaBH₄ (10 times higher than RuCl₃.3H₂O) was used as reducing agent. Ru metal% loading (the content of Ru) and the ratio of Mn: Co in manganese-cobalt microspheres were determined by EDS and ICP-AES methods, and the results are summarized in Table S1. Other single metal-based oxides such as SiO₂, Al₂O₃, and CeO₂ were loaded with ruthenium (4.0 wt%) using the same method.

Hydrogenation of HMF to BHMF/BHMTHF

Hydrogenation experiments of HMF to BHMF/BHMTHF were conducted in 100 mL of Parr reactor (Parr Instrument Company, Moline, IL, USA). For this purpose, 1.0 g (8.0 mmol) of HMF, 30 mL of methanol as a solvent, and 0.40 g of Ru-based catalyst (mole ratio of HMF/Ru = 50) was taken into the reactor and sealed. In order to eliminate the air from the reactor, H₂ gas was passed into the reactor three times. When the reactor was heated to the desired reaction temperature, the reactor was pressurized with H_2 gas. During the reaction, the pressure was maintained constantly using a gas reservoir equipped with a back-pressure regulator and a transducer. After completion of the reaction, the reactor was allowed to room temperature and depressurized. The product mixture was filtered to remove the insoluble catalyst, and the final solution was analyzed using High-Performance Liquid Chromatography (HPLC) instrument (Agilent Technologies 1200 series) equipped with UV-detector. Bio-Rad Aminex HPX-87 H pre-packed column was used as column material and dilute solution of H₂SO₄ (0.0005 M) in water was used as mobile phase. Based on the calibration curves obtained from the standard solutions of products (BHMF/ or BHMTHF), and HMF reactant, the conversion of HMF (C_{HMF},%), yield of product (BHMF/ or BHMTHF) (Y BHMF/BHMTHF,%), and the selectivity of product (BHMF/ or BHMTHF) (S_{BHMF/BHMTHF},%) were calculated using the following expressions.

$$\begin{split} C_{HMF}, & \% = \left(1 - \frac{\text{moleofHMFatparticulartime}}{\text{initialmoleofHMF}}\right) & X100 \\ Y_{BHMF/BHMTHF}, & \% = \left(\frac{\text{moleofaproduct(BHMF/orBHMTHF)}}{\text{initialmoleofHMF}}\right) & X100 \\ S_{BHMF/BHMTHF}, & \% = \left(\frac{Y_{BHMF/BHMTHF}}{C_{HMF}}\right) & X100 \end{split}$$

Instrumentation and sample analysis

The powder X-ray diffraction (XRD) patterns of the samples were established on a RIGAKU, MiniFlex X-ray diffractometer equipped with Cu-K α radiation (40 kV, 30 mA, $\lambda = 1.7902$ Å). The morphologies of samples were obtained by Scanning Electron Microscopy (SEM), JEOL (JSM-6701 F) instrument. Transmission Electron Microscopy (TEM) and High-Resolution Transmission Electron Microscopy (HRTEM) images were obtained by a JEOL (JEM-2100 F) instrument equipped with LaB6 filament and fitted with Energy Dispersive X-ray Spectrometer for elemental analysis. For TEM, the catalyst samples were dispersed in 2-propanol under sonication and then deposited on carbon-coated copper grids. After drying at ambient conditions, it was used for TEM analysis. X-Ray Photoelectron Spectroscopy (XPS) spectra were acquired by K-Alpha^{TM+} XPS spectrometer equipped with monochromatic aluminum (Al)-Ka (1486.6 eV) for X-ray source (for excitation of samples). X-Ray Photoelectron Spectroscopy (XPS) spectra were acquired by K-Alpha^{TM+} XPS spectrometer equipped with monochromatic aluminum (Al)-Ka (1486.6 eV) for X-ray source (for excitation of samples). The XPS spectra were recorded with the passenergy of 200 or 40 eV for the survey or core spectrum measurement, respectively. For XPS analysis, the samplewas mounted on a stainless steel sample holder with double adhesive carbon tape. Surface charge was compensated by a low energy electron flood gun. The peak fitting of the collected experimental data was done using Gaussian-Lorentzian functions and Shirley background subtraction and AVANTAGEsoftware was used. The binding energy (B.E.) scale was referenced by setting the C (1 s) binding energy (B.E.) of carbon to 284.6 eV. Brunauer-Emmett-Teller (BET) surface area was determined by nitrogen (N₂) adsorptiondesorption at -196 °C liquid N₂ temperature with a MICROMERITICS ASAP 2020, Tristar II analyzer. For each measurement, the sample was degassed at 250 °C for 12 h, then analyzed at -196 °C with N₂ gas at relative pressures (P/P₀) from 0.005 to 1.0 (adsorption) and 1.0 to 0.1 (desorption). The quantitative determination of different elements in solid catalysts and liquid samples (products mixture after oxidative esterification) was carried by inductively coupled plasma-atomic emission spectroscopy (ICP-AES, Thermo Scientific iCAP 6500 ICP spectrometer). Prior to ICP analysis, the samples of solid catalysts were dissolved in fresh aqua regia solution of hydrochloric acid and nitric acid (3: 1). The metal contents (amount of Ru loading) in the catalysts were also determined by Energy-Dispersive X-ray (EDX/EDS) Spectrometer Quantax 200, Bruker. The surface properties of supports and corresponding Ru nanoparticles were investigated by temperatureprogrammed desorption of ammonia (NH₃-TPD) technique. The sample (100 g) was pretreated in a flow-type fixed bed reactor at 300 °C for 3 h and cooled to 120 °Cin flow of helium (He). At this temperature, sufficient pulse of NH3 gas was injected until adsorption saturation, followed by purging He-gas with the flow of 30 mL/min for about 2 h. The temperature was then raised from 120-800 $^\circ C$ at a ramp rate 10 $^\circ C/$ min to desorb NH₃. The NH₃ desorbed was collected in a liquid N₂ trap and detected by on-line gas chromatography.

Results and discussion

Single metal oxides are often associated with distinct weakness such as low surface area, low acidic strength, and the poor reusability in a chemical reaction as a catalyst, which hampering their applications as support materials. To end this, an idea of preparing a solid mixed metal oxide of cobalt and manganese, was applied to use as a support material with ruthenium nanoparticles to enhance the acid strength, surface area, and structural properties. XRD patterns of MnCo₂O₄ and its precursor MnCo₂CO₃, prepared with a molar ratio of Mn and Co (1: 2) are represented in Fig. S2. All the diffraction patterns in MnCo₂O₄ are well in accordance with the MnCo₂O₄ (JCPDS no. 23-1237) [43,45]. The formation of MnCo₂O₄ is confirmed by the disappearance of peaks from MnCo₂CO₃ and the existence of new peaks in pattern of MnCo₂O₄ (JCPDS 11-692). Moreover, the morphologies of MnCo₂O₄ and MnCo₂CO₃ were investigated by SEM analysis. SEM images of MnCo₂O₄ showed 2.0-4.0 µm sized particles (spheres like structures) having multi-porous nature (Fig. S3a, 3b). However, the SEM images of MnCo₂CO₃ shows distinct size of particles and a smooth surface having less porosity (Fig. S3c and 3d). The size of ruthenium particles as expected in nano-sizes was further proven by TEM analysis. TEM and HR-TEM images of $Ru/MnCo_2O_4$ catalyst as represented in Fig. S3 (e) and (f) could not give any information on the size of Ru-nanoparticles. Multi-pores can further be seen clearly from a high magnification SEM image of MnCo₂O₄, which shows that several nanoparticles with a size range of 45-50 nm are aggregated (Fig. S4). Hence, both the size (~3.4 nm) and metal dispersion (39.2 %) are confirmed by CO-chemisorption studies, and the results are summarized in (Table S2). Elemental mapping images acquired during TEM analysis, as shown in Fig. S5, showed several red spots of ruthenium metal nanoparticles on a black background exhibited from MnCo₂O₄ spinels microspheres. The textural properties of MnCo2O4 spinels and Ru-based catalysts are summarized in Table S2. The specific surface area (SA) in the P/P_0 range of 0.00-0.45 and the pore volume were obtained from Brunauer-Emmett-Teller (BET) and Barrett-Joyner- Halenda (BJH) methods, respectively. As the results summarized in Table S2, the specific surface area of MnCo₂O₄ (Mn: Co = 1: 2) is 151.1 m²/g, while the specific surface area of $CoMn_2O_4$ (Mn: Co = 2: 1) is 89.5 m²/g. Pore volumes of $MnCo_2O_4$ (Mn: Co = 1: 2) and $CoMn_2O_4$ (Mn: Co = 2: 1) are 0.2977 cm³/g and 0.2978 cm³/g, respectively. After the loading of ruthenium (4.0 % by weight), as expected, the surface area of Ru/ MnCo₂O₄ catalyst decreased from 151.1 m²/g down to 135.4 m²/g. Ru/ $MnCo_2O_4$ catalyst has the pore volume (0.3082 cm³/g) which is almost similar to that of $MnCo_2O_4$ (Mn: Co = 1: 2), indicating the pore volume has little effect on the catalytic performance.

X-ray photoelectron spectroscopy (XPS) analysis of Ru/MnCo₂O₄ catalyst was further carried out in order to see the valence states of Mn, Co, O, and Ru metal, and the results are shown in Fig. 1. Mn 2p spectrum shows the two pair of doublet peaks, the first pair has a doublet made of $2p_{3/2}$ at 641.4 eV and $2p_{1/2}$ 652.9 (eV), and another pair has another doublet made of $2p_{3/2}$ at 642.9 eV and $2p_{1/2}$ at 653.9 (eV). These two pair of doublet peaks confirm the co-existence of the Mn(II) and Mn(III). Similarly, the characteristic two pair of doublet peaks, a doublet of $2p_{3/2}$ at 781.6 eV and $2p_{1/2}$ at 796.7 (eV) and another doublet $2p_{3/2}$ at ~779.9 eV and $2p_{1/2}$ at 795.1 (eV) are responsible for the co-existence of Co(II) and Co(III), respectively. The obtained results, the existence of Mn and Co with oxidation states (III/II), are similar to previous results reported by Ma and co-workers [43,46]. On the other hand, O 1s spectrum shows the presence of three different peaks (1s A-C), indicating the three oxygen groups exist in the spinel lattice structure of MnCo₂O₄. The major 1 s A peak corresponds to the metal and oxygen bonds. While two 1 s B and 1 s C could be assigned to the hydroxyl group and surface adsorbed water molecules, respectively [47]. While overlapping of $3d_{3/2}$ peak and C 1s peak appeared at around 284.6 eVdid not give clear evidence for the existence of ruthenium nanoparticles (in Ru 3d region from 278 to 300 eV). Hence, the existence of ruthenium nanoparticles was further confirmed from Ru 3p region (from 455.0-475.0 eV). As shown in the spectrum of Ru 3p, a characteristic 3p_{3/2} peak appeared at 463.0 (eV) is due to the metallic ruthenium.

Temperature programmed reduction (TPR) studies were carried out to gain an insight into the metal-support interaction and the reduction of phases in Ru-based catalysts at different temperatures, and the results are depicted in Fig. S6. Sample of Ru/Co₂O₃ catalyst having a predominant phase of cobalt as Co₂O₃ and Co₃O₄ undergoes presumably reduction to metallic cobalt in a three-stage process at temperatures ranges 130–190 °C, 200–280 °C, and 280–375 °C. The first peak is attributed to the reduction of Co₂O₃ \rightarrow Co₃O₄. In addition, the second and third peaks are assigned to Co₃O₄ \rightarrow CoO and CoO \rightarrow Co, respectively. Ehrhardt et al. reported that when cobalt precursor (cobalt nitrate) is calcined in an inert atmosphere, it produced different phases of cobalt (a mixture of Co₂O₃ and Co₃O₄). While the sample of Ru/ MnO₂ catalyst shows three-stage processes at temperatures ranges 100–160 °C, 165–245 °C, and 248–330 °C. These three peaks are



Fig. 1. XPS spectra of the Ru/MnCo₂O₄ catalyst: Mn 2p, Co 2p, O 1s, and Ru 3p regions.

assigned to $MnO_2 \rightarrow Mn_2O_3$, $Mn_2O_3 \rightarrow Mn_3O_4$, and $Mn_3O_4 \rightarrow MnO$, respectively [48]. Metallic Mn was not detected at a higher range of temperature more than 330 °C. While the sample of Ru/MnCo₂O₄ catalyst showed disparate behavior, showing all these peaks shifted towards the lower temperature compared to the transitions from the sample of Ru/Co₂O₃ and Ru/MnO₂. The peak shift towards lower temperature is attributed to a strong interaction between ruthenium metal and MnCo₂O₄ spinels microspheres used as support material. It is worth mentioning that no any additional peak was observed responsible for the reduction of Ru(III) to metallic Ru(0) because all the samples of Ru-based catalysts were already reduced at room temperature with sodium borohydride (NaBH₄) as reducing agent.

It has been reported that several products such as BHMF, BHMTHF, 5-methyl furfural (MF), 5-methyl-2-furan methanol (MFM), 2,5-dimethylfuran (DMF), and 2,5-dimethylfuran (DM-THF) are formed during hydrogenation of HMF (Scheme 1). Moreover, ring-opening products such as 2-hexanol, 1,2-hexanediol (1,2-HD), and 1,2,6-hexanetriol (1,2,6-HT) are also expected to be formed under the reduction conditions [39,49]. Therefore, we first studied compositional product changes from the hydrogenation of HMF as a function of time (from 0.5–16 h) using Ru/MnCo₂O₄ as a catalyst, and the results are depicted in Fig. 2. It is observed that HMF is rapidly transformed into BHMF through the reduction of aldehyde group in HMF in the initial stage of



Fig. 2. A plot of relative concentration of HMF, BHMF, and BHMTHF versus reaction time. Reaction conditions: HMF = 1.0 g (8.0 mmol), catalyst (Ru/ $MnCo_2O_4$)=0.02 g, HMF/Ru = 100, solvent (methanol)=30 mL, T = 80 °C, P (H₂)=6.0 MPa, Str. Speed = 600 RPM.

the reaction. The amount of BHMTHF is as low as 5.0 % even after 3 h, indicating that the ring hydrogenation of BHMF proceeds at a slower rate. On further increasing the reaction time from 3 to 16 h, the amount



Scheme 1. Hydrogenation of HMF to BHMTHF via the formation of BHMF as an intermediate.



Scheme 2. A plausible reaction mechanism for the hydrogenation of HMF to BHMTHF via the formation of BHMF (Interaction of activated hydrogen atom with reactants HMF (Left) and BHMF (Right).

of BHMF starts to decrease, giving rise to the formation of BHMTHF as the final product. Based on the time course studies, we suggest that the BHMF appears to be a sole intermediate to BHMTHF.

Based on the results, a plausible reaction mechanism for the hydrogenation of HMF is proposed and illustrated in Scheme 2. In hydrogenation of HMF, it is articulated that hydrogen (H₂) gas was first spread into the methanol. At the gas-liquid interface, H₂ is dissolved and then spread from methanol to reactant HMF. In actual practice, H₂ is not reacted directly either to the carbonyl group (aldehyde group) of HMF or a furan ring of BHMF as intermediate. But, it was absorbed on the surface of catalyst having Lewis and Brønsted acid sites producing indivisual but activated hydrogen (H) on the catalyst surface (as shown in left side of Scheme 2). Infact, activated H is more reactive than gaseous H₂. HMF is interacted with the activated H on the catalyst surface which is an irreversible reaction. Then, the BHMF product is desorbed from the surface of catalyst and is diffused into the methanol. Meanwhile, BHMF product having a furan ring is also interacted, but at slower rate, with the activated H in similar manner to form BHMTHF (as shown in right side of Scheme 2). Therefore, it could be concluded that the hydrogenation of HMF proceeds through H₂ dissolution, diffusion, adsorption on catalyst active centers to produce activated H, and the formation of BHMF as well. The aldehyde group of HMF is finally reacted with activated H available on the surface of catalyst and produce BHMTHF via the formation of BHMF.

The effect of temperature on the hydrogenation of HMF was studied by varying the reaction temperature from 80 to 120 °C and the results were presented in Fig. 3. On increasing the reaction temperature from 80 to 100 °C, the yield of BHMTHF increased from 71.6%–97.3%. Simultaneously, the conversion of HMF also increased from 77.0%–98.7% when temperature increased from 80 to 100 °C. Beyond 100 °C, it could be noticed that there were no significant effect either on the conversion of HMF or yield of BHMTHF. At 100 °C, a negligible



Fig. 3. Reaction conditions:HMF = 1.0 g (8.0 mmol), Catalyst ($Ru/MnCo_2O_4$) = 0.40 g, HMF/Ru = 50, Solvent (methanol) = 30 mL, $P(H_2)$ = 8.2 MPa, t = 16 h, Str. Speed = 600 RPM. C: Conversion and Y: Yield.



Fig. 4. Reaction conditions:HMF = 1.0 g (8.0 mmol), Catalyst (Ru/MnCo₂O₄) = 0.40 g, HMF/Ru = 50, Solvent (methanol) = 30 mL, T = 100 °C, t = 16 h, Str. Speed = 600 RPM. C: Conversion and Y: Yield.

amount (1.4 %) of BHMF was found. The effect of hydrogen pressure on hydrogenation of HMF was also investigated by varying the hydrogen pressure from 4.1 to 8.9 MPa and the results were presented in Fig. 4. When the pressure was low as 4.1 MPa, both the conversion of HMF and yield of BHMTHF were quite low as 46.8 % and 44.4 %, respectively. On increasing the pressure from 4.1 to 8.2 MPa, HMF conversion and yield of BHMTHF increased gradually. However, on further increasing hydrogen pressure more than 8.2 MPa, no significant affect on the conversion of HMF and yield of BHMTHF could be observed.

In general, the nature of the solvent plays an important role in this catalytic hydrogenation reaction. The hydrogenation of HMF can also be very dependent upon the solvents used. To this end, different kinds of polar and non-polar solvent were evaluated for the hydrogenation of HMF, and the results are presented in Fig. 5. Interestingly, methanol used as a polar solvent gave the highest yield of BHMTHF (92.2 %) at 95.2 % conversion of HMF. For BHMTHF selectivity point of view, the use of methanol is considered to be the best choice in the hydrogenation of HMF. In comparison to methanol, used another polar solvent ethanol showed only 67.5 % of BHMTHF at 72.8 % conversion of HMF. While, water known as universal solvent was also found to give somewhat higher yield of BHMTHF (80.2 %) and 92.5 % conversion of HMF, which is considered to be better than ethanol. Moreover, isopropanol (IPA) gave very poor results towards both conversion of HMF and BHMTHF yield. Other typical polar solvents such as tetrahydrofuran (THF) and methyl tert-butyl ether (MTBE) showed very poor performances for this reaction. Non-polar solvents such as hexane and pentane did not offer any improvement either in the conversion of HMF orthe yield of BHMTHF, probably due to the high hydrogen gas solubility in protic polar solvent like methanol than non-polar solvent.

The effect of catalyst amount on hydrogenation of HMF was also studied by varying the amount of $Ru/MnCo_2O_4$ catalyst from 0.10 g to 0.50 g and the results are presented in Table 1. When the $Ru/MnCo_2O_4$

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Fig. 5. Hydrogenation of HMF in different kinds of solvents using Ru/MnCo₂O₄ catalyst. Reaction conditions: HMF = 1.0 g (8.0 mmol), catalyst = Ru/MnCo₂O₄, HMF/Ru = 100, solvent = 30 mL, t = 24 h, T = 100 °C, $P(H_2)$ = 8.2 MPa, Str. Speed = 600 RPM.

Table 1Effect of catalyst amount on hydrogenation of HMF.

Entry	Catalyst, g	HMF/Ru	C _{HMF} , %	Y _{BHMTHF} , %	Y _{BHMF} , %	S _{BHMTHF} , %
1	0.10	200	38.5	36.7	1.8	95.3
2	0.20	100	70.8	68.4	2.4	96.6
3	0.40	50	98.7	97.3	1.4	98.5
4	0.50	40	100.0	98.0	2.0	98.0

Reaction conditions: HMF = 1.0 g (8.0 mmol), T = 100 °C, $P(H_2)=8.2 \text{ MPa}$, Solvent (methanol) = 30 mL, t = 16 h, Str. Speed = 600 RPM. C: Conversion, Y: Yield, and S: Selectivity.

catalyst amount was low as 0.10 g, both the conversion of HMF and yield of BHMTHF were 38.5 % and 36.7 %, respectively (Entry 1). By increasing the amount of Ru/MnCo₂O₄ catalyst from 0.10 g to 0.40 g (Entry 1–3), HMF conversion increased remarkably to 98.7 % (Entry 3) simultaneously, the yield of BHMTHF increased to 97.3 % (Entry 1–3). On further increasing the amount of Ru/MnCo₂O₄ catalyst from 0.40 g to 0.50 g, the conversion of HMF reached maximum to 1.0 % and the yield of BHMTF increased slightly to 98.0 % (Entry 4). Increased amount of Ru/MnCo₂O₄ catalyst i.e. 0.50 g, had no significant effect on the conversion of HMF and the yield of BHMTHF, therefore the amount of Ru/MnCo₂O₄ catalyst was fixed as 0.40 g for further study in hydrogenation of HMF.

A series of metal oxides, single- and bimetal-based mixed oxides, supportedruthenium catalysts were investigated in the hydrogenation of HMF to BHMTHF, and the results are summarized in Table 2. Among all, Ru/MnCo₂O₄ catalyst is found to show the best performance for the hydrogenation of HMF, which gives not only the excellent yield of BHMF (98.5 %) at complete conversion of HMF (1.0 %) but also BHMTHF (97.3 %) at the high conversion of HMF (98.7 %) (Entry 2). This excellent results might be attributed to the availability of Brønsted acid sites (10.7 mmol/g) and increased Lewis acid sites (7.3 mmol/g) arising from the loading of ruthenium nanoparticles (Table S3 and Fig. S7) as well as intrinsic Brønsted acid sites of $MnCo_2O_4$ (8.2 mmol/g). In addition, we recently reported that 99.1 % yield of FDCA could be obtained from the oxidation of HMF using the same Ru/MnCo₂O₄ catalyst [21]. From the reduction and the oxidation of HMF studies, it can be cautiously stated that Ru/MnCo2O4 catalyst has a redox-active ability, and it can be ascribed to the existence of multiple oxidation states on Mn (III/II) and Co (III/II) in Ru/MnCo2O4 catalyst (see XPS in

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Entry	Catalyst	C _{HMF} , %	Y _{BHMTHF} , %	Ү _{внмғ} , %	S _{BHMTHF} , %
1	Ru/MnCo ₂ O ₄	100	1.5	98.5	98.5 ^b
2	Ru/MnCo ₂ O ₄	98.7	97.3	1.4	98.5
3	Ru/CoMn ₂ O ₄	95.9	92.7	3.1	96.7
4	Ru/MnO ₂	77.8	59.2	18.6	76.1
5	Ru/Co ₂ O ₃	65.3	48.5	16.8	74.3
6	MnCo ₂ O ₄	11.9	-	-	-
7	Ru/SiO ₂	95.1	78.0	17.0	82.1
8	Ru/Al ₂ O ₃	93.0	68.6	24.4	73.8
9	Ru/CeO ₂	91.9	73.0	18.9	79.4
10	Ru/C	100	65.3	-	65.3
11 ^c	No catalyst	-	-	-	-
12 ^d	MnCo ₂ O ₄	-	1.5		19.8

C: Conversion, Y: Yield, and S: Selectivity.

 a Reaction conditions: HMF = 1.0 g (8.0 mmol), HMF/Ru = 50, t=16 h, T = 100 °C, P(H₂)=8.2 MPa, Solvent (methanol)=30 mL, Str. Speed = 600 RPM.

^b Selectivity of BHMF after 4 h, when ratio of HMF/Ru = 100.

 c t = 24 h.

^d BHMF used as substrate (8.0 mmol).

spectra in Fig. 1). Many previous studies have also demonstrated that Mn and Co-based bimetal species with multiple oxidation states could promote the water-oxidation and water-reduction reactions [43], and the reaction for rare organic transformations [21,22,50]. Furthermore, the facile reduction at lower temperature revealed by of TPR studies using the Ru/MnCo₂O₄ catalyst is very related to the structural defect (the existence of M²⁺ species and surface oxygen vacancies) in Ru/ MnCo₂O₄ catalyst arisen from the spinels structure, which probably the reason for high activity in the hydrogenation of HMF to BHMF at lower reaction temperature i.e., 100 °C. Gao et al. reported the number of surface defects, which showed a key role during the hydrogenation of furfural [51]. Meanwhile, Ru/CoMn₂O₄ (Mn: Co = 2: 1) catalyst showed somewhat lower yield of BHMTHF (92.7 %) (entry3) than Ru/ $MnCo_2O_4$ (Mn: Co = 1: 2), which is due to the low surface area of $CoMn_2O_4$ (89.5 m²/g) than that of MnCo₂O₄ (151 m²/g) (Tables S2). Single metal oxides supported ruthenium catalysts, Ru/MnO2 and Ru/ Co₂O₃ catalysts, give only 59.2 % and 48.5 % yield of BHMTHF, respectively (Entry 4 and 5 in Table 2), and these results are far from the satisfactory level, showing the important role of MnCo₂O₄ spinel structure again. Also, MnCo₂O₄ itself gave very low conversion of HMF and even does not produceany hydrogenated products (entry 6). Therefore, the yield of BHMTHF is very dependent on the type of metal oxides as support material. As can be seen in Table 2, silica supported ruthenium catalyst, Ru/SiO₂, known as acidic catalyst delivers only 78.0 % yield of BHMTHF (entry 7), and Ru/Al₂O₃ affords only 68.6 % of BHMTHF yield (entry 8). Similarly, Ru/CeO2 gives a mixture of BHMF (18.5 % yield) and BHMTHF (73.0 % yield) (entry 9). The carbon-supported ruthenium, Ru/C, also gives only 65.3 % yield of BHMTHF under identical conditions (entry 10). The hydrogenation of HMF hardly proceeds in the absence of a catalyst (entry 11). To investigate the role of ruthenium on the ring hydrogenation of BHMF, separate hydrogenation of BHMF was also carried out in the presence of MnCo₂O₄. However, a trace amount of BHMTHF (1.5 % yield) is observed (entry 12), indicating the pivotal role of Ru nanoparticles on the ring hydrogenation of BHMF formed as an intermediate during the reaction towards BHMTHF.

Moreover, Ru/MnCo₂O₄ catalyst is found to show the selective synthesis of BHMF or BHMTHF just by changing the reaction time from 4 hto 16 h (Scheme 3). As shown in Scheme 3, BHMF with 98.5 % yield is obtained after 4 h (HMF/Ru = 100), while BHMTHF with 97.3 % yield is obtained after 16 h (HMF/Ru = 50). As earlier mentioned in time course studies, the rate of formation to BHMTHF is much slower than that of BHMF. Hence, the synthesis of BHMTHF with 97.3 % yield



Scheme 3. Tuneable synthesis of BHMF/BHMTHF from hydrogenation of HMF. Reaction conditions: $HMF = 1.0 \text{ g} (8.0 \text{ mmol}), T = 100 \text{ °C}, P(H_2) = 8.2 \text{ MPa}, Solvent (methanol) = 30 \text{ mL}, Str. Speed = 600 RPM.$



Fig. 6. Photo images of purified BHMF (solid sample) and purified BHMTHF (viscous liquid).

needed a longer reaction time and more catalyst. In addition, the separation of BHMF (from the product mixture obtained after 4 h) and BHMTHF (from the product mixture obtained after 16 h) is detailed in supporting information. Photo images of purified BHMF and BHMTHF are provided in Fig. 6. Moreover, the structure and purity of BHMF and BHMTHF are confirmed by ¹H-NMR and ¹³C-NMR spectroscopy, respectively. Fig. S8 and Fig. S9, while ¹H-NMR and ¹³C-NMR spectra of BHMTHF are shown in Fig. S10 and Fig. S11.

Catalyst reusability

The catalyst reusability was investigated in the HMF hydrogenation in the presence of $Ru/MnCo_2O_4$ used as a catalyst, and the results are presented in Fig. 7. To avoid the loss of the catalyst, the centrifugation method was used after every run to separate the catalyst from the product mixture. The recovered catalyst was washed thoroughly with methanol (3 times), dried in an oven at 45 °C under vacuum for 10 h,



Fig. 7. Reusability of Ru/MnCo₂O₄catalyst in hydrogenation of HMF.

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and then reused. The molar ratio of HMF/Ru was kept constant as 50. The results shown in Fig. 7 disclose that the catalyst is active and reusable for four successive runs, but a minor loss in both conversions of HMF and the yield of BHMTHF is observed. To inspect the reason for the minor deactivation of Ru/MnCo₂O₄ catalyst during the reaction, the product solutions were examined by ICP to detect possible leached metals (Ru, Mn, and Co). The ICP results summarized in Table S4 (from Run #1 to #4) show that insignificant amount of ruthenium (range from 1.6 to 2.7 ppm), manganese (range from 49.6-185.5 ppm), and cobalt (range from 14.1-121.7 ppm) were leached out. However, the structural stability of reused Ru/MnCo2O4 catalyst after four successive runs was found to be positive when examined by SEM and SEM images are presented in Fig. 8. No any rupture in particles of Ru/MnCo₂O₄ was observed, clearly indicating that Ru/MnCo₂O₄ catalyst is highly stable after the hydrogenation of HMF. Furthermore, XPS of fresh and reused Ru/MnCo₂O₄ catalyst after four runs (Fig. S12) showed no obvious difference in the spectrum of Mn or Co, confirming the existence of the initial Mn and Co with multiple oxidation state (III/II). Moreover, it could be known that Ru metal surface could possibly be covered with the reduced species of the metal oxide supports and this phenomenon was found in many cases as reported in the literature [52-54]. However, MnCo₂O₄ used as spinel support in this study is quite stable than other metal oxides.

Conclusions

Solid mixed metal oxide, comprising cobalt and manganese-based, $MnCo_2O_4$ spinels support was prepared via simple co-precipitation method and used as support material for ruthenium nanoparticles as catalyst. Catalytic performance of Ru/MnCo₂O₄ was investigated in the HMF hydrogenation for producing two possible furan diols such as a functional group reduced product BHMF, and another fully ring-hydrogenated product BHMTHF. It was found that Ru/MnCo₂O₄ was able



Fig. 8. SEM images of fresh MnCo₂O₄ spinels microspheres-(a), reused Ru/MnCo₂O₄ catalyst after four runs-(b–c), and high-magnification SEM image of reused Ru/MnCo₂O₄ catalyst after four runs-(d).

to selectively produce two useful diols such as BHMF and BHMTHF from the hydrogenation of HMF just by changing reaction conditions without any additive. Notably, Brønsted acidity on the surface of $MnCo_2O_4$ spinels support and increased Lewis acidity by the help of ruthenium nanoparticles were the main motives to produce high yields of BHMF and BHMTHF. Finally, BHMF with 98.5 % yield and BHMTHF with 97.3 % yield were achieved using Ru/MnCo₂O₄ as a single catalyst. It is also worth mentioning that the redox ability of Ru/MnCo₂O₄ was the main factor resulting in both reduction and oxidation of HMF, which was revealed by XPS studies. Moreover, methanol among other solvents is proved to be an appropriate solvent to produce BHMF/BHMTHF. Ru/MnCo₂O₄ catalyst was found to be very useful for several successive runs without considerable loss of its original activity or morphological changes.

Declaration of Competing Interest

There are no conflicts to declare.

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Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:https://doi.org/10.1016/j.mcat.2019.110722.

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