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On the Nature of Catalytic Active Sites on Molybdenum Catalysts

The question of the nature of the active catalytic sites on molybdenum-based catalysts is still controversial.

Alumina-supported and unsupported molybdenum catalysts were studied in our laboratory (*1–4*). Catalytic reactions were performed at 350°C either in a flow system or in a batch reactor, using C_6 saturated hydrocarbons like 2-methylpentane as reactants. Alumina-supported catalysts were prepared by reduction in a hydrogen flow of MoO_3/Al_2O_3 containing 6 wt% of MoO_3 (*2, 4*). Unsupported Mo catalysts were Mo films produced by evaporation of a Mo metallic wire and studied in a batch reactor or Mo metallic powder pretreated and studied under hydrogen flow (*3*).

On Mo metallic films in a batch reactor (with the same hydrocarbon-to-hydrogen ratio (0.007) as that in the flow system) we obtained a high level of activity mainly in extensive hydrogenolysis (*2*).

On Mo metallic powder in the flow reactor, we obtained much less activity but with a high selectivity in isomerization (over 90%) (*2*).

On MoO_3/Al_2O_3 reduced in hydrogen flow at 550, 750, or 950°C for 2 h with a high heating rate to reach the reduction temperature (+150°C/15 min), we obtained an increase in activity and isomerization selectivity as the reduction temperature increased. After reduction at 550°C, the total activity (α_T) was 1.8% and the isomerization selectivity (Si) was 35.4%. After reduction at 950°C, α_T was 2.4% and Si was 96.4%. ^{13}C labeling experiments permitted us to study the isomerization mechanisms. It was shown that up to and including a reduction temperature of 750°C, the reaction mechanisms were essentially acidic. After reduction at 950°C, the mechanisms changed. Our interpretation of the results was that the mechanisms became metallic. We proposed an isomerization mechanism on metallic molybdenum via a metallacycle intermediate evolving to a carbene–olefin intermediate giving exclusively bond-shift migration. This mechanism accounted for the relative migration rates of the alkyl groups studied by ^{13}C labeling experiments (*2, 3*). It was supported by an XPS study which showed that a reduction of MoO_3/Al_2O_3 under hydrogen flow at 950°C produced metallic molybdenum (*1*). This latter result was also found by Nakamura *et al.* (*5*). The supported catalyst reduced at 950°C behaved exactly like the unsupported metallic powder (*2*).

On MoO_3/Al_2O_3 reduced in hydrogen flow at 750 or 950°C for 6 to 20 h and/or with a low heating rate to reach the reduction temperature (+50°C/15 min), the catalytic results changed completely (*4*). In this case, high extensive hydrogenolysis activity was observed as for metallic Mo films. Depending on the pretreatment conditions, the isomerization sites of unsupported metallic molybdenum powder or the hydrogenolysis sites of molybdenum films can be produced on alumina-supported molybdenum catalysts.

These interpretations were contested by Burwell (*6*). Burwell *et al.* (*5, 7–10*) worked on $Mo(CO)_6/Al_2O_3$ and $MoO_3/\gamma\text{-}Al_2O_3$ reduced in flowing hydrogen at temperatures contained between 650 and 950°C. According to them, molybdenum was reduced to the metallic state under these conditions. They studied the catalytic reactions of several alkanes and found a high level of hydrogenolysis. They concluded that Mo(0)/

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Al_2O_3 is among the best cracking catalysts but the catalytic sites are rapidly and easily poisoned by O_2 and other gases (CO, H_2O, N_2). Burwell (*6*) suggested that in the cases where we obtained low hydrogenolysis activity and high isomerization selectivity (unsupported metallic Mo powder and $MoO_3/\gamma\text{-}Al_2O_3$ reduced under hydrogen flow at 950°C) the Mo catalytic sites were poisoned by oxygen coming from the reactant streams. We agree with the fact that Mo(0) is an active cracking site but we assert that Mo(0) can also be an isomerization site.

(i) Burwell does not pay much attention to the isomerization mechanisms on metallic molybdenum. The study of these isomerization reactions by ^{13}C labeling experiments can provide much information on the nature of catalytic active sites. On oxidized Mo, we obtained 16.7% of 3-methyl[3-^{13}C]pentane, 16.7% of 3-methyl [6-^{13}C]pentane, and 66.6% of 3-methyl [1-^{13}C]pentane plus 3-methyl[2-^{13}C]pentane and 33.3% of [1-^{13}C]hexane, 33.3% of [2-^{13}C]hexane, and 33.3% of [3-^{13}C]hexane for either reactant: 2-methyl[2-^{13}C]pentane or 2-methyl[4-^{13}C]pentane. This statistical distribution or "scrambling" of the label means that desorption is the low-rate step in the mechanism; the adsorbed molecule is subjected to several fast isomerization reactions before desorbing. This situation is typical of acidic catalysts. For instance, Moliere (*11*) obtained the same results on oxidized tungsten supported on alumina. On molybdenum catalysts which were reduced under drastic conditions (where the catalytic site is most probably Mo(0), even according to Burwell's work) the scrambling disappeared. We obtained ^{13}C distributions typical of a bond-shift mechanism, which is well established for classical metallic catalysts like Pt or Pd (*12, 13*).

(ii) If the Mo(0) hydrogenolysis sites were poisoned by oxygen from the reactant streams in our flow system, we would not obtain such a high level of extensive hydrogenolysis on $MoO_3/\gamma\text{-}Al_2O_3$ reduced at 750 or 950°C under what we called "particular" conditions (lower heating rate to reach the reduction temperature or longer plateau at the reduction temperature) (*4*). Using these conditions, the catalysts remained much longer under the influence of the reactant streams.

Our interpretation of the results is that metallic molybdenum presents two kinds of active catalytic sites: one giving hydrogenolysis at a high rate, another giving isomerization at a lower rate. The former can be found on metallic molybdenum films, the latter on metallic molybdenum powder. Both can be obtained on $MoO_3/\gamma\text{-}Al_2O_3$ in a flow system depending on the reduction conditions. The difference between the two sites might be the geometrical arrangement of the metallic molybdenum atoms of the active site giving different adsorption abilities and different electronic properties. More work is in progress in our laboratory in order to examine this point.

Burwell (*6*) also criticized our papers (*1–3*) because we did not refer to work (*5, 7–10*) which was relevant to ours. Our papers were submitted in July 1985 but were not published until March 1987. It was thus impossible to refer to most of the work cited by Burwell in Ref. (*6*). This is very unfortunate because discussion of the above points would have improved our paper.

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