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Hydroisomerisation of *n*-alkanes over partially reduced MoO_3: Promotion by CoAlPO-11 and relations to reaction mechanism and rate-determining step

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Abstract

The reaction mechanism and the rate-determining step (RDS) of the isomerisation of *n*-alkanes (C_4–C_6) over partially reduced MoO_3 catalysts were studied through the effects of the addition of an alkene isomerisation catalyst (i.e. CoAlPO-11). When an acidic CoAlPO-11 sample was mechanically mixed with the MoO_3, a decrease of the induction period and an increase of the steady-state conversion of *n*-butane to isobutane were observed. These data support previous assumptions that a bifunctional mechanism occurred over the partially reduced MoO_3 (a complex nanoscale mixture of oxide-based phases) during *n*-butane isomerisation and that the RDS was the skeletal isomerisation of the linear butene intermediates. The only promotional effect of CoAlPO-11 on the activity of partially reduced MoO_3 for C_5–C_6 alkane hydroisomerisation was a reduction of the induction period, as the RDS at steady-state conditions appeared to be dehydrogenation of the alkane in this case. However, lower yields of branched isomers were observed in this case, the reason of which is yet unclear.

Keywords: Isomerisation; Alkane; MoO_3; Aluminophosphate; Mechanism; Bifunctional; Dehydrogenation; Acidity

1. Introduction

The need to tackle global warming has renewed the interest in *n*-alkane isomerisation for the production of more efficient and cleaner fuels. The octane numbers (RON) of *n*-butane, *n*-pentane and *n*-hexane are 113, 62 and 19, respectively, while those of isobutane, isopentane and 2-methylpentane are 122, 100 and 82, respectively [1]. Isoalkanes can also be used for the formation of high-octane rate alkylates and ether compounds, after dehydrogenation to the corresponding alkene. The mechanism of alkane isomerisation has been discussed for years and is seemingly established. However, the details of the mechanism are sometimes still unclear and controversial [2]. The main problems to be solved include the formation route of carbenium ions, the acidic properties of the catalysts, the role of a metallic phases and hydrogen during isomerisation.

Catalysts based on molybdena (MoO_3) reduced at mild temperatures, e.g. 623 K, are active for the hydroisomerisation of C_4–C_7 alkanes [3–10]. These materials can be more selective than zeolite-supported platinum (in particular at high conversions), are more resistant to sulfur and nitrogen poisoning and do not catalyse the formation of significant levels of aromatics [5–7]. Further catalyst development has been hampered by the structural complexity of the material (complex mixture of oxide-based phases on the nanoscale [11]) and by contradictory statements regarding the associated mechanism of reaction. Katrib and co-workers [8,9] and Matsuda et al. [7] have proposed that a traditional bifunctional mechanism [12,13] operates, whereas Ledoux and co-workers [6] have proposed a metallocyclobutane intermediate-based mechanism. Matsuda et al. [7] and Katrib and co-workers [9] proposed that the dehydrogenation process was the rate-determining step in the case of the isomerisation of C_5–C_7 alkanes, while Meunier [10] suggested that the isomerisation of the linear butene intermediates was rate-determining in the case of C_4.

The data reported in the present article give an indication of the bifunctional nature of the alkane isomerisation mechanism taking place over reduced MoO_3 catalyst. The rate-determining step in the case of *n*-butane, *n*-pentane and *n*-hexane is

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identified at various times on stream and the promotional effect of the mechanical addition of an acidic medium-pore zeotype (i.e. CoAlPO-11) is demonstrated.

2. Experimental

Molybdenum oxide MoO_3 (Aldrich, purity >99.5%) and CoAlPO-11 (prepared by standard hydrothermal synthesis) were used for the catalytic tests. The CoAlPO-11 preparation method was similar to those reported in the literature [14–16]. Pseudoboehmite (Sasol Pural SB, 38 wt.% Al), phosphoric acid (Fluka, 85%) and cobalt acetate (Aldrich) were used as aluminium, phosphate and cobalt source, respectively. Di-*n*-propylamine (Aldrich, 99%) was used as template. The CoAlPO was synthesised under traditional hydrothermal conditions with a batch composition 1.0 P:0.96 Al:0.08 Co:1.0 T:80 H_2O. The pseudoboehmite was first suspended in 20 ml of distilled water. The phosphoric acid was then added to the slurry and the mixture was heated at 363 K for 30 min. The template and the cobalt acetate were added after cooling of the mixture to room temperature and the batch was stirred for 30 min. The final mixture was sealed in Teflon-lined stainless-steel autoclaves and put into a pre-heated oven at 433 K during 40 h. The content of the autoclave was then filtered, washed with water and dried at 373 K overnight. The analysis of the synthesis product was carried out by X-ray powder diffraction (PANalytical X'Pert pro using Cu Kα radiation).

High-purity butane and hydrogen were supplied by high-pressure cylinders from BOC. Gas flows were regulated by Aera mass flow controllers. High-purity *n*-pentane and *n*-hexane (Aldrich) were supplied through saturators. The catalytic activity was measured at 623 K in a plug-flow reactor, at a total pressure of 1 bar. The catalysts were calcined in situ at 723 K to combust the amine template present in the as-synthesised CoAlPO. The reactor effluents were measured by on-line gas chromatography (Perkin-Elmer 8700, fitted with a Chromosorb 102 column and a FID).

3. Results and discussion

3.1. Catalyst characterisation

The CoAlPO sample prepared by hydrothermal method exhibited a light blue colour and the XRD pattern (not shown) of this material corresponded to that of AlPO-11 (AEL-type structure) reported in the literature [16]. The cobalt content of the sample, as measured by ICP, was 4.0 wt.%. This material is referred to as CoAlPO-11 in the present paper.

3.2. Catalytic tests for n-butane isomerisation

The conversion of *n*-butane to isobutane measured over MoO_3, CoAlPO-11 and two mechanical mixtures of these materials is shown in Fig. 1. No activity was observed over CoAlPO-11 when this sample was used as the only catalytic material (Fig. 1, curve a). The isobutane yield observed over MoO_3 exhibited the typical sigmoidal shape observed over this oxide when used for alkane isomerisation (Fig. 1, curve b). This phenomenon is related to the kinetic of the processes leading to the formation of the active phase by reduction of MoO_3 and to a large surface area increase (typically up to 180 $m^2\ g^{-1}$ [11,17]). The catalytic sample made of a mechanical mixture of the two oxides (Fig. 1, curve c) yielded a significantly higher conversion to isobutane than that expected from the sum of the individual contributions. In addition, the delay to obtain a given level of conversion was significantly shortened. A further increase of isobutane yield and reduction of the induction period was obtained when a higher mass of CoAlPO-11 was utilised to make the mechanical mixture (Fig. 1, curve d).

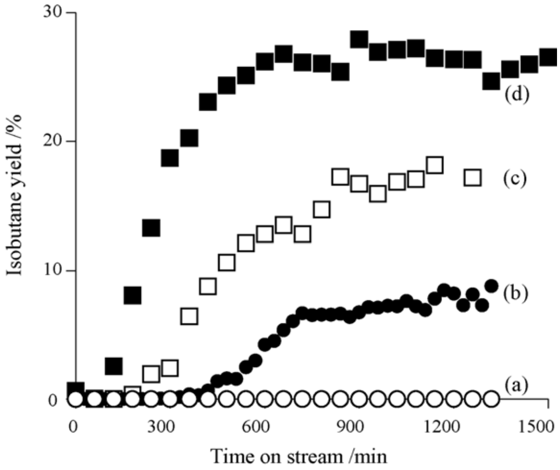

Fig. 1. Isobutane yield during the reaction of *n*-butane over: (a, ○) 50 mg CoAlPO-11, (b, ●) 50 mg MoO_3, (c, □) 50 mg CoAlPO-11 + 50 mg MoO_3 and (d, ■) 100 mg CoAlPO-11 + 50 mg MoO_3. Feed: 10% *n*-butane in H_2 at ambient pressure, total flow rate: 100 $cm^3\ min^{-1}$, *T*: 623 K.

The data shown in Fig. 1 clearly indicate that CoAlPO-11, an acidic microporous material, was totally inactive for the isomerisation of *n*-butane, but promoted the activity of reduced MoO_3 for this reaction. This result supports previous work by Meunier [10], who showed that a bifunctional mechanism was taking place during *n*-butane isomerisation and proposed that the rate-determining step (RDS) was the skeletal isomerisation of linear butenes to isobutene (Fig. 2). CoAlPO-11 is an active and selective catalyst for the skeletal isomerisation of butenes, like other one-dimensional 10-member ring channel zeotypes such as FER and TON [18]. CoAlPO-11 has also been used in combination with noble metals to give selective alkane hydroisomerisation catalysts [19]. The role of CoAlPO-11 in the present case was to favour the skeletal isomerisation of the minute concentration of butenes existing at steady-state conditions, which is typically lower than 1000 ppm [10].

The conversion of *n*-pentane to isopentane measured over MoO_3 and a mechanical mixture of MoO_3 and CoAlPO-11 is shown in Fig. 3. The plots showing the conversion of *n*-hexane to 2-methylpentane (Fig. 4) are essentially identical and the case of these two alkanes is discussed altogether. Similarly to the case of butane, the induction period was significantly shortened when CoAlPO-11 was present. Assuming that a bifunctional mechanism also operates in the case of pentane and hexane isomerisation as proposed by Matsuda et al. [7] and

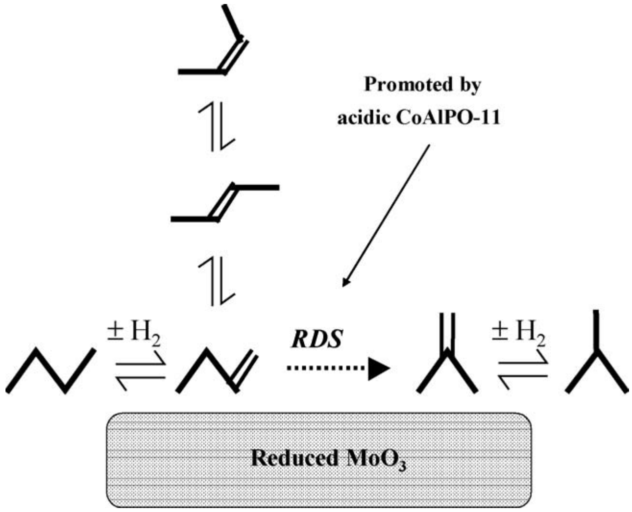

Fig. 2. Schematic representation of *n*-butane reaction pathway over reduced MoO_3. The dehydrogenation of *n*-butane to linear butenes is fast, while the skeletal isomerisation of the linear butenes to isobutene is slow. The latter step is that promoted by the acidic CoAlPO-11.

Katrib and co-workers [8,9], this observation indicates that the acidity of the sample was rate-limiting at early time on stream. This is in agreement with the isopropanol dehydration measurements [7,8], which showed that the acidity of MoO_3 was initially low but gradually increased with the extent of the reduction.

However, it is also clear that the steady-state value of conversion was not increased by the presence of CoAlPO-11. This observation supports the conclusions that the RDS in the case of longer alkanes (C_nH_{2n+2}, $n > 4$) was the alkane dehydrogenation [7,9]. The steady-state isoalkane yields was even lower as compared to the MoO_3 case (Figs. 3 and 4), possibly due to the formation of heavier products (e.g. dimers or cyclopentadiene [20]) leading to deactivation by coke formation. Some by-products formed over the CoAlPO-11 could have also led to a modification of the reduced MoO_3 microstructure in terms of surface area or/and composition.

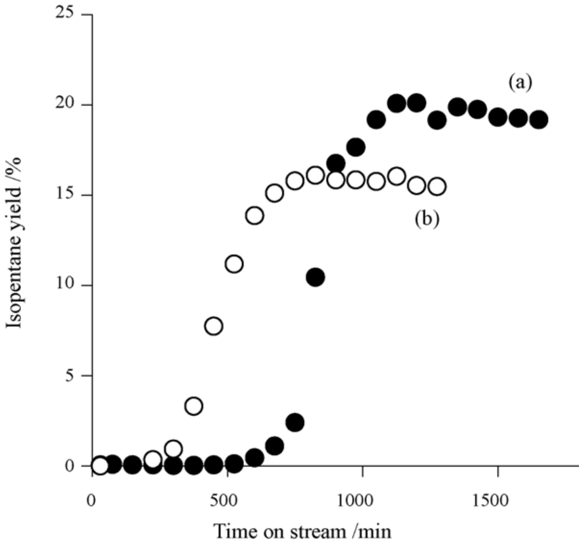

Fig. 3. Isopentane yield during the reaction of *n*-pentane over: (a, ●) 20 mg MoO_3 and (b, ○) 20 mg MoO_3 + 40 mg CoAlPO-11. Feed: 3% *n*-pentane in H_2 at ambient pressure, total flow rate: 100 $cm^3\ min^{-1}$, *T*: 623 K.

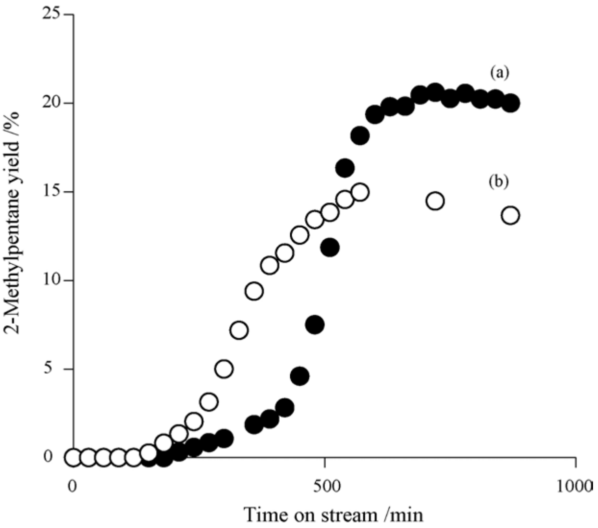

Fig. 4. 2-Methylpentane yield during the reaction of *n*-hexane over: (a, ●) 20 mg MoO_3 and (b, ○) 20 mg MoO_3 + 40 mg CoAlPO-11. Feed: 3% *n*-pentane in H_2 at ambient pressure, total flow rate: 100 $cm^3\ min^{-1}$, *T*: 623 K.

The difference in the hydroisomerisation RDS between the case of *n*-butane and that of the higher *n*-alkanes was most likely related to the higher activation energy required in the case of the skeletal isomerisation of the C_4-alkene intermediate [18]. Boronat et al. have showed by DFT calculations that the energy of the transition state is much higher in the case of the C_4, resulting in the higher activation energy and lower skeletal isomerisation rate, which becomes limiting in this case [21].

The nature of the phases associated with the metallic and acidic characters of the reduced MoO_3 sample is not fully clear. While Katrib and co-workers have clearly shown that the MoO_2 phase, which is observed over the active sample [11], exhibit a metallic character [22], the phase responsible for the acidity (e.g. MoO_2, amorphous oxide domains, oxycarbide) is more uncertain and needs to be further investigated.

4. Conclusions

A bifunctional mechanism occurs over partially reduced MoO_3 catalysts during *n*-butane isomerisation and the RDS is the skeletal isomerisation of the linear butene intermediates. Acidic Co-AlPO-11 can be mechanically added to the MoO_3-based catalyst to increase the isobutane yield and decrease the induction period. The only promotional effect of CoAlPO-11 is the reduction of the induction period in the case of higher alkanes ($>C_4$), for which the RDS at steady-state is alkane dehydrogenation.

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