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CHARACTERISATION AND ACTIVITY OF Cu-Zn-Al-Zr/ZSM-5 HYBRID CATALYSTS FOR CO_2 HYDROGENATION REACTION: EFFECT OF THE IMPROVISED PREPARATION TECHNIQUE

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ABSTRACT

An improvised preparation technique, namely ultrasonic spray precipitation (USP) was employed in preparing Cu-Zn-Al-Zr/ZSM-5 zeolite hybrid catalysts. The effects of the newly improvised technique on the physicochemical properties as well as the catalytic behavior of CO_2 hydrogenation reaction were studied. This technique exploits the capability of spraying effect in generating micro-droplets upon contact of catalyst precursors with precipitating agent and also the introduction of an ultrasonic energy in assisting the precipitation process. The characterisation data showed that the USP technique dictates the formation of ultrafine crystallite size (75–99 nm) as compared to conventional technique (CP). The addition of ZSM-5 zeolite had influenced the BET surface area and acidity characteristic (NH_3-TPD) of the catalysts regardless of the preparation method employed. Reducibility analysis (H_2-TPR) revealed that the USP catalysts can be easily reduced at low temperature range of 467–469 K and the existence of single reduction peak explains good interactions between different elements in the catalyst with the formation of single form of oxide species. Moreover, this study also showed that catalysts prepared by USP technique absorbed higher H_2 as compared to their respective CP-prepared catalysts. This trend was also in line with CO_2 conversion data in which Cu-Zn-Al-Zr/ZSM-5 zeolite hybrid catalyst recorded the highest conversion at 55.4 % (503 K, 30 bar, 10,000 h^{-1} GHSV).

INTRODUCTION

The current global concentration of CO_2 has reached an alarming level of 400 ppm [1]. CO_2 mitigation and sequestration therefore becoming an important research area to overcome issues on global warming. Many efforts have been carried out and one solution that is regarded to be the promising approach would be to consume the CO_2 by means of catalytic hydrogenation reaction to form valuable chemicals/fuels such as methanol and dimethyl ether (DME) [2,3]. Both compounds are considered as the future

alternative fuel due to their easily-handling properties as well as numerous potential benefits. Due to thermodynamic limitation and catalyst deactivation associated with CO_2 hydrogenation [4,5], a modified formulation (hybrid catalysts) based on Cu-Zn-Al methanol commercial catalyst should be feasible to catalysed the reaction [6,7]. Hybrid catalyst formulation is a combination of both catalytic function of methanol synthesis (MS) and methanol dehydration (MD) that facilitates the consecutive reactions in co-current production of methanol and DME [8,9].

Preparation of an industrial catalysts generally involved a series of operations depending on its desired final usage. In the case of multi-elemental catalyst, the most commonly used technique is co-precipitation which involves four major stages that are precipitation, aging, drying as well as calcination. Numerous studies were carried out in this field to optimize the parameters in each of these preparation stages and among which got more attention were precipitation and aging stage. Phase composition of precursors and final catalyst microstructure are extremely depended on both stages, which eventually will influence the catalytic performance [10]. Drop wise titration of a mixed metal nitrates with precipitating agent is the widely used method in precipitation stage due to its effectiveness. During precipitation process, the formation of solid precipitate is greatly depended on nucleation and crystallisation within the contact area between two liquids and it always difficult to maintain a regular boundary in microstructure mainly because of poor aggregation force or disorganized agglomeration effect of precursors [11]. Moreover, vigorous stirring action associated with drop wise titration could leads to a randomly nucleation, resulting a non-uniform particle size with poor porosity. It is believed that randomly nucleation could also inhibits active metal dispersion, particularly which involved multi-elemental precursors. These negative characteristics are the major weaknesses possessed by a catalyst prepared by conventional drop wise titration method. Recently, different techniques were explored to overcome such weaknesses. In this study, the objectives are to employ an improvised technique namely ultrasonic spray precipitation (USP) and to investigate its potential superiorities over the conventional precipitation (CP) on the catalyst properties as well as its reaction activity.

EXPERIMENTAL

Catalysts formulation based on Cu:Zn:Al:Zr (CZAZ) at 4:3:1:2 ratio with ZSM-5 zeolite (-Z) (equalized with Cu loading) were synthesised using both CP and USP method. In CP method, the mixture of Cu, Zn, Al and Zr nitrate solution was dropwise-titrated into Na_2CO_3 solution containing the pre-dispersed ZSM-5 zeolite under vigorous stirring. Alternatively, in USP method, the addition of precursors was achieved by means of spraying action under ultrasonic irradiation effect. Temperature and pH were maintained at 333 K and 7.0, respectively. The precipitate was aged for 3 h, washed multiple times with warm distilled water, filtered and dried overnight before calcined at 623 K for 4 h. The synthesised hybrid catalysts (with zeolite content) were denoted as CZAZ-Z (CP) and CZAZ-Z (USP) while non-hybrid catalysts were denoted as CZAZ (CP) and CZAZ (USP).

The surface morphology investigation was carried out using FEI Quanta FEG 650 FE-SEM at accelerating voltage of 15 kV and working distance of 6.3–9.2 mm. The physisorption analysis for surface area (BET) and pore size determination was performed using Micromeritics ASAP 2020. Prior to the analysis, catalyst sample was degassed at 423 K for 3 h. Reducibility (TPR-H_2) and acidity (TPD-NH_3) of the catalysts were characterised using Micromeritics AutoChem II 2920. In TPR-H_2 analysis, the sample was pretreated with He at 393 K for 1 h before the 10 % H_2-Ar gas mixture (50 ml/min) was replaced at heating rate of 10 K/min from 323 to 773 K. In TPD-NH_3 analysis, after the He pretreatment (623 K), the sample was saturated with 5 % NH_3-He gas mixture (50 ml/min) at ambient temperature for 1 h. Subsequently, the NH_3 desorption was monitored by TCD at temperature range of 323–973 K.

The catalytic activity and performance were tested in a fixed–bed reactor equipped with carbon- steel tube (i.d. of 9 mm, height 300 mm) and 20 microns inner porous plate. Prior to each test, 250 mg of catalyst sample was firstly pretreated before reduced at 503 K in H_2 flow for 1 h. After purging, reacting gases (CO_2/H_2/He at 1/3/2 ratio) were continuously fed into the reactor at 503 K, 30 bar and 10,000 h^{-1} GHSV. The post-reaction stream was analysed after 5 h by an on-line gas chromatograph (GC) equipped with multi–column (DB-1, Hayesep Q and Molsieve) separation system connected to TCD and FID detector.

RESULTS AND DISCUSSION

Physical and Chemical Properties

In USP technique, the combination of spraying action with ultrasonic irradiation has influenced the generation rate as well as growth rate of the crystal nucleation during precipitation stage, hence dictated the formation of uniform and ultrafine particles [12]. SEM analysis (figure 1) revealed that USP catalysts exhibited finer, more uniform with dense-stacking structure, particularly the CZAZ (USP) sample. In addition, less agglomeration can be noticed in CZAZ-Z (USP) hybrid catalyst whereby an individual spherical-shaped particles were fairly distributed and well-covered by much finer ZSM-5 zeolite particles.

These morphological characteristics should be the factor of co-precipitation stage, performed under ultrasonic irradiation that favours a better mixing effect among precursors which also enhanced their distribution onto the zeolite framework [13]. Moreover, sonocrystallization induces rapid nucleation that generally yields smaller crystals of a more narrow size distribution [14]. Unlike CZAZ-Z (USP), CZAZ-Z (CP) however displayed a randomly-shaped particle with larger and compact structure. The morphological trend was also in line with the crystallite size (d_C) data which revealed a smaller value for CZAZ-Z (USP) and CZAZ (USP) catalyst as compared to their respective paired catalyst. However, an opposite trend was observed in the BET surface area (SA_{BET}) analysis whereby both hybrid catalysts outnumbered the non-hybrid pair.

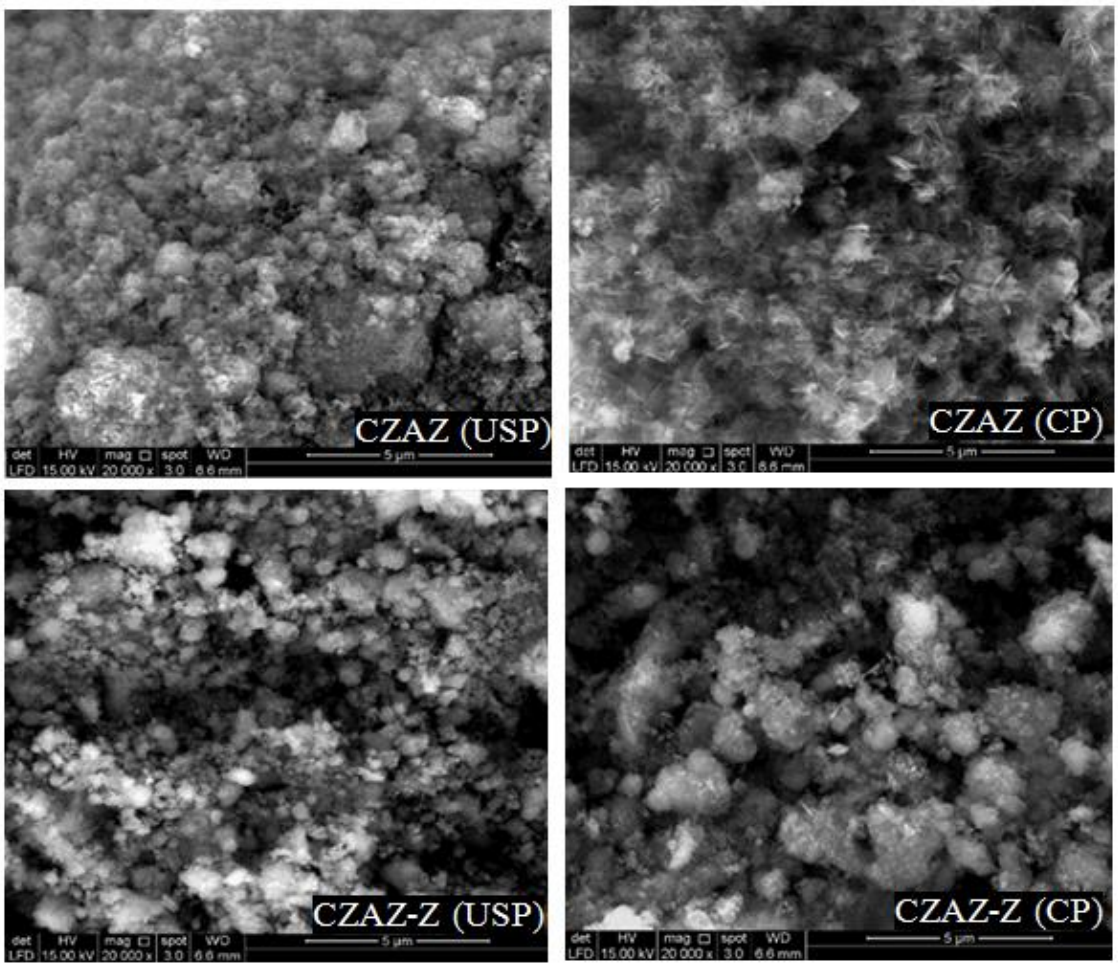

Figure 1: SEM images of the catalysts

Table 1: Quantative data of physicochemical properties

Sample	SA_{BET} [$m^2\ g^{-1}$]	APD [Å]	d_c [nm]	Reducibility Temp. [K] /[mmol/g_{cat}]	Acidity T_{d1}, T_{d2} [K]/[mmol/g_{cat}]
CZAZ (CP)	149	212	108	466.6 (3.40)	351, 796 (0.54)
CZAZ (USP)	96	178	99	467.5 (4.57)	359, 806 (0.71)
CZAZ-Z (CP)	182	120	82	476.2 (2.34)	348, 795 (0.90)
CZAZ-Z (USP)	167	122	75	468.6 (2.97)	354, 813 (1.00)

APD : average pore diameter d_c: crystallite size (Scherrer equation)

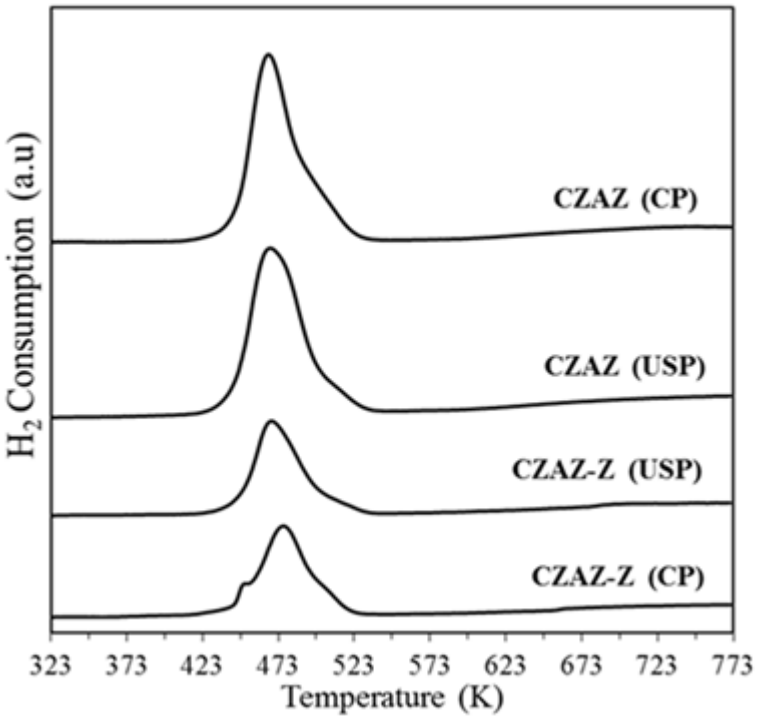

Figure 2: H2–TPR profiles

Based on the fact that the commercial ZSM-5 zeolite used in this study possessed a relatively higher surface area (302 m^2g^{-1}) and its finer particle characteristic make it easily to fill up into the multi-metallic porous structure, thus the addition of ZSM-5 zeolite to the hybrid catalysts (CZAZ-Zs) had influenced the surface area characteristic regardless of the preparation method.

In the reducibility analysis (H2-TPR), all catalysts have displayed a single reduction peak at a considerably low temperature (466 – 476 K) indicating an ease of reduction in one step. It suggests a good interaction between different species that produce a single form of oxide species regardless of preparation method employed. However, the noticeable peak shoulder on the right side for all the catalysts could be attributed to the ongoing reduction of bulk CuO phases while a left-side peak shoulder for CZAZ-Z (CP) hybrid catalyst might be ascribed to the reduction of dispersed CuO [15]. This feature was not exhibited by CZAZ-Z (USP) hybrid catalyst implying that the conventional precipitation technique favours the formation of more dispersed CuO phases. In terms of H2 consumption, catalysts prepared by USP technique surpassed the conventional-prepared catalysts.

The role of ZSM-5 zeolite and its acidity characteristic in hybrid catalyst was investigated by NH_3–TPD (Figure 3). Each catalyst had exhibited two desorption peaks indicating the existence of two acid sites. The first peak which appeared at low

temperature region (348 – 359 K) is normally associated with the desorption of weakly bound NH_3 while the second peak appeared at much higher temperature (795–813 K) is usually attributed to the strong NH_3 adsorbed at Brønsted acid sites [16]. The degree of acidity which manifested by total NH_3 uptake obviously showed an anticipated result. Both hybrid catalysts (CZAZ-Zs) with ZSM-5 zeolite content outnumbered the other pair of catalysts (CZAZs) by more than 30 %.

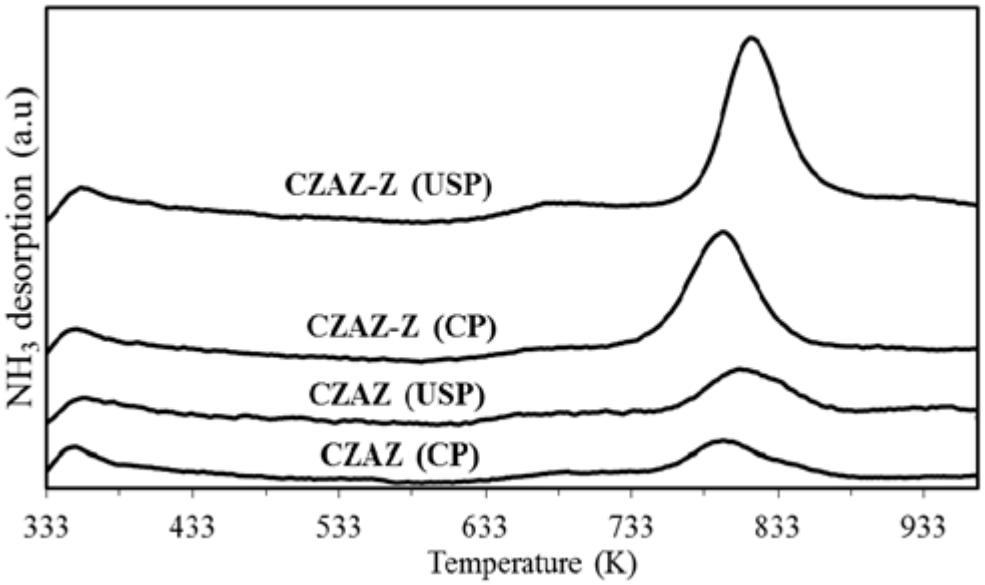

Figure 3: NH_3–TPD profiles

Majority of the NH_3 uptake was recorded at high temperature region revealing that these catalysts possessed strong acid sites characteristic. Moreover, preparation method employed was another factor that contributed to these important characteristics. Catalysts prepared by USP technique acquired more NH_3 uptake than that of CP technique suggesting that ultrasonic irradiation together with spraying effect have influenced the interaction between multi-metallic and ZSM-5 zeolite component during formation of more acidic structure.

Catalytic activity

CO_2 hydrogenation reaction using copper-based catalysts is less active due to thermodynamic limitation associated with more stable CO_2. Methanol selectivity is low as a consequence of the competing reverse water gas shift (RWGS) reaction, producing undesirable CO and adding more H_2O. Nevertheless, the modified Cu-Zn-Al-Zr–based catalysts in this study have improved CO_2 conversion, reaching up to 55.4 %. Interestingly, catalysts prepared by USP technique have shown higher CO_2 conversion than conventional ones (CP). However, it was not the case for CZAZ-Z (CP) which had achieved the least conversion despite of having the highest surface area. This finding could be explained in terms of the amount of active Cu surface possessed by this catalyst. It is widely accepted that hydrogenation reaction of CO_2 is initiated on the Cu

surface. Perhaps, there might be only limited amount of accessible active Cu surface on this catalyst relative to its total surface area which eventually inhibited catalytic performance. Similar trend was also observed in terms of methanol selectivity for hybrid catalysts (CZAZ-Zs) in which CZAZ-Z (USP) had achieved the highest selectivity of 20.7 %. Formation of hydrocarbon (HCs) products were partly influenced by methanol dehydration (MD) step of reaction which associated by the acidity of the catalysts. Moreover, hydrocarbons selectivity (HCs) which contributed only between 2.5 – 4.4 % also exhibited the effect of preparation technique used.

Table 2: Catalytic performance of CO_2 hydrogenation

Sample	CO_2 conversion [%]	Product selectivity [%]			
		CH_3OH	HCs*	H_2O	CO
CZAZ (CP)	46.7	20.5	2.5	7.0	70.0
CZAZ (USP)	55.2	20.4	4.4	9.6	65.5
CZAZ-Z (CP)	46.3	20.3	3.3	7.7	68.7
CZAZ-Z (USP)	55.4	20.7	3.6	7.7	68.0

* HCs : hydrocarbons

Analysis of other by-products (H_2O and CO) revealed that RWGS reaction generally remain dominant over the main reaction, resulting in high CO selectivity in the product stream (above 65 %). Both catalysts prepared by conventional technique (CPs) produced more CO as compared to their respective pair (USPs). Even though CZAZ (USP) exhibited the least CO selectivity (65.5 %), it also balanced by the highest H_2O selectivity which is disadvantageous for catalyst durability [17]. Instead, by adding ZSM-5 zeolite, the hybrid catalysts (CZAZ-Zs) are capable of reducing H_2O selectivity while also inhibiting CO selectivity at certain extent.

SUMMARY

The introduction of spray-titration technique together with ultrasonic irradiation during precipitation stage have improved the catalyst's physicochemical characteristics and reaction activity, hence justifying the superiority of this improvised preparation technique over the conventional ones.

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