A Dual Catalyst Bed System for the Elimination of Hydrogen from CO₂ Feed Gas in Urea Synthesis

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A dual catalyst bed system (Au/Fe₂O₃ + Pt–Pd/Al₂O₃) for eliminating hydrogen from the CO₂ feed gas in urea synthesis is found to be far superior to commercially available and patented catalysts in catalytic activity. At relatively low temperatures, hydrogen is eliminated and coexistent CO is also oxidized completely to useful CO₂. This can avoid effectively the accidental explosion of hydrogen–oxygen–ammonia mixed gases, thus ensuring the safety of urea synthesis.

1. Introduction

The removal of hydrogen from the CO₂ feed gas for urea synthesis by catalytic oxidation is an important technology to avoid explosion due to the accumulation of hydrogen. The catalysts used for the elimination of hydrogen from the CO₂ feed gas in urea production plants are mainly supported Pt or Pt–Pd catalysts,^{1,2} such as CN-101 catalyst (Pt/Al₂O₃) made by Engelhard, Iselin, NJ, and DH-2 (Pt–Pd/Al₂O₃) and D-438 (Pd–FeO_x/Al₂O₃) catalysts made by LZCP, Lanzhou, China.³ This elimination of hydrogen from the CO₂ feed gas is necessary in order to prevent any possible accidental explosion of the feed gas mixture in the process of making urea.^{2,4} The conventionally used supported Pt or Pd catalysts for such a purpose have two drawbacks, namely, the high reaction temperature (around 473 K for industrial applications) and sulfur poisoning. Although the application of supported gold catalyst enhances the reaction activities and resistance to sulfur poisoning,⁴ it is desirable to seek a new type of catalyst with high catalytic activity at low temperature.

2. Concept for a Dual Catalyst Bed System

The use of Pt or Pd catalysts needs to a relatively high temperature to remove hydrogen in the presence of a small yet appreciable amount of CO (0.1–0.2%) in the CO₂ feed gas. This coexistent CO competes favorably with hydrogen for adsorption and reaction on the surface of Pt or Pd catalysts.⁵ Pt and Pd catalysts are well-known to have very high catalytic activity in removing hydrogen with oxygen, even at close to room temperature, for instance, on Pd/C⁶ and Pt–Pd/Al₂O₃⁷ catalysts. However, it is difficult for these metals to suppress the CO content in the CO₂ feed gas unless operated at a temperature above 373 K. In consideration of this coexistent CO, an ideal catalyst bed system for

the elimination of hydrogen from the CO₂ feed gas for urea synthesis should possess a high activity to eliminate the CO as well as hydrogen in the feed gas, so that the catalyst bed system can be operated at a low temperature to eliminate the hydrogen effectively. It is difficult for one catalyst to possess two kinds of high low-temperature catalytic activities of eliminating CO and hydrogen at the same time. The supported Au catalyst reported elsewhere^{8,9} exhibits the high CO eliminating activity. Some works on selective oxidation of hydrogen and carbon monoxide mixed gases were reported.^{6,10,11} In this paper, we report a dual catalyst bed system, in which a supported Au catalyst is used in combination with a supported Pt–Pd catalyst, which realizes the co-elimination of CO and hydrogen from the CO₂ feed gas at a relatively low temperature, thus resulting in a considerable savings of energy.

3. Experimental Section

3.1. The supported Au catalyst samples were synthesized via coprecipitation from aqueous HAuCl₄ and the nitrate of the corresponding metal oxide support. The appropriate precursor solutions were added to a solution of sodium carbonate, and the catalysts were thus obtained after being dried, calcined, or subjected to various heat and oxygen treatments^{12–14} (generally treated in oxygen at 473–623 K). The gold loading was adjusted to 1 atom % [=100Au/(Au + Fe)]. Pt–Pd/Al₂O₃ catalyst [5 wt % Pt (mol)/Pd (mol) = 1] was prepared by conventional impregnation, according to the procedure described previously.^{2,15,16} Commercial catalyst samples used were DH-2 (Pd–Pt/Al₂O₃ industrial catalyst made by LZCP) and CN-101 (Pt/Al₂O₃ commercial catalyst made by Engelhard).

3.2. The activity of catalysts was evaluated with a fixed-bed continuous flow reactor at atmospheric pressure. A mixture of the CO₂ feed gas (H₂, 1%; CO, 0.1%; O₂, 1.5%; CO₂, 95%; N₂, 2.4%) was passed through the catalyst bed at a flow rate of 225 mL/min (feed gas space velocity 27 000 h^{–1}, except where specially stated). The reaction products were analyzed using gas chromatography (SC-8). The activity of the catalysts for CO–O₂ reaction was indicated by the lowest temperature at which the conversion of CO is “complete”; i.e., the residual CO in the exit gas is less than 50 ppm. The activity of the catalyst H₂–O₂ reaction was expressed

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Table 1. Surface Area and Composition of Catalysts

catalyst	metal component	support	S_{BET} of the catalyst (m ² /g)
CN-101 Pt/Al ₂ O ₃ (Engelhard) ¹	Pt	γ -Al ₂ O ₃	101.0
DH-2 Pt–Pd/Al ₂ O ₃ (LZCP) ¹	Pt, Pd	γ -Al ₂ O ₃	179.1
Au/Fe ₂ O ₃ (LZCP)	Au	γ -Fe ₂ O ₃	136.4
Au/NiFe ₂ O ₄	Au	γ -Fe ₂ O ₃ , NiO	108.2
dual catalyst bed system (Au/Fe ₂ O ₃ + Pt–Pd/Al ₂ O ₃)	Au	γ -Fe ₂ O ₃	
	Pt, Pd	γ -Al ₂ O ₃	

Table 2. Catalytic Activity of Elimination of CO

catalyst	T^0 (K)	catalyst	T^0 (K)
Au/Fe ₂ O ₃	<288	Au/NiFe ₂ O ₄	289
Au/ZnO	353	Pt/Al ₂ O ₃ (CN-101)	403
Au/MgFe ₂ O ₄	301	Pt–Pd/Al ₂ O ₃ (DH-2)	408

Table 3. Comparison of the Activity for the Elimination of Hydrogen

catalyst	T^0 (K)
DH-2 (Pd–Pt/Al ₂ O ₃)	398
CN-101 (Pt/Al ₂ O ₃)	393
Au/Fe ₂ O ₃	358
Au/MgFe ₂ O ₄	403
Au/NiFe ₂ O ₄	403
dual catalyst system ^a (Au/Fe ₂ O ₃ + Pt–Pd/Al ₂ O ₃)	332

^a Feed gas flow rate: 225 mL min^{−1}.

by the lowest temperature at which the H₂ is “completely” converted; i.e., the residual H₂ in the exhaust gas is less than 20 ppm.^{2,3} The lowest temperature of complete conversion is denoted by T^0 . The lower the T^0 , the higher the activity.

4. Results and Discussion

The specific surface area and composition of catalysts related to this work are listed in Table 1. The dual bed system consists of two catalysts (catalyst₁ and catalyst₂ are separately composed and not in contact). catalyst₁, which meets the incoming CO₂ feed gas first, is a suitable supported Au catalyst for the elimination of carbon monoxide. Then catalyst₂ meets the incoming CO₂ feed, which is a supported Pt–Pd catalyst for the elimination of hydrogen. The activity for the removal of CO from the CO₂ feed gas was investigated first. The results (Table 2) show that Au/Fe₂O₃, Au/NiFe₂O₄, and Au/MgFe₂O₄ catalysts can eliminate CO from the CO₂ feed gas at room temperature, Au/ZnO can catalytically remove CO at 353 K, and Pt/Al₂O₃ and Pt–Pd/Al₂O₃ catalysts can work at considerably higher temperatures.

In the dual catalyst bed system, catalyst₁ is any one of the catalysts (Au/Fe₂O₃, Au/NiFe₂O₄, or Au/MgFe₂O₄); Au/Fe₂O₃ is chosen in this work, while Pt–Pd/Al₂O₃ is chosen as catalyst₂. The comparison of activity for the elimination of hydrogen from CO₂ feed gas is shown in Table 3. It is seen that the dual catalyst system can decrease the residual hydrogen concentration in the exit CO₂ feed gas to less than 20 ppm at 332 K. The CO in the feed gas is certainly converted to CO₂ completely at this temperature according to the data given in Table 2. This purified feed gas can then be safely used in urea synthesis. Compared with CN-101, DH-2, and Au/

Fe₂O₃^{4,17} catalysts, the dual catalyst bed system is far superior to these industrially used and patented catalysts in activity and can catalyze the reaction between H₂ and O₂ to H₂O in the CO₂ feed gas at relatively low temperatures, at which CO is also oxidized completely into useful CO₂ that can be absorbed by ammonia.⁴ This can effectively avoid the accidental explosion of hydrogen–oxygen–ammonia mixed gases and ensure the safety of urea production. Compared with the single catalyst bed, the disadvantages of the dual bed system are complex catalyst used and more catalyst cost. In the urea making, the CO₂ feed gas from the absorbed tower is usually heated around 413–473 K for catalytic elimination of hydrogen on the Pt and Pd catalysts mentioned above. This dual catalyst system thus can result in significant energy savings in the process of eliminating hydrogen from the CO₂ feed gas.

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