Enhanced adsorption behaviour of hydrogen on CO or N₂ preadsorbed Rh/TiO₂ surface

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Adsorption isotherms of CO, N₂ and H₂ have been measured on Rh/TiO₂. The observed enhancement in H₂ adsorption on the preadsorbed N₂ surface is considered as a favourable precursor for ammonia synthesis. This is similar to the influence of preadsorbed CO on H₂ adsorption facilitating CO-hydrogenation under SMSI condition.

Strong metal support interaction (SMSI)¹ in supported metal catalyst systems is an interesting area of research importance. Several explanations have been put forward to explain the seemingly simple interaction, which is, still not well understood. Reducible oxides such as titanium dioxide contribute to the SMSI. Formation of Ti³⁺ species during pretreatment operations such as reduction and evacuation at high temperature is a primary step in the origin of SMSI². Migration of TiOₓ species to the metal surface is also accepted as a mechanism of SMSI³. One of the favoured mechanisms proposed is based on the transfer of electrons from the reducible support to metal crystallites⁴. The above mechanisms have been proposed to explain the so-called SMSI behaviour, namely, the suppression in hydrogen and carbon monoxide adsorption and enhancement of CO-hydrogenation by metals supported on reducible oxides after high temperature pretreatments compared to low temperature pretreatments. Even though CO and N₂ are isoelectronic, the individual adsorption behaviour with reduction temperature has been found to be quite different⁵. Co-adsorption of CO and hydrogen on supported rhodium catalysts has been reported⁶. This study is of particular relevance to Fischer-Tropsch synthesis. Similar studies on the adsorption behaviour of N₂ and H₂ may be useful in understanding ammonia synthesis, since the stability of the precursors controls the rate of formation of ammonia. In order to understand the effect of precursor for these reactions, sequential adsorption studies of CO and hydrogen as well as N₂ and hydrogen have been undertaken.

Materials and Methods
Rh/TiO₂ (~1 wt% Rh) was prepared by impregnating TiO₂ anatase (Tioxide International, UK, pore volume = 0.3 cm³ g⁻¹; and surface area = 70 m² g⁻¹) with an aqueous solution of RhCl₃·3H₂O. It was dried overnight at 423 K and then calcined in air at 623 K for 3 hr. The catalyst was reduced both at low temperature (LTR, 573 K) and high temperature (HTR, 773 K) and tested for SMSI⁷. A conventional all glass high vacuum apparatus was used for measuring the gas uptake. The catalyst (~0.3 g) attached to the adsorption system was reduced under LTR and the adsorption measurements were carried out at room temperature after degassing at 573 K to reach a pressure of 10⁻⁵ torr. Carbon monoxide adsorption isotherms were measured at room temperature in the following sequence: (i) CO on the bare surface; (ii) degassing for 1 hr at room temperature; (iii) hydrogen on the preadsorbed CO; (iv) reduction in hydrogen at 573 K for 3 hr and degassing at the same temperature; (v) hydrogen on the bare surface; (vi) degassing for 1 hr at room temperature; and (vii) CO on the preadsorbed hydrogen. The above isotherms were built to a pressure of 200 torr by incremental addition of the gases and waiting for 1 hr before taking the pressure readings. Similarly N₂ adsorption isotherms and the sequential adsorption of N₂ and H₂ and H₂ and N₂ were carried out. The catalyst was reduced at different temperatures and the adsorptions of CO and N₂ were carried out separately at room temperature.

Results and Discussion
The effect of reduction temperature on CO and N₂ adsorption is shown in Fig. 1 (inset). It is observed that CO adsorption decreases with reduction temperature whereas nitrogen adsorption increases. This difference in adsorption behaviour can be explained as follows. In the case of CO, the molecule adsorbs both on the metal as well as on the Ti³⁺ sites⁸. As the
Fig. 1—CO(A) and N₂(B) adsorption isotherms over Rh/TiO₂ at room temperature [(1) CO; (2) H₂; (3) CO on H₂; (4) N₂; (5) H₂ on N₂; and (6) N₂ on H₂. Inset represents the effect of reduction temperature on CO (— - -) and N₂ (— ○ —) adsorption].

Temperature (Fig. 1, inset). There is an increase in N₂ adsorption due to Ti³⁺ sites under SMSI condition. This study, thus, provides evidence for the enhancement of H₂ adsorption on the preadsorbed N₂ surface of Rh/TiO₂. The special feature of N₂ adsorption can be conveniently exploited for ammonia synthesis since dissociation of N₂ is the rate-determining step for this process. This is supported by the striking similarity of an increase in methane formation in CO-hydrogenation under SMSI conditions.

References