



Mechanistic insight into the heterogeneous catalytic transfer hydrogenation over Cu/Al₂O₃: Direct evidence for the assistant role of support

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ABSTRACT

The catalytic transfer hydrogenation (CTH) between alcohol and alkene was investigated over Cu/Al₂O₃ catalyst *via* mechanical mixture of the supported catalyst and the pure support. It is found that the CTH activities are highly depended on the amount and acid/basic properties of the mechanically mixed support, clearly indicating the assistant role of support. In addition, only alkene with high activity of hydrogenation can really act as hydrogen acceptor. Based on these, a new bifunctional reaction pathway is proposed. Alcohol dehydrogenates to form alkoxide on Al₂O₃ surface ($R_1CH(OH)R_2 \rightarrow R_1CH(O)R_2 + H$), and H atom migrates to the metallic Cu patches *via* reverse hydrogen spillover, while extraction of α -hydrogen forming ketone ($R_1CH(O)R_2 \rightarrow R_1C(O)R_2 + H$) occurs on Cu or Cu–Al₂O₃ interface. On the metallic Cu patches, alkene hydrogenates yielding alkane ($R_3CH=CHR_4 + 2H \rightarrow R_3CH_2CH_2R_4$). This mechanism can give a better explanation for the observed acceleration or deceleration role of hydrogen acceptor to alcohol dehydrogenation.

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1. Introduction

Catalytic transfer hydrogenation/dehydrogenation (CTH) is of promising alternative for alcohol anaerobic oxidation, in which the usage of dangerous or toxic oxidant can be obviated [1–4]. The dehydrogenation of secondary alcohol to ketone or aldehyde has also been widely used as an important hydrogen resource for the reduction of organic compounds instead of the traditional hydrogenation where high pressure H₂ is required [4,5]. Furthermore, there are several advantages in the gas-phase CTH reaction, e.g., good energy efficiency, optimal hydrogen utilization and improvement of the equilibrium of the dehydrogenation reaction [6–9]. In order to facilitate catalyst design, it is required to understand reaction pathway from an atomic-scale.

Many attempts have been paid for the comprehensive understanding of the mechanism of the homogeneous CTH, especially for ruthenium complex [4,5,10–12]. Among the breakthroughs, the most important one is the discovery of metal ligand bifunctional catalysts, in which the process of hydride transfer is suggested to be not the single effect of metal sites [10,11]. As for the heterogeneous CTH over supported catalysts, the major effort is devoted to understand the intermediate of hydride-metal from the view of a

single active phase [13–15]. Actually, hydrogen acceptor (HA, such as the alkene) and hydrogen donor (HD, such as alcohol) may react through respective pathway and/or on different active sites. For example, many studies have proved that the support plays an assistant role into the dehydrogenation of alcohol [16–19].

A few reports have shown that the activities of CTH reaction differ over different kinds of support [1,20–21]. However, the possible assistant role of the support has never been considered into the mechanistic studies of the CTH over the supported catalyst. In this work, we focus on investigating the effect of support to fully understand the fundamental steps involved into the heterogeneous CTH.

The cases of heterogeneous CTH mainly rely on noble catalysts or oxide catalyst for classical Meerwein–Ponndorf–Verley reaction, e.g., Pd/C, Ru(OH)_x/Al₂O₃, MgO/Al₂O₃ and ZrO₂ [13–15,21–25]. Prominently, an active copper catalyst is reported, which makes the CTH process under very mild conditions [1,2,26]. The CTH reaction over this novel catalyst system promises the set up of a green and safe protocol for alcohol anaerobic oxidation. Recently, several gas-phase heterogeneous CTH processes over copper based catalyst have been developed by our group [6,7]. It promotes us to preliminarily understand the CTH mechanism over the copper based catalysts.

Here we put forward the discovery that the Al₂O₃ plays an important assistant role in the CTH reaction between alkene and alcohol over Cu/Al₂O₃ *via* mechanically mixed catalyst and its support. A reaction mechanism is proposed based on hydrogen

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spillover. The proposed mechanism explains the accelerated or decelerated phenomenon in the CTH reactions from a bifunctional view.

2. Experimental

2.1. Catalyst preparation

In order to get a well-dispersed catalyst to rationalize the role of each active component, a low-loading copper catalyst (namely Cu/Al₂O₃) was prepared from a well-known deposition–precipitation method [27]. The commercial Al₂O₃ (Nanjing Catalyst Co., PR China, 20–40 mesh) was mixed to a solution of Cu(NO₃)₂·3H₂O and urea, and the slurry was held in a water bath at 70 °C for 24 h under continually stirring. During the stirring process at constant temperature, hydroxide ions were generated by the hydrolysis of urea and were precipitated with Cu²⁺ slowly. After precipitation, the solid was separated by filtration, washed with water, dried overnight at 110 °C, and calcined at 450 °C for 4 h.

The mechanical mixture catalysts were prepared with different proportion of Cu/Al₂O₃ and Al₂O₃ (crushed into each powder, >300 mesh). The powder was suspended and stirred in *n*-pentane (5 ml/g of solid), and the solvent was removed by evaporation at 110 °C for 12 h. The mixed powder was palletized, then crushed and sieved to the original particle size (20–40 mesh). Here the Cat and Sup stand for the supported catalyst (Cu/Al₂O₃) and the pure support (Al₂O₃), respectively. The mechanical mixture catalysts are identified in the format of Cat(*x*)Sup(100 – *x*) by relative weight of catalyst and support.

$$x = \frac{\text{wt.\% Cu/Al}_2\text{O}_3}{\text{wt.\% Cu/Al}_2\text{O}_3 + \text{wt.\% Al}_2\text{O}_3} \times 100$$

It must be firstly noted that the Cat100Sup0 is different from the supported catalyst Cu/Al₂O₃, for several additional physical processes (i.e., crushing and palletizing process) are included in the preparation of Cat100Sup0.

2.2. Catalyst characterization

The bulk composition of the support catalyst and pure support was determined by atomic absorption spectroscopy (AAS) on a TJA AtomScan16 absorption spectro-photometer. The Cu loading of Cu/Al₂O₃ is 3.5% (weight ratio) by AAS. The main impurities are Fe, Na and Si in the Al₂O₃, and the weight ratio of them is 0.08%, 0.12% and 0.12%, respectively.

The Brunauer–Emmett–Teller surface area (*S*_{BET}) and pore volumes of the catalysts and support were measured by N₂ physisorption at –196 °C using a Tristar 3000 system (Micromeritics, USA). Samples were degassed at 120 °C for 6 h before measurement using a D/max-RA. X-ray diffractometer (Rigaku, Japan) with Cu Kα radiation (λ = 0.154 nm) operated at 40 kV and 100 mA. The Cu/Al₂O₃ mainly contains two crystallite peaks: γ-Al₂O₃ and CuO. The crystallite size of γ-Al₂O₃ in Cu/Al₂O₃ is almost identical with that in its support (Fig. 1).

The specific Cu surface area was obtained in an Autochem 2910 (Micromeritics, USA) apparatus with a reported method named s-TPR [28]. The samples were firstly pre-reduced in situ in a 5% H₂/Ar flow (60 ml/min) at 255 °C for 90 min. When the Cu⁰ surface was oxidated by N₂O and the system temperature cooled to 40 °C, the H₂/Ar flow was replaced to a N₂O flow for 30 min. The H₂-TPR was carried out on the freshly oxidized Cu₂O surface in order to reduce Cu₂O to Cu from 40 to 600 °C (Heating rates in 10 °C/min). The amount of H₂-uptake was evaluated by the experimental s-TPR curves and calibration measurements with CuO (Beijing Chemical Company, >99 wt.% purity). The surface metal was obtained by the

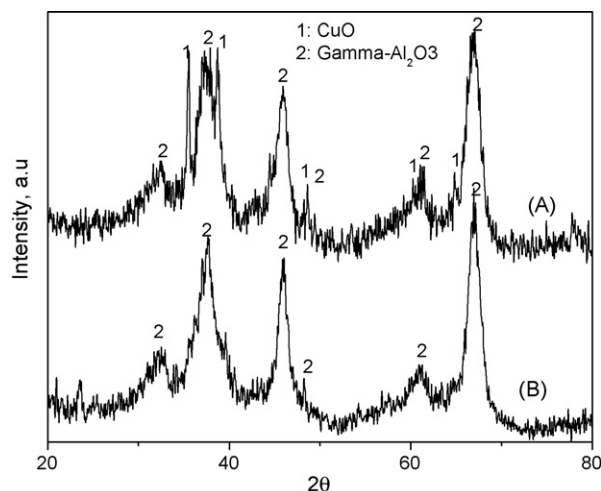


Fig. 1. XRD profiles of (A) the Cu/Al₂O₃, (B) the fresh commercial Al₂O₃.

amount of H₂-uptake. The Cu⁰ metallic surface area of Cu/Al₂O₃ measured is 6.7 m²/g_{cat} by s-TPR, and the metal dispersion is nearly 30%. The Cu⁰ metallic surface area of other mechanical mixture catalysts is also investigated, however, the accuracy and repeatability is found to be poor because of their low metal loading.

The temperature programmed reduction (H₂-TPR) analysis was performed in a conventional apparatus with a thermal conductivity detector (TCD). The sample loading was 100 mg with exception of Cat100Sup0 (loading was 50 mg). The samples were dried under Ar flow at 150 °C for 60 min, and then cooled to 100 °C. The reduction was carried out from 100 up to 550 °C (6 °C/min) under a 30 ml/min flow rate of 5% H₂/Ar mixed gas. In order to investigate the possible adsorbed *n*-pentane, the thermogravimetry/mass spectrometry (TG–MS) of Cat50Sup50 from 30 to 650 °C was also carried out, and the possible adsorbed *n*-pentane was found to be under detection by TG–MS.

The temperature programmed desorption of NH₃ (NH₃-TPD) analysis was conducted in a self-made vessel. The catalyst sample (150 mg) was degassed in situ for 2 h at 600 °C and argon flow. Then, the sample was brought to saturation level using an NH₃/Ar at 100 °C for 1 h. After the reactant excess was eliminated by flowing dry Ar at the same temperature, the temperature was raised using a 10 °C/min ramp and the desorption signals were recorded by TCD.

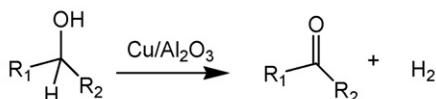
The temperature programmed desorption of CO₂ (CO₂-TPD) was performed in a Micromeritics ASAP 2010 apparatus. Firstly, sample (200 mg) was in situ heated in a helium flow at 600 °C for 1 h to desorb the impurities. Secondly, CO₂ adsorption on catalyst was conducted at 40 °C for 1 h and the sample was purged with helium at 40 °C for 1 h to remove physical adsorbed species. Finally, CO₂-TPD was carried out with increasing to 600 °C (Heating rates in 10 °C/min).

2.3. Catalytic activity test

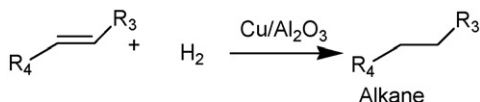
The CTH reactions between alkene and alcohol are illustrated in Scheme 1. 2-Pentanol (2-POL) and different kinds of alkene (styrene, cyclohexene and 1-hexene) were chosen as the probe reactant.

The reactions were performed in a 100 ml stirred stainless autoclave. A typical experiment was performed as follows. Firstly, catalysts were suspended in inert solvent (1, 4-dioxane), and they were in situ pre-reduced at 6 MPa H₂ and 255 °C under continuous stirring at 1000 rpm for 4 h. After the autoclave was cooled to

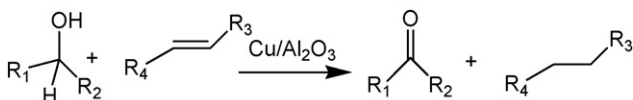
Equation1 Alcohol dehydrogenation



Equation2 Alkene hydrogenation



Equation3 The CTH between alcohol and alkene

**Scheme 1.** The reaction equations between the probe reactants in this work.

room temperature and depressurized to atmospheric pressure, the reactant mixture was added to the autoclave. Then N₂ flow was injected for several times in order to remove the residual H₂. At the end of the reaction, the autoclave was cooled to room temperature, and then the gas and liquid samples were withdrawn. The concentrations of the liquid samples were determined by the internal standard method (*n*-tetradecane worked as internal standard). The liquid samples were measured by a gas chromatographs equipped with a capillary column (OV-101) and a flame ionization detector. The gas samples were analyzed by a gas chromatograph equipped with a molecular packed column and a TCD.

3. Results and discussion

3.1. Hydrogen acceptor selection

For selecting a suitable alkene and investigating the effect of alkene on the activity of the alcohol dehydrogenation, three kinds of alkene were chosen as the possible hydrogen acceptor (HA). As shown in Table 1, a great difference in the activity of hydrogenation is observed among three kinds of alkene. Table 2 shows the activities of the 2-POL dehydrogenation reaction with different alkene. The yield of 2-PON increases from 40.1% to 58.4% at reaction time of 8 h when styrene works as HA, which shows that styrene significantly accelerates the dehydrogenation of 2-POL. This result is consistent with the reports by Zaccheria et al. [1,2]. Otherwise, as shown in Table 2 (entry 2), the hydrogen-transfer efficiency is approximately 100%, i.e., the hydrogen from 2-POL nearly completely transfer to styrene. It is indicated that the CTH reaction surely occurs between 2-POL and styrene. In order to investigate whether the rate acceleration is just a shift of the thermodynamic equilibrium in the presence of styrene, the 2-POL dehydrogenation

Table 1Hydrogenation of different alkene over Cu/Al₂O₃ or Al₂O₃

Entry	Alkene	Catalyst	Reaction time (h)	Conversion (%)	Selectivity ^a (%)
1	Cyclohexene	Cu/Al ₂ O ₃	3	0	0
2	Styrene	Cu/Al ₂ O ₃	0.33	99.0	95.6
3	1-Hexene	Cu/Al ₂ O ₃	3	4.5	88.9
4	Styrene	Al ₂ O ₃	2	8.6	0 ^b

Reaction conditions: alkene (2 g), catalyst (1 g), solvent (50 g), 3 MPa H₂, temperature 150 °C.

^a The selectivity of cyclohexane, *n*-hexane or ethylbenzene, respectively.

^b Close to the possible experimental errors.

Table 2Dehydrogenation of 2-POL with different hydrogen acceptor over Cu/Al₂O₃

Entry	HA	Reaction Time (h)	2-PON yield (%)	Hydrogen-transfer efficiency ^a (%)
1	None	5	22.2	–
		8	40.1	–
		20	60.2	–
2	Styrene	5	49.1	99.3
		8	58.4	97.1
3	1-Hexene	8	37.8	12.4
4	Cyclohexene	8	2.0	0

Reaction conditions: 2-POL (2 g), hydrogen acceptor/hydrogen donor = 1.5 (mol/mol), catalyst (2 g), solvent (50 g), 0.3 MPa N₂, reaction temperature 180 °C.

^a Hydrogen-transfer efficiency = (moles of hydrogen-transfer to alkene/moles of hydrogen from 2-POL) × 100.

with/without styrene is also investigated as a function of reaction time. Without styrene as HA, the yield of 2-PON increases as the increase of reaction time and attains 60.2% at reaction time of 20 h. It is proved that the measurement without styrene and at reaction time of 5 h is carried out far from thermodynamic equilibrium, and the yield of 2-PON greatly increases with styrene as HA. Accordingly, the rate acceleration is not a simple shift of the thermodynamic equilibrium (Table 2, entry 1–2). Unlike styrene, cyclohexene and 1-hexene are incapable of accelerating the 2-POL dehydrogenation. As for the condition in the presence of 1-hexene, the 2-PON yield is similar with that of the 2-POL dehydrogenation without HA. However, the hydrogen to 1-hexene is much less than that from 2-POL (Table 2, entry 3), which shows a real CTH reaction does not take place between 2-POL and 1-hexene. Cyclohexene even greatly lowers the activity of CTH over Cu/Al₂O₃ (Table 2, entry 4). In summary, the activity order of the CTH reaction is identical to that of the alkene hydrogenation and it is suggested that only alkene with high activity of hydrogenation is really active as HA.

Among the three kinds of alkene, only styrene accelerates the CTH and a real CTH reaction occurs between 2-POL and styrene. Therefore, styrene is selected for further investigations and the yield of 2-PON is defined as the activity of the CTH reaction infra.

3.2. Effect of the amount of Al₂O₃ on the CTH activity

Table 3 gives the activity of the CTH reaction between 2-POL and styrene over the mechanical mixture catalysts. The yield of 2-PON is nearly equal to zero over the Al₂O₃, which shows that the single Al₂O₃ is identified as ineffective catalyst under the experimental conditions (Table 3, entry 6). Surprisingly, the activity of the CTH reaction increases monotonously and dramatically when the amount of Al₂O₃ increases in the mechanical mixture catalysts (Table 3, entries 1–6). For example, the 2-PON yield of Cat25Sup75

Table 3

The CTH activities between 2-POL and styrene over different catalysts

Entry	Catalyst code	Net Cat plus Sup (g)	Net Cat (g)	2-PON yield (%)
1	Cat100Sup0	1	1	4.0
2	Cat75Sup25	1.33	1	18.9
3	Cat50Sup50	2	1	35.8
4	Cat25Sup75	4	1	68.3
5	Cat11Sup89	9	1	88.1
6	Al ₂ O ₃	2	0	0 ^b
7	Cu/Al ₂ O ₃	1	1	17.2
8	Cu/Al ₂ O ₃ ^a	1	1	6.2

Reaction conditions: 2-POL (2 g), styrene/2-POL = 1.5 mol/mol, solvent (50 g), N₂, 180 °C, reaction time 8 h.

^a Cu/Al₂O₃ (crushed into powder, >300 mesh).

^b Close to the possible experimental errors.

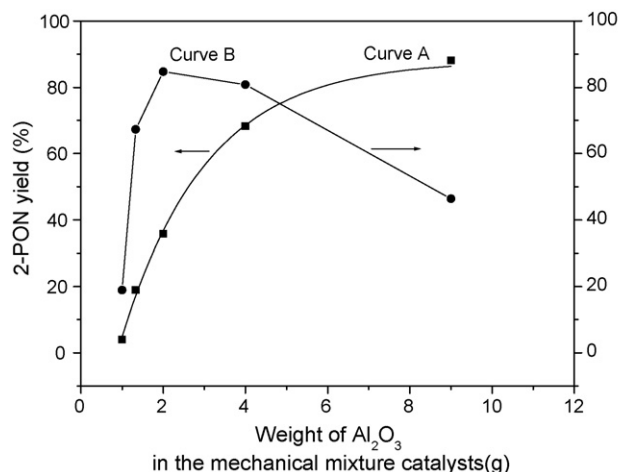


Fig. 2. Catalytic performance over the mechanical mixture catalysts as a function of the weight of Al_2O_3 in the mechanical mixture catalysts for CTH reaction.

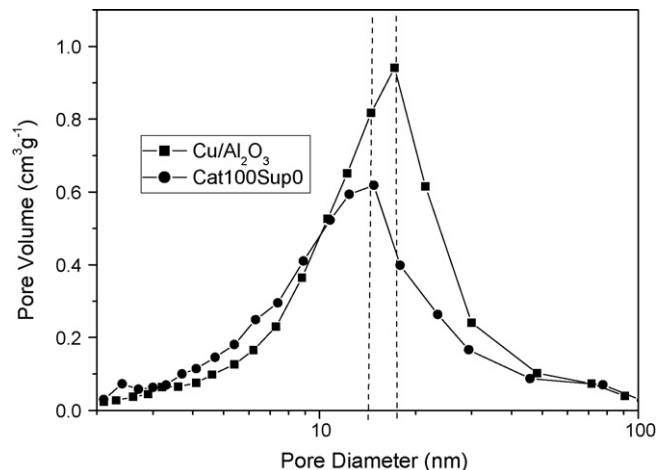


Fig. 4. The pore-size distribution of $\text{Cu}/\text{Al}_2\text{O}_3$ and Cat100Sup0 .

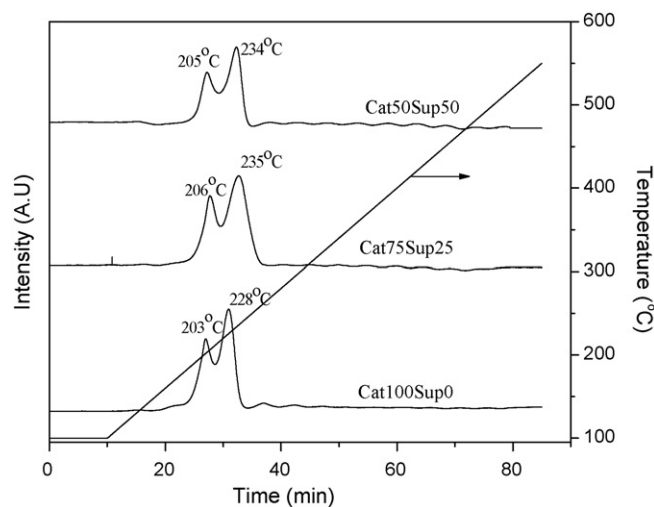


Fig. 3. H_2 -TPR profiles of Cat100Sup0 , Cat75Sup25 and Cat50Sup50 .

is 4 times as large as that of $\text{Cu}/\text{Al}_2\text{O}_3$. It is likely demonstrated that Al_2O_3 plays an important assistant role.

Fig. 2 (Curve A) presents the activities of the CTH as a function of the weight of Al_2O_3 . When the weight of Al_2O_3 increases in the mechanical mixture catalysts, a linear increase of the 2-PON yield is initially observed. When the weight of the mechanical mixed Al_2O_3 is high, the activity of the CTH trends to be levelled. As shown in curve B, a closer inspection presents that the dehydrogenation rate of 2-PON ($R_{2\text{-PON}}$) reaches a maximum at Cat50Sup50 ($R_{2\text{-PON}} = \text{Yield}_{2\text{-PON}} \times \text{Initial mol of 2-POL (mol)}/\text{Reaction time (s)} \times \text{catalyst weight (g)}$). It is suggested that optimal metal loading is necessary to maximize activity of the CTH reaction.

One may argue whether the reduction behavior is affected by the mechanically mixed Al_2O_3 . The H_2 -TPR profiles of mechanical mixture catalysts present a direct evidence to rule out this

hypothesis. The H_2 -TPR profiles of Cat100Sup0 , Cat75Sup25 , and Cat50Sup50 are given in Fig. 3. The range of reduction temperature and the hydrogen consumption peak center are almost identical. This indicates that the reduction performances are insensitive to the amount of the mechanically mixed Al_2O_3 in the mechanical mixture catalysts.

It is worth noting that the activity of CTH is greatly different over $\text{Cu}/\text{Al}_2\text{O}_3$ (20–40 mesh), $\text{Cu}/\text{Al}_2\text{O}_3$ (>300 mesh) and Cat100Sup0 (20–40 mesh). The three catalysts are identical in the chemical composition and only different in physical forms. The texture performance of $\text{Cu}/\text{Al}_2\text{O}_3$ and Cat100Sup0 was investigated. As shown in Table 4, when the $\text{Cu}/\text{Al}_2\text{O}_3$ is converted into Cat100Sup0 through a series of physical changes, the S_{BET} , average pore size and pore volume decrease, which means that the crush process may partly destroy physical structure. Furthermore, the pore-size distribution suggests that the mid pore is partly destroyed or plugged (Fig. 4). Thus, the texture performance is also important to the activity of the CTH reaction.

3.3. Effect of the calcined temperature of Al_2O_3 on the CTH activity

Previous reports show that the acid/basic sites vary with the calcined temperature [29,33]. In order to estimate the effect of the Al_2O_3 properties on the activity of the CTH reaction, a series of mechanical mixture catalysts was prepared with Al_2O_3 powder at different calcined temperature (600–800 °C) as mechanical addition.

Firstly, the Al_2O_3 powders with different calcined temperature were determined by XRD, N_2 physisorption and TPD techniques. No new phase is detected in the bulk phase of Al_2O_3 . The diffraction peaks become slightly sharper at 800 °C, showing that the crystallite size of Al_2O_3 increases a little. As shown in Table 5, the S_{BET} decreases while the total pore volume changes slightly and the average pore-size increases from 600 to 800 °C. Figs. 5 and 6 show that the NH_3 -TPD and CO_2 -TPD patterns of Al_2O_3 calcined at 600 or 800 °C. The NH_3 -TPD of the samples shows two desorp-

Table 4
The textural performance of Al_2O_3 , $\text{Cu}/\text{Al}_2\text{O}_3$ and Cat100Sup0

Catalyst	BET surface area ($\text{m}^2/\text{g cat}$)	Micropore area ($\text{m}^2/\text{g cat}$)	Total pore volume ($\text{cm}^3/\text{g cat}$)	Average pore size (nm)
Al_2O_3	134.4	10.5	0.443	13.2
$\text{Cu}/\text{Al}_2\text{O}_3$	129.9	8.26	0.479	14.7
Cat100Sup0	128.7	9.3	0.383	11.4

Table 5

The CTH activities between 2-POL and styrene over Cat50Sup50 with the mechanically mixed Al_2O_3 powder at different calcined temperature and the characterization results of Al_2O_3 at different calcined temperature

T^a ($^\circ\text{C}$)	2-PON yield (%)	S_{BET} ($\text{m}^2/\text{g cat}$)	Pore volume ($\text{cm}^3/\text{g cat}$)	Average pore size (nm)	Basicity ($\mu\text{mol/g}$) ^b	
					Weak/medium	Strong
Uncalcined	35.8	134.4	0.44	13.2	ND ^c	ND
600	37.3	131.2	0.49	14.8	262	30
650	27.3	128.8	0.49	15.2	255	39
700	12.3	116.6	0.48	16.4	242	41
800	10.8	114.3	0.49	16.6	189	47

Reaction conditions: 2-POL (2 g), styrene/2-POL = 1.5 mol/mol, solvent (50 g), N_2 , 180°C , reaction time 8 h.

^a Calcined temperature, the Al_2O_3 powder was calcined in air for 6 h.

^b Basicity: Amount of adsorbed CO_2 .

^c ND: not determined.

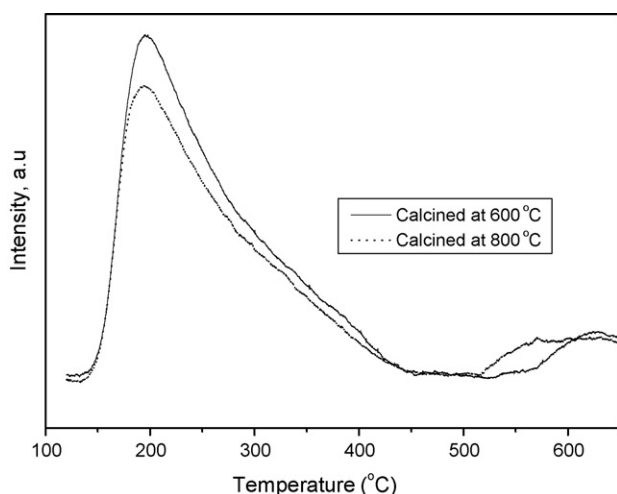


Fig. 5. NH_3 -TPD profiles of Al_2O_3 calcined at 600 and 800°C .

tion signal maxima. One at low temperature is at $\sim 195^\circ\text{C}$. To the Al_2O_3 calcined at 600 or 800°C , the other at high temperature is at ~ 630 and $\sim 530^\circ\text{C}$, respectively. It indicates that the intensity of strong acid sites changes. The total amount of acidic sites decreases by 14.6% with the high calcined temperature, which is consistent with the previous reports [29]. As for the CO_2 -TPD, two desorption peaks exist at ~ 100 and $\sim 430^\circ\text{C}$. The peaks at 100°C are ascribed to the weak and medium basic sites, and the other ones to strong basic sites. With the calcined temperature from 600 to 800°C , the

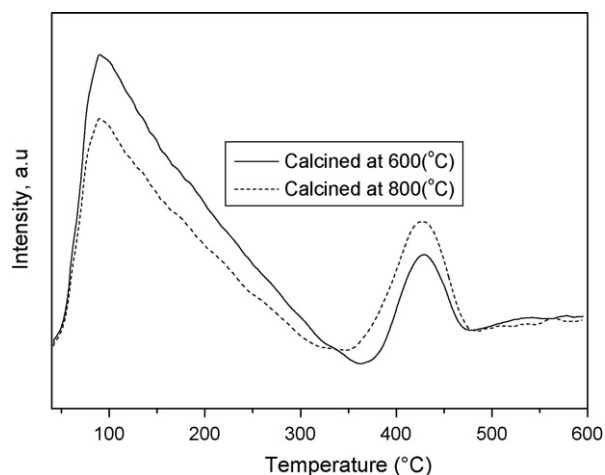


Fig. 6. CO_2 -TPD profiles of the Al_2O_3 calcined at 600 and 800°C .

amount of adsorbed CO_2 on weak and medium basic sites decreases from 262.4 to $189.0 \mu\text{mol/g}$ while the amount of CO_2 adsorbed on strong basic sites enhances from 29.6 to $45.6 \mu\text{mol/g}$. The amounts of adsorbed CO_2 on Al_2O_3 at different calcined temperature are listed in Table 5. The characterization results show that the acid and basic sites of the Al_2O_3 powders decreased when the calcined temperature increased from 600 to 800°C .

Table 5 shows the activity of the CTH reaction reduces when the calcined temperature of Al_2O_3 enhances. The yield of 2-PON sharply decreases from 37.3% to 10.8% when the calcined temperature of Al_2O_3 increases from 600 to 800°C . It means that the acid/basic properties of Al_2O_3 have great effect on the activity of the CTH reaction and the important assistant role of support is further demonstrated. Furthermore, one hypothesis can be ruled out, that is, the activity of the CTH reaction may be improved by mechanical addition of Al_2O_3 through the alternative dispersion of the metal particles. The accuracy and the repeatability of s-TPR technique are poor because of the low metal loading in the mechanically mixed catalysts (3.5%–0.8%), thus it is unreasonable to estimate this case by measure of the Cu^0 surface areas. But this case can be safely excluded by the fact that the activities change with the mechanically mixed Al_2O_3 at different calcined temperature.

3.4. Mechanism proposal

The results show that the activity of CTH reaction is associated with the amount and properties of the mechanically mixed Al_2O_3 . It is strongly indicated that the support plays an important assistant role in the CTH reaction between alcohol and alkene. A reaction mechanism based on hydrogen spillover (Scheme 2) is proposed and clarified.

Step 1: The tested catalysts were low loading (0.39%–3.5%), and the Cu surface area of $\text{Cu}/\text{Al}_2\text{O}_3$ is only $6.7 \text{ m}^2/\text{g}_{\text{cat}}$, which is much less than its S_{BET} ($196 \text{ m}^2/\text{g}_{\text{cat}}$). The alcohol is also proved to be easily adsorbed onto Al_2O_3 surface [17,19,30,31]. Thus it is concluded that alcohol should mainly be adsorbed on Al_2O_3 surface.

Step 2: The alcohol dehydrogenation includes two reaction steps as following (A) the alcohol dissociation into alkoxide and hydrogen ($\text{R}_1\text{CH}(\text{OH})\text{R}_2 \rightarrow \text{R}_1\text{CH}(\text{O})\text{R}_2 + \text{H}$), (B) the extraction of the α -hydrogen from alkoxide ($\text{R}_1\text{CH}(\text{O})\text{R}_2 \rightarrow \text{R}_1\text{C}(\text{O})\text{R}_2 + \text{H}$) [19,29–32]. Wang et al. reported that isopropanol can directly dehydrogenate to acetone in low yield over the nanocrystallite sol-gel Al_2O_3 , and the formation of acetone was suggested to depend on the surface basic sites [29,33]. However, Zaki et al. proved that pure Al_2O_3 was completely inactive for alcohol dehydrogenation and metal sites was needed for the reaction step B [19]. In our experiments, the CTH reaction is not observed over Al_2O_3 , it further proves the proposed by Zaki et al. [19]. On the other hand, both Wang et al. and Zaki et al. reported that the main product was propene from isopropanol dehydration [19,29]. It is generally accepted that

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