Claims

1. A supported for preparation of isobuthylene from halomethane, characterized by carrying out hydrogen reduction activation before using it, catalyst comprising a support and a metallic active component supported on the support; the metallic active component contains zinc oxide and zinc halide, and the content of zinc oxide is 0.5 wt.%-20 wt.%, the content of zinc halide is 10 wt.%-50 wt.%, and the content of the support is 40 wt.%-88 wt.% based on the total weight of the catalyst.

2. The supported catalyst according to claim 1, wherein the content of zinc oxide is 1 wt.%-15 wt.%, the content of zinc halide is 15 wt.%-40 wt.%, and the content of the support is 50 wt.%-84 wt.% based on the total weight of the catalyst.

3. The supported catalyst according to claim 1 or 2, wherein the zinc halide is selected from one or more of zinc fluoride, zinc chloride, zinc bromide and zinc iodide, and the support is selected from one or more of aluminum oxide, silicon oxide and ZSM-5 molecular sieve.

4. The supported catalyst according to any one of claims 1-3, further comprising a promoter selected from one or more of Ti, Zr, Ce and La, and the content of the promoter calculated on element is 0.1 wt.%-10 wt.% based on the total weight of the catalyst.

5. The supported catalyst according to claim 4, wherein the promoter is Zr, and the weight content of the promoter calculated on element is 0.5 wt.%-5 wt.% based on the total weight of the catalyst.

6. The supported catalyst according to any one of claims 1-5, wherein it is determined by NH_3-TPD method that the total acidity of 450°C or less in the catalyst is

0.5 mmol/g-1.3 mmol/g, and the acidity of 250°C-350°C is 20%-90% of the total acidity of 450°C or less.

7. A method for preparing a supported catalyst according to any one of claims 1-6 including the following steps: introducing zinc oxide to a support and then contacting gaseous-phase halogen-containing compound with the support containing the introduced zinc oxide, and the contact conditions make the zinc oxide on the support partially converted into zinc halide, wherein the dose of zinc oxide makes the content of the support be 40%-88% based on the total weight of the obtained supported catalyst, and the contact conditions make the content of zinc oxide on the support be 0.5%-20%, and the content of zinc halide be 10%-50%.

8. The method according to claim 7, wherein gaseous-phase halogen-containing compound contacts the support containing the introduced zinc oxide in a form of a mixed gas of gaseous-phase halogen-containing compound and inert gas, and the concentration of gaseous-phase halogen-containing compound in the mixed gas is not less than 20 v/v%.

9. The method according to claim 8, wherein the gaseous-phase halogen-containing compound is one or more of monohalomethane, bihalomethane and trihalomethane.

10. The method according to claim 8 or 9, wherein the mean of contact includes putting the support containing the introduced zinc oxide in a continuous flow fixed bed reactor, raising temperature to 150°C-400°C in an inert atmosphere, and inputting gaseous-phase halogen-containing compound or a mixed gas containing gaseous-phase halogen-containing compound with the space velocity $50h^{-1}$-1000 h^{-1}, the contact pressure 0.1MPa-0.5MPa and the time 0.5h-8h.

11. Use of the supported catalyst according to any one of claims 1-6 in the preparation of isobutylene.

12. A method for preparation of isobutylene from halomethane including carrying out hydrogen reduction activation of the supported catalyst according to any one of claims 1-6 to make the content of halogen in the activated catalyst be 20 wt.%-90 wt.% of the total content of halogen in the supported catalyst without reduction, then contacting halomethane with the activated catalyst to prepare isobutylene.

13. The method according to claim 12, wherein the contact conditions include reaction temperature 150°C-350°C, reaction pressure 0.1MPa-5MPa and space velocity $50h^{-1}$-$1000h^{-1}$.

14. The method according to claim 12, wherein the conditions of hydrogen reduction activation make the content of halogen in the catalyst be 30 wt.%-80 wt.% of the total content of halogen in the catalyst before reduction.

15. The method according to any one of claims 12-14, wherein the means of hydrogen reduction activation includes raising temperature of the catalyst to 300°C-600°C in an inert atmosphere; then inputting hydrogen or a mixed gas of hydrogen and inert gas in which the volume percentage of hydrogen in the mixed gas is 10%-95% at a space velocity of $200h^{-1}$-$2000h^{-1}$ and holding pressure at 0.1MPa-0.5MPa for 2h-16h.

16. The method according to any one of claims 12-15, wherein halomethane is one or more of monohalomethane, bihalomethane and trihalomethane.

17. The method according to any one of claims 12-16, wherein the contact takes place in a fixed bed, fluidized bed, fixed fluidized bed, moving bed, slurry bed or bubbling bed reactor.